V — CONCLUSÃO

A etapa final da análise de dados cinéticos consiste em uma análise crítica das estimativas dos parâmetros. Em princípio, deve-se aceitar o conjunto de parâmetros estimados pelo método que conduz aos menores desvios entre o valor experimental e a predição do modelo. Porém, dependendo das condições experimentais, assim como da variância da constante de velocidade observada, o simplex ponderado pode ser mais indicado. No caso de ajustes de equações lineares, o uso da simples soma dos quadrados dos desvios é apropriado quando a variância é constante. Para situações onde a variância relativa desta variável é constante, a ponderação com $w_i = [MeO^-]^2$ é recomendada.

Para ajustes de parâmetros de equações não-lineares, como a investigada por Knipe (eq. 8), a escolha do tipo de ponderação é mais complexa. Somente um estudo sistemático dos erros experimentais e seus efeitos na equação do modelo poderia indicar a ponderação apropriada. Sem esta informação, o pesquisador deveria considerar o uso de mais do que um tipo de ponderação. O método simplex para otimização permite convenientemente que avaliações de parâmetros sejam realizadas com diferentes ponderações.

REFERÊNCIAS

[1] Draper, N.R.; Smith, H. *"Applied Regression Analysis"*, Wiley, Chichester, New York, 1981.

[2] Nelder, J.A.; Mead, R. *Comput. J.*, (1965), 7, 308.

[3] Kragten, J.; De Jagher, P.C.; Decnop-Weever, L.G. *Anal. Chim. Acta*, (1986), 180, 457.

[4] Spendley, W.; Hext, G.R.; Himsworth, F.R. *Technometrics*, (1962), 4, 441.

[5] Knipe, A.C.; McGuinness, S.J.; Watts, W.E. *J. Chem. Soc., Chem. Commun.*, (1979), 842.

[6] Knipe, A.C.; McGuinness, S.J.; Watts, W.E. *J. Chem. Soc., Perkin Trans.,* (1981), 193.

ARTIGO

CYCLOADDITION REACTIONS OF DIMETHYL ACETYLENEDICARBOXYLATE WITH 1-, 2- AND 3-SUBSTITUTED INDOLES USING BORON TRIFLUORIDE-DIETHYL ETHER CATALYSIS[1]

J. Augusto R. Rodrigues* and Lidia I. Verardo

Universidade Estadual de Campinas, Instituto de Química, 13083 – Campinas, Brazil

ABSTRACT

Reactions of dimethyl acetylenedicarboxylate with 1-, 2- and 3- substituted indoles with boron trifluoride-diethylether catalysis were carried out at low temperatures (0–25ºC). Thermally unstable cyclobutenes were isolated, mainly in apolar solvents, which isomerized to benzazepines. Possible mechanisms for the cycloaddition and thermal isomerization are discussed. The other compounds isolated were Michael adducts and dihydro-2-oxocarbazoles.

The products obtainable from the reaction of indoles and dimethyl acetylenedicarboxylate (DMAD) depend greatly on the conditions of the reaction and have been investigated extensively by Acheson.[2] Treatment of indole with DMAD gives many products arising either from initial electrophilic attack at the 3-position to give maleate or fumarate,[3] or from cyclisation to a cyclobutene intermediate followed by ring opening to a benzazepine[4] and subsequent reactions. In methanol, 1- and 2-methylindoles yield the corresponding fumarates[3] while 1-methylindole with DMAD in anhydrous acetonitrile also gives benzazepine and carbazole-1,2,3,4-tetracarboxylate.[3,4] The latter was the major isolated product from the reaction of indole and DMAD without solvent.[5] In aqueous methanol 1-methylindoles possessing a tri-, tetra-, or penta-methylene chain bridge between the 2,3-positions yielded a variety of lactones.[6,7,8] When the reaction was carried out in aqueous acetonitrile, low yields of cyclobutene were found in some cases.[9] Reaction of DMAD with 1-, 2-, and 3-alkyl substituted indoles in acetic acid gave the corresponding dihydrocarbazoles as the only isolated products in 15 to 25% yields.[10] When the reaction was carried out with 1-methyl-2-ethoxyindole, it was suggested that the DMAD attacks the indole at the 3-position to form a dipolar adduct which undergoes a ring closure to give a cyclobutene derivative that collapses into benzazepine.[11] Cyclobutenes

were isolated in good yields for the first time from photo-chemical reactions of indoles with DMAD.[12] The photoaddition of 1,3-dimethylindole and DMAD gave seven different products: 2-maleate, 2-fumarete, cyclo-butene, benzazepine, and the 2:1 adducts of indole: DMAD.[13] Taylor et al.[14] have reported that the boron trifluoride etherate (BTE) catalyzed reaction of 1,2,3-tri-methylindole and 1,3-dimethylindole with DMAD gave the corresponding benzazepines and dihydro-2-oxocar-bazole, both in low yields. As indicated in a preliminary report,[1] we have repeated the reaction of 1,2,3-trimethy-lindole and 1,3-dimethylindole with DMAD and, for the first time, have isolated the cyclobutenes in good yields under thermal conditions.

Nearly all the reactions studied by Acheson were carried out under refluxing conditions and in most cases on a large scale so that it would be possible to isolate products with low yields. In contrast, the reaction of 1,2,3-trimethylin-dole with DMAD and a few drops of BTE gave excellent overall yields. The reaction was carried out at low tempera-tures (0−25ºC) after which it is possible to isolate pro-ducts that are unstable at higher temperatures.[1] In order to obtain more information concerning the structural features, reactivity and mechanism we have now extended the study of this reaction to other indoles.

RESULTS AND DISCUSSION

Reactions of 2,3-dimethylindole with DMAD in 40 ml of benzene with 1 ml of BTE for 6 days at room tempera-ture gave three compounds. The ^{1}H NMR spectrum of an orange solid (1) isolated from the chromatographic column in 48% yield, showed an upfield (δ 1.45 and 1.48) chemical shift of the methyl groups when compared with 2,3-dime-thylindole (δ 2.19). The reaction of the orange solid with acetyl chloride-Na_2CO_3 gave the acetyl derivative (2), which upon heating was converted to benzazepine (7). The formation of (7) may be interpreted as a ring expansion from (2) by thermal decomposition. The structures of
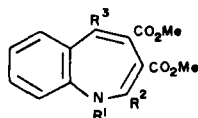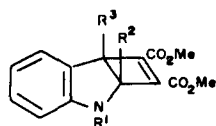

(1)	R^1= H , R^2= R^3 = Me	(7)	R^1 = Ac, R^2 = R^3 = Me
(2)	R^1 = Ac, R^2= R^3= Me	(8)	R^1 = Me, R^2 = R^3 = H
(3)	R^1= Me, R^2=R^3 = H	(9)	R^1 = Me, R^2 = Ph, R^3=H
(4)	R^1= R^2=R^3= Me	(10)	R^1 = R^2 = R^3 = Me
(5)	R^1= Me, R^2=H, R^3=Me	(11)	R^1 = Me, R^2 = H, R^3 = Me
(6)	R^1=Me, R^2=Ph, R^3= H		

(1) and (2) were confirmed by ^{13}C NMR (Table). The absence of a deshielding of H-7 of the aromatic ring as well as strong steric effects from MeCO-NMe expected in the endo of (2) as shown by models, allow us to predict the exo conformer for (2). It is not surprising that we were

unable to isolate the thermolysis product of (1) since it is well known that 1-non-substituted benzazepines are unstable.[15,16]

Structural analysis of the second product indicated that it was a 1:2 adduct of 2,3-dimethylindole with DMAD. ^{1}H NMR and IR data suggested that it was a misture of maleate and fumarate isomers. During separation by thick layer chromatography, one isomer transformed into the other and only one product was isolated as yellow crystals in 11% yield. The ^{1}H NMR spectrum showed an upfield chemical shift of the methyl group (δ 1.70) when compared with 2,3-dimethylindole. The singlet at δ 6.30 (1H) was assigned to a vinylic maleate hydrogen.[17] Under reflux in CCl_4, this product was converted into colourless crystals whose structure was assigned to be (14). Thus the thermo-labil yellow crystal should be (12).

Under reflux in CCl_4 the mixture of (12) and (13) was isomerized to benzazepine (14) in 83% yield.
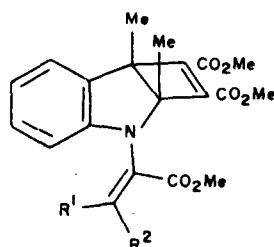
(12) R^1 = H, R^2 = CO_2Me

(13) R^1 = CO_2Me, R^2 =H
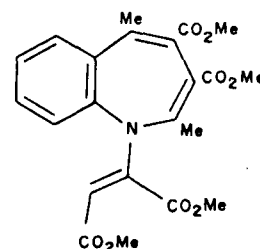
(14)

The third compound was an orange solid isolated in 28% yield whose mass spectrum and chemical analysis showed a loss of MeOH relative to the starting materials. The IR showed an ester absorption at 1 715 cm^{-1} and an unsatu-rated carbonyl at 1 630 cm^{-1}, which is compatible with dihydro-2-oxocarbazole (15). This compound was methy-lated with MeI-K_2CO_3-CH_3CN to give, in 98% yield, the dienone (16), which was compared with an authentic sample.[1]
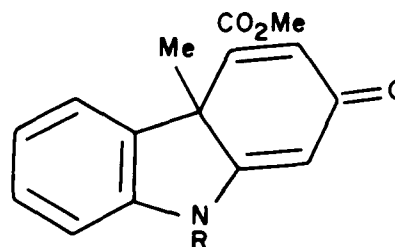
(15) R = H

(16) R = Me

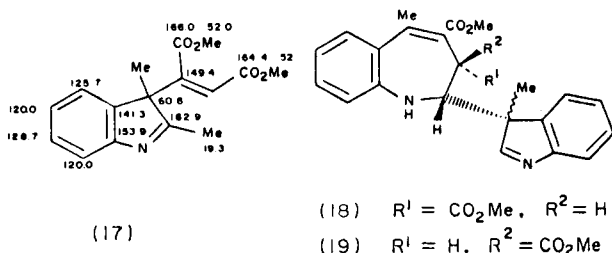When the reaction was carried out in benzene at 0-4°C for 40 hours, 25% of the starting material was recovered. We isolated (1) in 6% yield, and (15) in 12% yield as well as an orange solid (48% yield) that was identified as (13).
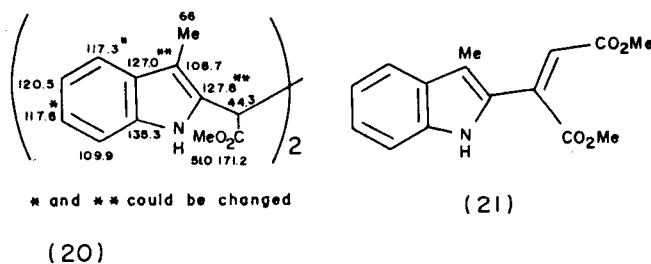
To verify the influence of the solvent, the reaction was run in acetonitrile at room temperature for 5 days. The products isolated were the cyclobutene (1) (10%), the maleate (12) (6%), the fumarate (13) (7%), the dienone (15) (36%) and a pale yellow solid, m.p. 90-92°C (25% yield). The molecular ion, M^+ 287 of its mass spectrum revealed a 1:1 adduct. The IR showed a signal at 1730 cm^{-1} (C = 0) and at 1 640 cm^{-1} (C = 0) and at 1 640 cm^{-1} (C = N), while the ^1H NMR spectra had a singlet at δ 5.79 with integration for 1 H, suggesting a vinylic fumarate or maleate hydrogen. The stereochemistry was determined by ^{13}C NMR which revealed a $^3H_{CO_2H}$ coupling of 12 Hz characteristic of maleate derivatives.[18,19] These results allow us to suggest its structure as (17). This is the first time that this type of compound has been isolated from reactions of indoles with DMAD.

The reaction of 3-methylindole (skatole) with DMAD in benzene with BTE at 0-4°C for 19 h gave four compounds. Three are 2:1 adducts (skatole: DMAD). ^1H NMR of the first showed only one NH proton. The 5-methyl doublet at δ 2.08 with J = 1 Hz is due the homoallylic coupling[20] since it was simplified by double irradiation of the double quartet (J = 8 and 1 Hz) at 4.28. The i.r. spectrum gave absorptions at 3 420 (NH), 1 745 (C = 0) and 1 665 cm^{-1} (C = N). These data are consistent with (18).

The reaction of 1-methylindole with DAMD in hexane-CCl_4 with BTE, after 3 hours at 0-4°C gave a mixture of two compounds in 36% yield after isolation by preparative thick layer chromatography: a cyclobutene (3) and a benzazepine (8), with total recovery of unreacted starting material. On standing in ethanolic solution at room temperature (3) rearranged to (8). The presence of (3) was determined by comparing the ^1H NMR signals with those in the literature.[12] It is interesting to compare our results with Acheson et al.,[4] who reported that a large scale reaction of 1-methylindole with DMAD under acetonitrile reflux during 6 days gave five to seven compounds (low overall yield) depending on the presence or absence of water in the solvent. Recently this reaction was repeated by Acheson et al.[21] in dichlorometane at 10 kbar to give the benzazepine (8) in 20% yield. On the other hand, good yields of (3) were obtained by Davis and Neckers[23] when the reaction was carried out using ultraviolet irradiation.

The reaction of 1-methyl-2-phenylindole with DMAD in CCl_4 with BTE at 0-4°C for 3 days gave the benzazepine (9) in 88% yield and the maleate (22) and fumarete (23) in 2% yield.

(20)

* and ** could be changed

(21)

(17)

(18) $R^1 = CO_2Me$, $R^2 = H$
(19) $R^1 = H$, $R^2 = CO_2Me$

(22) $R^1 = Ph$, $R^2 = CO_2Me$, $R^3 = H$
(23) $R^1 = Ph$, $R^2 = H$, $R^3 = CO_2Me$
(24) $R^1 = Me$, $R^2 = CO_2Me$, $R^3 = H$
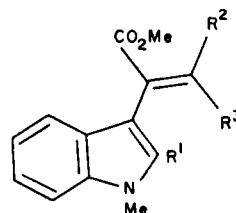(25) $R^1 = Me$, $R^2 = H$, $R^3 = CO_2Me$

The second compound was the epimer (19) with the protons at C-2 and C-3 at δ 4.28 and 3.38, respectively, with J = 12 Hz. These two substances were eluted together from the column and isolated by preparative thick layer chromatography. The yield was 21% for (18) and 10% for (19). When this mixture was left 24 h in a CH_2Cl_2 solution, the ^1H NMR gave a 1:1 proportion. These two compounds have never been isolated before in reactions of indoles with DMAD.

The third substance isolated in 44% yield gave a ^1H NMR spectrum characteristic of a symmetric structure consistent with (20). The last compound, isolated in 17% yield, was the maleate (21).

The cyclobutene (6) could not be isolated, but was suggested by t.l.c. where the orange spot decreased with time while the yellow spot of (9) increased. In the case of 1,2-dimethyl-indole, the reaction carried out at 0-4°C for 3 hours gave maleate (24) in 58% yield and fumarate (25) in 20% yield. Neckers was able to obtain a cyclobutene in 11% yield from the photocycloaddition of DMAD to 1,2-dimethylindole,[22] and Johnson has isolated (24) and (25) after 7 days in aqueous methanol without catalyst.[23]

In our preliminary report we described the reaction of 1,2,3-trimethilindole with DMAD in benzene at 0-4°C with

BTE, where we isolated only the cyclobutene (4) in 82% yield.[1] When this reaction was carried out in acetonitrile at 25°C we isolated (4) in 6% yield, (16) in 72% yield and a new compound (26) in 10% yield, which was not identified at the time.

165.2 52.0
CO₂Me
124.8
18.2 140.0 O
Me 164.7
122.9
129.9 54.2
119.6 107.3 O
129.1 Me
147.7 N 19.2
107.4 Me
27.9
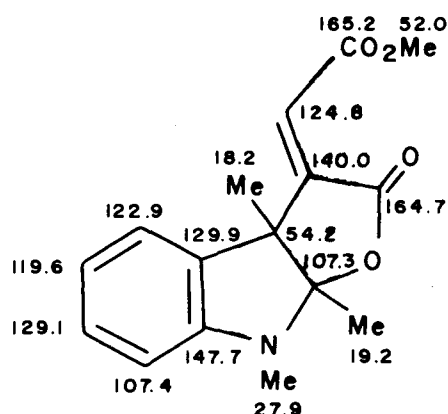
(26)

In order to collect more information about the structures of the cyclobutenes, we obtained the ^{13}C NMR spectra (Table). Also included are two compounds that we have described previously: (4) and (5).[1] We started the assignments at C-1 in (5) that presented a doublet at δ 70.1. By comparison we assigned the signals for C-1 of the other structures. The sp^2 aromatic carbons were compared with indolines, indolenines and indole.[24] The chemical shifts of C-6 and C-7 were determined by analogy with cyclobutene derivatives[25] and 1,4-dicarbonyl compounds.[26] The models for C-18 and C-19 are well know in the literature.[27]

Most of the cyclobutenes isolated are highly coloured and exhibit absorption maxima in their u.v. spectra (EtOH) at 390-435 nm. These bands correspond to intramolecular charge-transfer between aniline π donor and dimethylcarboxylate π acceptor moieties. The cyclobutene (2) is colourless as a result of the strong electron withdrawing COMe bond to nitrogen of the aniline π donor moiety. Neckers et al.[13] arrived at the same conclusion but their arguments are in contradiction to those of Iamamura.[28] This intramolecular charge-transfer interaction is an example of an only recently recognised charge-transfer interaction within one molecule where the donor and acceptor moieties are aligned in two parallel planes.[28]

The thermal isomerizations of cyclobutenes to benzazepines take place with relative ease because the electron-donor and-acceptor are substituted at appropriate positions.[29] In contrast, the thermolysis of (2) which has an electron withdrawing substituent at the nitrogen, required much higher temperatures. Similar results were obtained recently by Ikeda et al.,[16] who reported the synthesis of some 3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-dienes with substituents only on the nitrogen. With the N-benzyl derivative they observed ring opening in refluxing xylene, but the N-acetyl and N-benzoyl derivatives required tempe-

ratures over 300°C. At this temperature they obtained benzazepines and others compounds.

For (2+2) cycloaddition of electron-rich alkenes with electron deficient alkenes, Huisgen[30] has provided conclusive evidence for a two-step reaction via a 1,4-dipolar intermediate even in apolar solvents. By analogy with these reactions, Acheson and Elmore[2] have suggested that all reactions of indoles with DMAD can be interpreted as starting with initial electrophilic attack to give a zwitterion which then undergoes further reactions depending on the circunstances. If we analyse the results we have obtained we can distinguish three different reaction products: (2+2) cycloadducts, Michael adducts and dihydro-2-oxo-carbazoles. The formation of both the latter two compounds can be rationalized by assuming a common 1,4-dipolar-charged-intermediate which results from nucleophilic addition of the indoles to the electron deficient carbon-carbon triple bond of the acetylene. In our reactions at low temperature (0-4°C) in apolar solvents with only a few drops of BTE, the predominant or even the sole compound isolated[1] was the (2+2) cycloadduct. In contrast, in polar medium the predominant product was the oxocarbazoles or the Michael adducts and the minor compound was the cyclobutene. These results allow us to conclude that in apolar solvents the (2+2) cycloadduct might be formed by a concerted thermally-allowed process in agreement with the theoretical work of Epiotis for polar reactions.[31] In polar solvents the conversion of an initially formed tied-ion pair type 1,4-dipolar intermediate into a charge-separated type will be assisted by solvation. Similar results were obtained by Reinhoudt in reactions between acetylenic esters and enamines.[32]

The influence of the Lewis acid catalyst on the formation of cyclobutenes has been attributed to a lowering of the energy of the frontier orbitals because of complexation to the Lewis acid.[33] The affirmation of Acheson et al.[10] that DMAD does not need BTE catalysis to induce reaction with indoles is not absolutely correct since at the temperature of refluxing acetic acid the (2+2) cycloadducts are not stable. Under the conditions used by Acheson, the temperature and the reaction medium favor the two step process which becomes the predominant pathway over the (2+2) cycloaddition. This explains how the different products are formed, even using similar reagents and solvents, and only varying the reaction conditions.

CONCLUSIONS

We have developed a viable route to the cyclobutenes (1) to (6) under thermal conditions. To obtain these cyclobutenes in good yields it is necessary to carry out the reaction in non-polar solvents and to control the temperature carefully. We have evidence that the cyclobutenes might be formed by a concerted (2+2) thermally allowed process. In polar solvents, the predominant products are Michael adducts, the dienone (15) or (16), while the minor compounds are cyclo-addition products.

EXPERIMENTAL

IR spectra were recorded as KBr discs (for solids) and as thin films (for liquids) on a JASCO A-202 instrument (calibrated against polystyrene). UV spectra were recorded using a Bausch & Lomb 2000 spectrophotometer. ^{1}H NMR spectra were obtained as $CDCl_3$ solutions using a Varian T-60 or Varian XL-100 instrument. ^{13}C NMR spectra were obtained using a Varian XL-100 instrument. Mass spectra were obtained on a Varian Mat 311 A instrument at 70 eV using a direct insertion probe. Preparative thick layer chromatography (p.l.c.) was carried out on plates coated with silica gel PF 254 (Merck). Melting points are uncorrected. DMAD was distilled before using. Petroleum refers to light petroleum, b.p. 30-60°C.

Reaction of 2,3-Dimethylindole with Dimethyl Acetylene-dicarboxylate. — (a) A solution of DMAD (525 mg, 3.7 mmol) and 2,3-dimethylindole (507 mg, 3.5 mmol) in dry benzene (40 ml) was purged with nitrogen and after the addition of BTE (0.9 ml) was kept 6 days at room temperature. The solvent was removed and the residue chromatographed on a column (silica). (i) Elution with diethyl ether-petroleum, 1:5, gave *6,7-bis (methoxy-carbonyl)-1,5-dimethyl-3,4-benzo-2-azabicyclo [3.2.0] hepta-3,6-diene* (*1*) (482 mg, 48%) as orange crystals m.p. 101-103°C (Found: C, 66.94; H, 6.04, N, 4.78. $C_{16}H_{17}NO_4$ requires C, 66.89; H, 5.96; N, 4.87%); $v_{max.}$ 3 265 (NH), 1 725, 1 700 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 234 (ϵ 8 700) and 400 nm (1 030); δ_H (60 MHz, $CDCl_3$) 1.45 (3 H, s, Me), 1.48 (3 H, s, Me), 3.71 (6 H, s, OMe), 4.34 (1 H, br, N-H, D_2O exchangeable), 6.28-7.23 (4H, m, aromatic); m/z 287 (M$^+$, 54%), 214 (90), 145 (100). (ii) Elution with diethyl ether-petroleum, 1:4, gave a solid mixture. P.l.c. of this mixture (hexane-diethyl ether, 1:3, 5 consecutive elutions) gave only *dimethyl 2'-[6,7-bis(methoxycarbonyl)-1,5-dimethyl-3,4-benzo-2-azabicyclo [3.2.0]hepta-3,6-dien-2-yl] maleate* (*13*) (87 mg, 11%) as yellow crystals m.p. 94-96°C (hexane-diethyl ether, 1:1) (Found: C, 61.54; H, 5.43; N, 3.01. $C_{22}H_{23}NO_8$ requires C, 61.53; H, 5.40; N, 3.26%); $v_{max.}$ 1 745, 1 705 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 234 (ϵ 14 180) and 335 nm (12 280); δ_H (60 MHz, $CDCl_3$) 1.56 (3 H, s, Me), 1.70 (3 H, s, Me), 3.79 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.84 (6 H, s, O-Me), 6.30 (1 H, s, olefinic H), 6.65-7.46 (4 H, m, aromatic); m/z 429 (M$^+$, 15%) 287 (20), 184 (100), 156 (24). (iii) Elution with diethyl ether — ethyl acetate, 1:5, gave *2,4a-dihydro-4-methoxy-carbonyl-4a-methyl-2-oxocarbazole* (*15*) (250 mg, 28%) as orange crystals m.p. 168°C (decomp.) (benzene) (Found: C, 71.01; H, 5.14; N, 5.34. $C_{15}H_{13}NO_3$ requires C, 70.58; H, 5.13; N, 5.49%); $v_{max.}$ 3 425 (NH), 1 715, 1 630 cm^{-1} (C=O); λ_{max} (EtOH) 238 (ϵ 9 570), 272 (6 650), and 406 nm (6 660); δ_H (100 MHz, $CDCl_3$) 1.90 (3 H, s, 4a-Me), 3.91 (3 H, s, OMe), 5.84 (1 H, d, J 1.6 Hz, 1-H), 6.90 (1 H, d, J 1.6 Hz, 3-H), 6.75-8.10 (4 H, m, aromatic), 8.50 (1 H, br, N-H, D_2O exchangeable; m/z 255 (M$^+$, 100%), 240 (15), 239 (86), 212 (17), 168 (37), 167 (15).

(b) A solution of DMAD (897 mg, 6.32 mmol) and 2,3-dimethyl-indole (896 mg, 6.18 mmol) in dry benzene (2 ml) was purged with nitrogen and after BTE (0.3 ml) was added, kept 40 h at 0-4°C. The solvent was removed

and the residue was chromatographed on a column (silica). (i) Elution with diethyl ether-petroleum, 1:20, furnished the starting material (25%). (ii) Elution with diethyl ether-petroleum, 1:5, gave (*1*) (106 mg, 6%). (iii) Elution with diethyl ether-petroleum, 1:4, gave *dimethyl 2'-[6,7-bis(methoxycarbonyl)-1,5-dimethyl-3,4-benzo-2-azabicyclo [3.2.0]hepta-3,6-dien-2-yl] fumarate* (*12*) (651 mg, 48%) as orange crystals m.p. 99-101°C (diethyl ether-petroleum) (Found: C, 61.68; H, 5.37; N, 3.17. $C_{22}H_{23}NO_8$ requires C,61.53; H, 5.40; N, 3.26%); $v_{max.}$ 1 725, 1 705 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 328 (ϵ 2 140) and 390 nm (2 230); δ_H (60 MHz, CCl_4) 1.50 (3 H, s, Me), 1.54 (3 H, s, Me), 3.40 (3 H, s, OMe), 3.72 (6 H, s, OMe), 3.75 (3 H, s, OMe), 6.62 (1 H, s, olefinic H), 6.10-7.40 (4 H, m. aromatic); m/z 429 (M$^+$, 13%), 287 (17), 184 (100), 156 (24). (iv) Elution with diethyl ether-ethyl acetate, 1:5, gave (*15*) (190 mg, 12%).

(c) A solution of DMAD (577 mg, 4.06 mmol) and 2,3-dimethyl-indole (576 mg, 3.97 mmol) in dry acetonitrile (3 ml) was purged with nitrogen and after BTE (0.8 ml) was added, kept 5 days at room temperature. The solvent was removed and the residue was chromatographed on a column (silica). (i) Elution with diethyl ether-petroleum, 1:5, gave (*1*) (114 mg, 10%). (ii) Elution with diethyl ether-petroleum, 1:4, gave a mixture of (*12*) and (*13*) (113 mg, 13%). (iii) Elution with diethyl ether-ethyl acetate, 1:4, gave *dimethyl 2'-(2,3-dimethyl-3H-indol-3-yl) maleate* (*17*) (285 mg, 25%) as pale yellow crystals m.p. 90-92°C (diethyl ether-hexane) Found: C, 67.1; H, 5.9; N, 4.6. $C_{16}H_{17}NO_4$ requires C, 66.9; H, 6.0; N. 4.9%); $v_{max.}$ 1 730 (C=O), 1 640 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 214 nm (ϵ 26 990); δ_H (60 MHz, CCl_4) 1.37 (3 H, s, 3-Me), 2.22 (3 H, s, 2-Me), 3.45 (3 H, s, OMe), 3.64 (3 H, s, O-Me), 5.79 (1 H, s, olefinic H), 6.99-7.56 (4 H, m, aromatic); m/z 287 (M$^+$, 65%), 228 (100), 212 (21), 196 (21), 168 (100), 155 (26), 144 (25), 129 (34), 128 (33), 115 (25).

6,7-bis (Methoxycarbonyl)1,5-dimethyl-2-acetyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (*2*). — To a solution of the cyclobutene (*1*) (112 mg, 0.4 mmol) in dry benzene (2 ml) was added anhydrous sodium carbonate (100 mg) and the mixture was stirred at 0-4°C. A solution of acetyl chloride (1.1 g, 14 mmol) in dry benzene (2 ml) was added dropwise and two new portions of sodium carbonate were added at intervals of 30 minutes. The temperature was raised to room temperature and at the end of 2 h the reaction mixture was filtered and the residue washed eith benzene (25 ml). Evaporation of the combined solutions left an oil which was eluted through a short column of silica (5 g) with dichloromethane to give (*2*) (105 mg, 82%) as colourless crystals, m.p. 130-131°C (dichloromethane-petroleum) (Found: C, 65.78; H, 5.76; N, 4.16. $C_{18}H_{19}NO_5$ requires C, 65.64; H, 5.81; N, 4.25%); $v_{max.}$ 1 735, 1 720, 1 650 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) br line; δ_H (60 Mz, $CDCl_3$) 1.57 (3H, s, 5-Me), 1.83 (3 H, s, 1-Me), 2.43 (3 H, s, COMe), 3.77 (3 H, s, OMe), 3.84 (3 H, s, OMe), 6.87-7.73 (4 H, m, aromatic); m/z 329 (M$^+$, 36%), 298 (15), 214 (100), 145 (54), 144 (30).

1-Acetyl-2,5-dimethyl-3,4-bis (methoxycarbonyl)-1H-1-benzazepine (*7*). — The cyclobutene (*2*) (107 mg, 0.33

mmol) was heated at 245ºC for 3 min. The dark residue was chromatographed on a column (silica; dichloromethane) and gave the benzazepine (7) (95 mg, 89%) as colourless crystals, m.p. 117-119ºC (diethyl ether-petroleum) (Found: C, 65.64; H, 5.74; N, 4.09. $C_{18}H_{19}NO_5$ requires C, 65.64; H, 5.81; N, 4.25); $v_{max.}$ 1 725, 1 670 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 227 (ϵ 16 730) and 265 nm (7 400); δ_H (100 MHz, CDCl$_3$) 1.86. 2.20 (total 3 H, 2 x s, 2-Me), 2.51, 2.54 (total 3 H, 2 x s, 1-COMe), 2.62 (3 H, s, 5-Me), 3.72 (3H, s, OMe), 3.74 (3 H, s, OMe), 7.20-7.80 (4 H, m, aromatic); m/z 329 (M$^+$, 12%), 298 (30), 297 (70), 255 (20), 254 (25), 214 (100), 168 (20), 145 (16).

Dimethyl 2'-[2,5-Dimethyl-3,4-bis (methoxycarbonyl)-1H-1-benzazepin-1-yl]Maleate (14). — A mixture of (12) and (13) (232 mg, 0.54 mmol) was refluxed in carbon tetrachloride for 2 days. The solvent was removed and the residue recrystallised from dichloromethane-petroleum to give (14) (193 mg 83%) as colourless crystals, m.p. 133-134ºC (Found: C, 61.17; H, 5.32; N. 3.20. $C_{22}H_{23}NO_8$ requires C, 61.53; H, 5.40; N, 3.26%); $v_{max.}$ 1 730, 1 705 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 235 (ϵ 14 150) and 263 nm (15 450); δ_H (60 MHz, CDCl$_3$) 2.47 (3 H, s, 5-Me), 2.62 (3 H, s, 2-Me), 3.65 (6 H, s, OMe), 3.72 (3 H, s, OMe), 3.77 (3 H, s, OMe), 4.89 (1 H, s, olefinic H), 7.16-7.79 (4 H, m, aromatic); m/z 429 (M$^+$, 10%), 184 (100), 156 (56), 115 (28).

Reaction of 3-Methylindole with Dimethyl Acetylenedicarboxylate. — To a solution of DMAD (750 mg, 5.28 mmol) and 3-methylindole (642 mg, 4.90 mmol) in dry benzene (5 ml), purged with nitrogen and cooled to 0ºC, was added BTE (0.6 ml). The solution was kept 19 h at 0ºC. The solvent was removed and the residue chromatographed on a column (silica, 40 g). (i) Elution with diethyl ether-hexane, 1:4, gave a mixture of two components which was subjected to p.l.c. (silica, 7 consecutive elutions with benzene). The first component (at R$_F$ 0.6) was assigned the structure trans-2,3-dihydro-3α, 4-bis (methoxycarbonyl)-5-methyl-2-(3'-methylindol-3'-yl)-1H-1-benzazepine (19) (102 mg, 10%) and was obtained as colourless crystals, m.p. 195-196ºC (cyclohexane-carbon tetrachloride) (Found: C, 70.9; H, 6.0; N, 6.8 $C_{24}H_{24}N_2O_4$ requires C, 71.3; H, 6.0; N, 6.9%); $v_{max.}$ 3440 (NH), 1 740 (C= O), and 1 610 cm^{-1} (C = N); $\lambda_{max.}$ (CHCl$_3$) 228 (ϵ 32 750), 284 (11 500) and 294 nm (11 350); δ_H (100 MHz, CDCl$_3$) 1.73 (3 H, s, 3'-Me), 2.12 (3 H, d, J 1.0 Hz, 5-Me), 3.38 (1 H, d, J 12.0 Hz, 2-H), 3.83 (6 H, s, OMe), 4.28 (1 H, dq, J 12.0 and 1.0 Hz, 3-H), 4.50 (1 H, br, NH, D$_2$O exchangeable), 5.96 (1 H, s, 2'-H), 6.45-7.72 (8 H, m, aromatic) (irradiation at δ 2.12 caused the double quartet at 4.28 to collapse to a doublet); m/z 404 (M$^+$, 22%), 254 (100), 241 (13), 202 (16), 170 (28), 131 (20), 130 (18). A second component (at R$_F$ 0.5) was assigned the structure cis-2,3-dihydro-3α-4-bis-(methoxycarbonyl)-5-methyl-2-(3'-methylindol-3'-yl)-1 H-1-benzazepine (18) (205 mg, 21%) and was obtained as colourless crystals, m.p. 211-213ºC (dichloromethane-diethyl ether) (Found: C, 71.3; H, 6.0; N, 6.8. $C_{24}H_{24}N_2O_4$ requires C, 71.3; H, 6.0; N, 6,9%); $v_{max.}$ 3 420 (NH), 1 745 (C= O) and 1 665 cm^{-1} (C = N); $\lambda_{max.}$ (EtOH) 226 (ϵ 20 540), 286 (7 920), and 294 nm (7 500); δ_H (100 MHz, CDCl$_3$) 1.57 (3 H, s, 3'-Me),

2.08 (3 H, d, J 1.0 Hz, 5-Me), 3.62 (1 H, d, J 8.0 Hz, 2-H), 3.67 (3 H, s, OMe), 3.78 (3 H, s, OMe), 4.28 (1 H, dq, J 8.0 and 1.0 Hz, 3-H), 4.78 (1 H, br, NH, D$_2$O exchangeable), 5.92 (1 H, s, 2'-H), 6.50-7.63 (8 H, m, aromatic) (irradiation at δ 4.28 causes the doublet at 2.08 to collapse to a singlet); m/z 404 (M$^+$, 100%), 273 (56), 214 (32), 213 (21), 192 (57), 170 (51), 144 (20), 131 (47), 130 (24). (ii) Elution with diethyl ether-hexane, 1: 1, gave 1,2-bis(methoxycarbonyl)-1,2-bis-(3'-methylindol-2'-yl)-ethane (20) (435 mg, 44%) as colourless crystals, m.p. 233-246ºC (decomp.) (dichloromethane-cyclohexane) (Found: C, 70.9; H, 6.0; N, 6.7. $C_{24}H_{24}N_2O_4$ requires C, 71.3; H, 6.0; N, 6.9%); $v_{max.}$ 3 395 (NH), 1 710 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 224 (ϵ 53 970), 285 (17 700) and 293 nm (15 890); δ_H (60 MHz, CDCl$_3$) 1.73 (6 H, s, 3'-Me), 3.73 (6 H, s, OMe), 4.64 (2 H, s, 1-H), 6.85-7.54 (8 H, m, aromatic), and 8.37 (2 H, br, NH, removed by D$_2$O); m/z 404 (M$^+$, 23%), 202 (100), 160 (80), 144 (9), 143 (10), 142 (8), 125 (9). (iii) Elution with diethyl ether gave dimethyl 2'-(3-methylindol-2-yl) maleate (21) (227 mg, 17%) as pale yellow crystals, m.p. 142-143ºC (dichloromethane-cyclohexane) (Found: C, 66.1; H, 5.5; N, 5.0. $C_{15}H_{15}NO_4$ requires C, 65.9; H, 5.5; N, 5.1%); $v_{max.}$ 3 385 (NH), 1 700 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 212 (ϵ 24 750), 253 (7 900) and 352 nm (23 430); δ_H (60 MHz, CDCl$_3$) 2.35 (3 H, s, 3-Me), 3.73 (3 H, s, OMe), 3.97 (3 H, s, OMe), 6.18 (1 H, s, olefinic), 6.92-7.67 (4 H, m, aromatic), and 8.43 (1 H, br, NH, D$_2$O exchangeable); m/z 273 (M$^+$, 86%); 241 (15), 214 (28), 213 (20), 181 (15), 155 (100), 128 (15).

Reaction of 1-Methylindole with Dimethyl Acetylenedicarboxylate — To a solution of DMAD (119 mg, 0.84 mmol) and 1-methylindole (92 mg, 0.70 mmol) in dry CCl$_4$-hexane, 1:3, (2 ml), after purging with nitrogen and cooling to 0ºC, was added BTE (0.1 ml). The solution was kept 3 h at 0ºC. The solvent was removed and the residue immediately subjected to p.l.c. (silica; dichloromethane as eluent). This gave an intense red component which was removed from the plate by extraction of the silica with diethyl ether to give a mixture of two closely running components. The ^{1}H n.m.r. spectrum showed a mixture of (3) and (8), 1: 1. A solution of this mixture in ethanol overnight gave a precipitate of (8) (69 mg, 36%) as orange crystals, m.p. 109-110ºC (lit.[3] 107-108ºC). A second component, R$_F$ 0.9, was a mixture of 1-methylindole and DMAD. No others components were detected under the conditions described above.

Reaction of 1-Methyl-2-phenylindole with Dimethyl Acetylene-dicarboxylate. — (a) To a solution of DMAD (498 mg, 3.51 mmol) and 1-methyl-2-phenylindole[34] (593 mg, 2.86 mmol) in dry carbon tetrachloride (7 ml), purged with nitrogen and cooled to 0-4ºC, BTE was added (0.2 ml). The solution was kept 24 h at 0-4ºC. The solvent was removed and the residue chromatographed on a column (silica, 50 g). (i) Elution with hexane-dichloromethane, 9:1, gave a mixture of starting material (545 mg). (ii) Elution with hexane-dichloromethane, 5: 1, gave a mixture of isomers (22) and (23). Recrystallization from dichloromethane-petroleum gave dimethyl 2'-(1-methyl-2-phenylindol-3-yl) maleate (22) (80 mg, 8%) as pale yellow

crystals, m.p. 109-110°C (Found: C, 72.24; H, 5.47; N, 3.97. $C_{21}H_{19}NO_4$ requires C, 72.19; H, 5.48; N, 4.01%); $v_{max.}$ 1 735 and 1 710 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 232 (ϵ 18 600), 277 (16 240) and 349 nm (13 820); δ_H (60 MHz, CCl_4) 3.41 (3 H, s, 1-Me), 3.51 (3 H, s, OMe), 3.71 (3 H, s, OMe), 6.25 (1 H, s, olefinic), and 7.06-7.96 (9 H, m, aromatic); m/z 349 (M$^+$, 100%), 290 (33), 289 (47), 258 (81), 232 (55), 231 (30), 216 (18), 144 (14). The second solid from recrystallization was dimethyl 2'-(1-methyl-2-phenylindol-3-yl) fumarate (23) (160 mg, 16%), and was obtained as orange crystals, m.p. 123-124°C (Found: C, 72.14; H, 5.52; N, 3.98. $C_{21}H_{19}NO_4$ requires C, 72.19; H. 5.48; N, 4.01%); $v_{max.}$ 1 730 and 1 720 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 236 (ϵ 16 850), 294 (12 150), and 372 nm (2 630); δ_H (60 Mz, CCl_4) 3.38 (3 H, s, 1-Me), 3.44 (3 H, s, OMe), 3.71 (3 H, s, OMe), 6.80 (1 H, s, olefinic) and 6.78-7.68 (9 H, m, aromatic); m/z 349 (M$^+$, 100%), 289 (35), 259 (18), 258 (68), 231 (45), 230 (26). (iii) Elution with hexane-dichloremethane, 1:1, gave 1-methyl-2-phenyl-3,4-bis(methoxycarbonyl)-1H-1-benzazepine (9) (210 mg, 21%) as yellow crystals, m.p. 135-136°C (dichloromethane-cyclohexane) (Found: C, 72.24; H, 5.64; N, 3.88. $C_{21}H_{19}NO_4$ requires C, 72.19; H, 5.48; N, 4.01%); $v_{max.}$ 1 735 and 1 710 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH). 258 nm (ϵ 17 530); δ_H (60 MHz, $CDCl_3$) 2.74 (3 H, s, 1-Me), 3.42 (3 H, s, OMe), 3.80 (3 H, s, OMe), 6.82-7.66 (9 H, m, aromatic) and 7.87 (1 H, s, 5-H); m/z 349 (M$^+$, 18%), 206 (14) 218 (35), 117 (100).

(b) To a solution of DMAD (180 mg, 1.27 mmol) and 1-methyl-2-phenylindole (217 mg, 1.04 mmol) in dry carbon tetrachloride (7 ml), purged with nitrogen and cooled to 0-4°C, was added BTE (0.1 ml). The solution was kept 3 days at 0-4°C. The solvent was removed and the residue chromatographed on a column (silica, 40 g). (i) Elution with hexane-dichloremethane, 5:1, gave a mixture of isomers (22) and (23). Recrystallization from dichloro-methane-petroleum gave (22) (4 mg, 1%) and (23) (4 mg, 1%). (ii) Elution with hexane-dichloromethane, 1:1, gave (9)(319 mg, 88%).

Reaction of 1,2-Dimethylindole with Dimethyl Acetylenedicarboxylate. – A mixture of DMAD (232 mg, 1.68 mmol) and 1,2-dimethylindole (179 mg, 1.23 mmol) was purged with nitrogen, cooled to 0-4°C and BTE (0.2 ml) was added. The reaction was kept 3 h at 0-4°C. The reaction mixture was chromatographed on a column (silica, 25 g). Elution with diethyl ether-hexane, 1:5, gave a mixture of isomers (24) and (25). Recrystallization from methanol gave dimethyl 2'-(1,2-dimethylindol-3-yl) maleate (24) (205 mg, 58%) as pale yellow crystals, m.p. 136-137°C (Found: C, 66,70; H, 5,87; N, 5,06. $C_{16}H_{17}NO_4$ requires C, 66.89; H, 5.96; N, 4.87%); $v_{max.}$ 1 735 and 1 715 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 222 (ϵ 6 240), 274 (3 680), and 351 nm (5 760); δ_H (60 MHz, $CDCl_3$) 2.40 (3 H, s, 2-Me), 3.56 (3 H, s, 1-Me), 3.76 (3 H, s, OMe), 3.89 (3 H, s, OMe), 6.13 (1 H, s, olefinic) and 6.98-7.83 (4 H, m, aromatic); m/z 287 (M$^+$, 100%), 228 (80), 169 (31), 168 (38). The

Table. ^{13}C N.m.r. δ values and multiplicities of cyclobutenes measured in $CHCl_3$ solutions at 25.2 MHz.^{a}

Compd. Carbon	(1)	(2)	(4)^b	(5)	(12)
1	68.4 s	73.3 s	71.9 s	70.1 d	73.0 s
3	148.6 s	142.9 s	149.8 s	150.3 s	143.5 s^c
4	129.8 s	131.6 s	129.3 s	128.6 s	131.1 s
5	57.6 s	56.0 s	56.5 s	53.8 s	57.6 s
6	144.2 s	143.7 s	143.8 s	145.6 s	146.8 s
7	138.7 s	139.1 s	137.1 s	134.6 s	137.7 s
8	124.7 d	125.1 d	123.9 d	123.2 d	124.4 d
9	118.4 d	123.5 d	116.7 d	116.0 d	121.5 d
10	128.5 d	128.7 d	128.8 d	128.3 d	128.5 d
11	110.1 d	115.8 d	106.3 d	106.1 d	111.5 d
12	160.8 s	162,1 s	160.4 s	160.0 s	160.5 s
13	51.6 q	52.1 q	51.1 q	50.8 q	51.5 q
14	160.8 s	160.7 s	160.8 s	160.3 s	160.0 s
15	51.6 q	51.9 q	51.1 q	50.8 q	50.8 q
16	15.0 q	16.2 q	15.1 q	18.1 q	13.9 q
17	17.6 q	16.6 q	15.1 q		15.7 q
18		169.7 s	29.1 q	31.9 q	143.1 s^c
19		25.8 q			107.4 d
20					164.7 s
21					51.5 q
22					165.5 s
23					52.1 q

^{a} The δ values are in ppm downfield from Me_4Si: δ (Me_4Si) = δ ($CHCl_3$) + 77.2 ppm. ^{b} Solvent CCl_4, (Me_4Si) = δ (CCl_4) + 96,0 ppm. ^{c} These assignments could be interchanged.

second solid from recrystallization was *dimethyl 2'-(1,2-dimethylindol-3-yl)fumarate* (*25*) (71 mg, 20%), obtained as orange crystals, m.p. 129-130°C (Found: C, 66.93; H, 5.96; N, 4.91. $C_{16}H_{17}NO_4$ requires C, 66.89; H, 5.96; N, 4.87%); $v_{max.}$ 1 725 and 1 715 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 223 (ϵ 9 640), 281 (5 460), and 284 nm (1 980); δ_H (60 MHz, $CDCl_3$) 2.76 (3 H, s, 2-Me), 3.60 (3 H, s, 1-Me), 3.66 (3 H, s, OMe), 3.78 (3 H, s, OMe), 7.05 (1 H, s, olefinic) and 6.96-7.40 (4 H, m, aromatic); m/z 287 (M^+, 100%), 228 (50), 227 (10), 168 (16), 167 (21).

Reaction of 1,2,3-Trimethylindole with Dimethyl Acetylene-dicarboxylate. – A solution of DMAD (591 mg, 4.2 mmol) and 1,2,3-trimethylindole[35] (526 mg, 3.3 mmol) in dry acetonitrile (20 ml) was purged with nitrogen and after the addition of BTE (0.8 ml) was kept 16 h at 25°C. The solvent was removed and the residue chromatographed on a column (silica, 50 g). (i) Elution with diethyl ether-hexane, 1:9, gave the cyclobutene (*4*) (60 mg, 6%) as a red oil (ii) Elution with diethyl ether gave methyl (Z)-3a, 8a,8-trimethyl-2-oxo-8H-furo[2,3-b]indol-3(2H)-ylidene acetate (*26*) (95 mg, 10%) as pale yellow crystals m.p. 91°C (decomp.) (dichloromethane-petroleum) (Found: C, 66.67; H, 5.92; N, 4.86. $C_{16}H_{17}NO_4$ requires C, 66.87; H, 5.96; N, 4.87%); $v_{max.}$ 1 750 and 1 720 cm^{-1} (C = O); $\lambda_{max.}$ (EtOH) 249 (ϵ 9 840), 291 (2 320), and 321 nm (1 620); δ_H (60 MHz, $CDCl_3$) 1.41 (3 H, s, 3a-Me), 1.68 (3 H, s, 8a-Me), 2.99 (3 H, s, 8-Me), 3.86 (3 H, s, OMe), 6.48 (1 H, s, olefinic), 6.39-7.40 (4 H, m, aromatic); m/z 287 (M^+, 100%), 256 (19), 243 (23) 228 (19), 214 (75), 213 (43), 185 (67), 184 (97), 169 (20), 168 (24), 158 (17). (iii) Elution with ethyl acetate-diethyl ether, 1:4, gave the dienone (*16*) (632 mg, 72%) as orange crystals, m.p. 147-148°C (diethyl ether-hexane).

2,4a-Dihydro-4-methoxycarbonyl-4a,9-dimethyl-2-oxo-carbazole (*16*). – To a cold solution of (*15*) (117 mg, 0.46 mmol) in dry acetonitrile (10 ml) was added potassium carbonate (600 mg). The suspension was stirred and methyl iodide (2.3 g, 16 mmol) was added. After 1 day at 25°C the reaction was filtered and washed with acetonitrile. The solvent was evaporated and the residue was purified by column chromatography (silica, 8 g). Elution with diethyl ether-ethyl acetate, 4:1, gave de dienone (*16*) (121 mg, 98%) as orange crystals, m.p. 147-148°C (diethyl ether-hexane).

ACKNOWLEDGEMENTS

REFERENCES

1 Part 1, Rodrigues J.A.R.; Verardo, L.I., *J. Heterocycl. Chem.*, (1983) *20*, 1263.

2 Acheson R.M.; Elmore, N.F., *Adv. Heterocycl. Chem.*, (1978) *23*, 263.

3 Acheson, R.M.; Bridson, J.N.; Cecil, T.R. and Hands, A.R., *J. Chem. Soc., Perkin Trans.* 1, (1972), 1569.

4 Acheson, R.M.; Bridson, J.N. and Cameron, T.S.; *J. Chem. Soc., Perkin Trans.* (1972) 968.

5 Noland, W.E.; Kuryla, W.C. and Lange, R.F.; *J. Am. Chem. Soc.*, (1959) *81*, 6010.

6 Acheson, R.M.; Choi, M.C.K. and Letcher, R.M.; *J. Chem. Soc., Perkin Trans.* 1 (1981), 3141.

7 Letcher, R.M.; Choi, M.C.K.; Mack, T.C.W. and Acheson, R.M. *J. Chem. Soc.,* Perkin Trans. 1 (1983), 505.

8 Letcher, R.M.; Lai, T.F.; Cheung, K.K.; Choi, M.C.K. and Mack, T.C.W., *J. Chem. Soc.,* Perkin Trans. 1, (1983), 2175.

9 Letcher, R.M.; Choi, M.C.K. and Acheson, R.M., *J. Chem. Soc.,* Perkin Trans. 1, (1983), 515.

10 Letcher, R.M.; Choi, M.C.K.; Acheson, R.M. and Prince, R.J., *J. Chem. Soc.,* Perkin Trans. 1, (1983), 501.

11 Plieninger H. and Wild, D., *Chem. Ber.*, (1966), *99*, 3070.

12 Davis, P.D. and Neckers, D.C., *J. Org. Chem.*, (1980), *45*, 456.

13 Davis, P.D.; Neckers, D.C. and Blount, J.R., *J. Org. Chem.* (1980), *45*, 462.

14 Fried, F.; Taylor, J.B. and Westwood, R., *J. Chem. Soc.*, Chem. Commun. (1971), 1226.

15 Dewar, M.T.S. and Trinajstic, N. *Tetrahedron* (1970), *26*, 4269.

16 Ikeda, M.; Ohno, K.; Takahashi, M. Uno, T.; Tamura, Y. and Kido, M., *J. Chem. Soc.,* Perkin Trans. 1, (1982), 741.

17 Jackman, L.M. and Wiley, R.H., *J. Chem. Soc.*, (1960), 2881.

18 Vogeli, V. and Von Philipsborn, W., *Org. Magn. Reson.*, (1975), *7*, 617.

19 Letcher, R.M. and Acheson, R.M., *Org. Magn. Reson.*, (1981), *16*, 316.

20 Paquette, L.A., *J. Am. Chem. Soc.*, (1964), *86*, 4096, and references therein.

21 Matsumoto, K.; Nakamura, S.; Uchida, T. and Acheson, R.M., *Heterocycles*, (1980), *14*, 1959.

22 Davis, P.D. and Neckers, D.C., *Tetrahedron Lett.*, (1978), 2979.

23 Johnson, D.C., *Diss. Abstr.*, (1962), *23*, 834.

24 Van B. Verpoorte, T.A.; Riegman, R.L.M.; Hylands, P.J. and Bisset, N.G., *Org. Magn. Reson.*, (1984), *22*, 328; Fritz, H. and Winkler, T., *Helv. Chim. Acta*, (1976), *59*, 903; Gontarel, R.; Pais, M.; Gottlieb, H.E. and Wenkert, E. *Tetrahedron Lett.*, (1978), 1235; Srinivasan, P.R. and Lichter, R.L., *Org. Magn. Reson.*, (1976), *8*, 198.

25 Masamuni, S.; Nakamura, N.; Suda, M. and Ona, H., *J. Am. Chem. Soc.*, (1973), *95*, 8481.

26 Berger, S. and Rieger, A., *Tetrahedron*, (1972), *28*, 3123.

27 Cooper, J.W., "Spectroscopic Techniques for Organic Chemists", *John Wiley & Sons,* New York, (1980); Breitmaier, E. and Voelter, W., "^{13}C NMR Spectroscopy Methods and Applications in Organic Chemistry", 2nd. ed., Verlag Chimie, Weinheim, 1978.

28 Iamamura, K.; Nakazawa, T. and Murata, I., Angew. Chem., Int. Ed. Engl., (1980), *19*, 543.

[29] Cook, A.G., in "Enamines", ed. A.G. Cook, Marcel Dekker, New York, (1969), p. 230.

[30] Huisgen, R., *Acc. Chem. Res.*, (1977), *10*, 117.

[31] Epiotis, N.D., *J. Am. Chem. Soc.*, (1973), *95*, 1191.

[32] Reinhoudt, D.W.; Verboom, W.; Visser, G.W.; Trompenaars, W.P.; Harkema, S. and van Hummel, G.J., *J. Amer. Chem. Soc.*, (1984), *106*, 1341.

[33] Hall, R.H.; den Hertog, H.J.; Jr. and Reinhoudt, D.N., *J. Org. Chem.*, (1982), *47*, 967.

[34] Kissman, H.M.; Farnsworth, D.W. and Witkop, B. *J. Am. Chem. Soc.*, (1952), *74*, 3948.

[35] Janetzky, E.F. and Verkade, P.E., *Rec. Trav. Chim.*, (1946), *65*, 691.

ARTIGO

ESTUDOS EM FILMES ANÓDICOS DE ÓXIDO DE TÂNTALO

Uílame Umbelino Gomes[a],
José Francisco Julião[b] e Daltro Garcia Pinatti[c]

[a]*Departamento de Física — Universidade Federal do Rio Grande do Norte — 59072 — Natal — RN;*
[b]*Departamento de Física — Universidade Federal do Ceará — 60000 — Fortaleza — CE;*
[c]*Instituto de Física — Universidade Estadual de Campinas — 13100 — Campinas — SP e*
Fundação de Tecnologia Industrial — Centro de Materiais Refratários — 12600 — Lorena — SP

ABSTRACT

Polycrystalline Tantalum Electrodes have been anodized in 1% H_3PO_4 electrolytic solution forming Ta_2O_5 anodic Films of different colors. The film thickness was determined as function of the anodic voltage. The differential capacitance method is used to obtain Mott-Schottky plots to find the donor density and a tentative was made to correlate the film thickness to the depletion layer width.

1. INTRODUÇÃO

O processo de oxidação anódica do Ta, a exemplo do Nb[1], resulta em filmes superficiais de Ta_2O_5 com coloração e propriedades semicondutoras fortemente dependentes da espessura dos filmes[1,2]. A espessura dos filmes pode ser controlada através do potencial de anodização[1,3]. A cinética de crescimento desses filmes tem sido estudada através dos trabalhos de Young[4], Haring[5] além de outros[7,8,9].

Após o processo de formação do filme anódico, o sistema Ta - Ta_2O_5 eletrólito (H_3PO_4 1%), pode ser descrito através do modelo de um capacitor de placas planas e paralelas onde a capacitância total (C) é a capacitância da camada de cargas espaciais do filme de Ta_2O_5. Nesse caso a relação entre a capacitância (C), área (A) e espessura do filme (X) é dada pela equação[10],

$$C = \Sigma \ \Sigma o A / X \qquad (1)$$

onde Σ é a constante dielétrica relativa do Ta_2O_5 e Σo a constante dielétrica do vácuo. No caso de materiais porosos, por exemplo, sinterizados de metais refratários, a área é um parâmetro extremamente importante a ser determinado. Através de medidas experimentais de C e X, o valor de A pode ser obtido a partir da Eq. 1.

A medida de capacitância diferencial pelo método de detecção sensível à fase (DSF), feita com auxílio de um amplificador "lock-in", usando um sistema de três eletrodos[11], apresenta sensíveis vantagens sobre a medida efetuada com uma ponte de capacitância[12]. Pelo método DSF observa-se o comportamento da capacitância em função da polarização externa aplicada ao eletrodo de Ta. Através de gráficos Mott-Schottky pode-se obter informações sobre o potencial de banda plana (V_{BP}), densidade de doadores e largura da camada de depleção de cargas do filme anódico.

Neste trabalho são apresentados filmes anódicos de Ta_2O_5, estudada a relação entre espessura dos filmes e o potencial de anodização, onde a espessura foi determinada através da lei de Faraday assim como pesagem em microbalança. Sequencialmente, foram feitas medidas de capacitância em função da polarização do filme e através de gráficos Mott-Schottky determinou-se a largura da camada de depleção de elétrons (L) e densidade de doadores (N_D) para cada caso, como também o potencial de banda plana do filme de Ta_2O_5.

2. PARTE EXPERIMENTAL

As amostras, folhas laminadas de Ta foram obtidas de lingotes refinados em forno de feixe eletrônico, produzidas no Centro de Materiais Refratários da Fundação de Tecnologia Industrial-Lorena(SP). A preparação