methanol, melted at 137–139°. Mixed m.p. with IV 123–129°; λ_{max} (methanol): 284 mμ (12,600).

Anal. Calcd. for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.33; H, 7.22; N, 10.35.

Infrared showed no NH absorption either in potassium bromide or in solution ($Cl_2C{=}CCl_2$, CS_2). NMR (tetramethylsilane standard): τ (p.p.m.) 4.77, 4.98.

Attempts at preparation of IVa from 2-benzalcyclohexanone phenylhydrazone in ethanol–hydrochloric acid using longer heating times gave a mixture of pyrazolines IVa and IV.

Isomerization of IVa *to* IV. When pyrazoline IVa was heated in glacial acetic acid under reflux for 4 hr. and the product was chromatographed, pyrazoline IV was isolated in 30% yield. The two pyrazolines were not isomerized by chromatography over aluminum oxide, each isomer being recovered unchanged.

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Diels-Alder Reactions of 1-Carbomethoxypyrroles and Dimethyl Acetylenedicarboxylate

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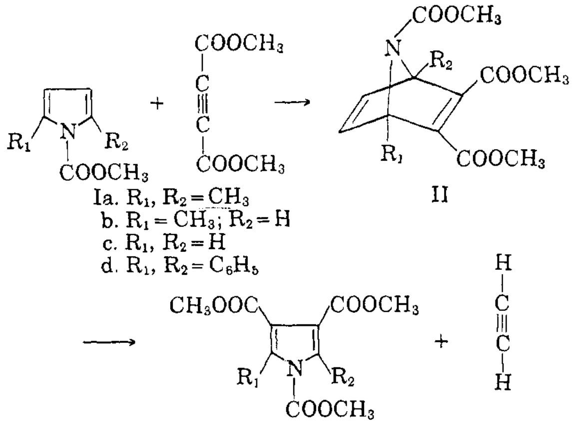
As part of a research program directed toward the study of electron deficient nitrogen compounds it appeared desirable to synthesize derivatives of 7-azabicyclo[2.2.1]hepta-2,5-diene (II). A possible entry into this ring system seemed to be given by the Diels-Alder reaction of a suitably substituted pyrrole with dimethyl acetylenedicarboxylate. Two examples of normal additions of dienophiles to pyrroles have been reported in the recent literature. The addition of benzyne to 1-methylpyrrole[1] and the reaction of acetylenedicarboxylic acid with 1-benzylpyrrole[2] both give moderately stable, normal Diels-Alder adducts in poor yields. All other examples of attempted diene syntheses involving pyrroles led to α-substitution products,[3] although initial normal addition followed by rearrangement cannot be excluded as a possible mechanism for these reactions.



Ia. $R_1, R_2 = CH_3$
b. $R_1 = CH_3$; $R_2 = H$
c. $R_1, R_2 = H$
d. $R_1, R_2 = C_6H_5$

IIIa. $R_1, R_2 = CH_3$
b. $R_1 = CH_3$; $R_2 = H$
c. $R_1, R_2 = H$

It was hoped that carbomethoxy substitution on nitrogen would decrease the aromatic character of the pyrrole and would tend to stabilize the adduct sufficiently to allow normal Diels-Alder addition to occur in preparative yields. Furthermore, alkyl substituents on both the 2 and 5 positions should minimize the possibility of an α-substitution reaction. When equimolar quantities of methyl 2,5-dimethylpyrrole-1-carboxylate (Ia) and dimethylacetylenedicarboxylate were heated to 160° a crystalline product was isolated from the reaction mixture which was identified as trimethyl 2,5-dimethylpyrrole-1,3,4-tricarboxylate (IIIa) by spectral and chemical evidence. The NMR spectrum revealed the presence of two equivalent allylic methyl groups (7.75 τ) and two equivalent (6.35 τ) and one different (6.15 τ) methoxy groups. Base-catalyzed hydrolysis led to 2,5-dimethylpyrrole-3,4-dicarboxylic acid, which was characterized as its diethyl ester. In a subsequent run the gas which began to escape from the reaction mixture at 140° was identified as acetylene.

The formation of IIIa seems to be explained best by assuming the transient formation of the normal adduct II which undergoes a reverse Diels-Alder reaction to give the observed product.[4] Attempts to obtain the initial adduct at temperatures below 140° resulted in the recovery of starting material.

The scope of this reaction has been extended to include the formation of trimethyl 2-methylpyrrole-1,3,4-tricarboxylate (IIIb) and trimethylpyrrole 1,3,4-tricarboxylate (IIIc) from methyl 2-methylpyrrole-1-carboxylate (Ib) and methyl pyrrole-1-carboxylate (Ic), respectively, and dimethyl acetylenedicarboxylate.[5] The latter two cases demonstrate that α-alkyl substitution is not a necessary factor in determining the mode of decomposition of the Diels-Alder adduct.

The attempted reaction of methyl 2,5-diphenylpyrrole-1-carboxylate (Id) with dimethyl acetylenedicarboxylate resulted in recovery of starting material. Similarly, attempted use of maleic anhy-

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[4] A similar reverse reaction is the thermal decomposition of 1-methyl-2,3-dicarboethoxycyclohexene-2 oxide-1,4 to ethylene and 2-methyl-3,4-dicarboethoxyfuran, K. Alder and H. F. Rickert, *Ber.*, **70**, 1354 (1937).

[5] While this work was in progress R. M. Acheson and J. M. Vernon [*J. Chem. Soc.*, 457 (1961)] reported the formation of trimethyl pyrrole-1,3,4-tricarboxylate by the same method.

dride, dimethyl fumarate, diphenylacetylene, and tetracyanoethylene as dienophiles in the aforementioned reactions was unsuccessful.

EXPERIMENTAL

Methyl 2,5-dimethylpyrrole-1-carboxylate. A suspension of the salt from 81.0 g. (0.85 mole) of 2,5-dimethylpyrrole[6] and 33 g. (0.85 mole) of potassium in 750 ml. of anhydrous ether was prepared by the method of Reynolds.[7] The suspension was cooled in an ice-salt bath, and with vigorous stirring 82.3 g. (0.86 mole) of methyl chloroformate was slowly added through a dropping funnel. The precipitated potassium chloride was removed by filtration and washed with ether. Evaporation of the ether at reduced pressure and distillation of the residue yielded 78.0 g. (59%) of a colorless oil which slowly solidified, b.p. 86–90° (21 mm.), m.p. 38°; ultraviolet spectrum (methanol): λ_{max} 250 mμ (5350).

Anal. Calcd. for $C_8H_{11}NO_2$ (153.18): C, 62.72; H, 7.24; N, 9.15. Found: C, 62.85; H, 7.26; N, 9.13.

Methyl 2-methylpyrrole-1-carboxylate. To a stirred suspension of the salt resulting from the reaction of 7 g. (0.18 mole) of potassium with 14.8 g. (0.18 mole) of 2-methylpyrrole[8] in 100 ml. of ligroin (90–100°) was added 19.0 g. (0.20 mole) of methyl chloroformate through a dropping funnel. The solution was filtered and distilled yielding 12.6 g. (51%) of a sweet-smelling oil, b.p. 63–65° (10 mm.), n^{20}_D 1.493, ultraviolet spectrum (methanol): λ_{max} 242 mμ (3640), 227 mμ (7280).

Anal. Calcd. for $C_7H_9NO_2$ (137.14): C, 61.30; H, 5.15; N, 10.21. Found: C, 61.35; H, 5.21; N, 10.14.

Methyl pyrrole-1-carboxylate. With vigorous stirring 49.0 g. (0.52 mole) of methyl chloroformate in 150 ml. of anhydrous ether was added through a dropping funnel to a suspension of pyrrole potassium salt[7] in 500 ml. of anhydrous ether from 33.5 g. (0.50 mole) of pyrrole and 19 g. (0.5 mole) of potassium at a rate to prevent uncontrolled refluxing. The solution was filtered and the ether was evaporated at reduced pressure. Distillation of the resulting brown oil yielded 41.2 g. (66%) of a sweet-smelling oil, b.p. 71–73° (21 mm.); n^{20}_D 1.487; ultraviolet spectrum (methanol): λ_{max} 230 mμ (8300).

Anal. Calcd. for $C_6H_7NO_2$ (125.13): C, 57.58; H, 5.64; N, 11.19. Found: C, 57.46; H, 5.60; N, 11.27.

Methyl 2,5-diphenylpyrrole-1-carboxylate. In a 250 ml. three-neck flask fitted with a gas inlet tube, reflux condenser with drying tube and a magnetic stirrer were placed 5.0 g. (0.02 mole) of 2,5-diphenylpyrrole[9] and 50 ml. of ligroin (b.p. 90–100°). The ligroin was warmed to dissolve the pyrrole and *ca.* 1 g. (0.02 mole) of potassium was added. After refluxing and stirring the mixture for 3 hr. under dry nitrogen, 2.5 g. (0.03 mole) methyl chloroformate was added and refluxing was then continued for 30 min. The mixture was cooled slightly and 5 ml. of glacial acetic acid was added with rapid stirring to react with tiny fragments of excess potassium. The contents of the flask were poured into 200 ml. of water and 100 ml. of benzene. The organic layer was dried over magnesium sulfate and evaporated at reduced pressure leaving a greenish brown oil which subsequently solidified. Recrystallization from ligroin (b.p. 90–100°) gave 4.3 g. (67%) of pale yellow cubic crystals, m.p. 98–100°. An analytical sample was sublimed at 90–95° (0.04 mm.), m.p. 100°; ultraviolet spectrum (methanol): λ_{max} 292 mμ (17,200), 224 mμ (13,500), 202 mμ (30,500).

Anal. Calcd. for $C_{18}H_{15}NO_2$ (277.31): C, 77.96; H, 5.45; N, 5.05. Found: C, 77.98; H, 5.65; N, 4.93.

Reaction of methyl pyrrole-1-carboxylates with dimethyl acetylenedicarboxylate. Equimolar amounts of the methyl pyrrole-1-carboxylates and dimethyl acetylenedicarboxylate were placed in a 50-ml. two-neck flask fitted with a gas take-off tube running into a solution containing ammoniacal cuprous chloride. The flask was heated in an oil bath and flushed with nitrogen to carry the acetylene into the cuprous chloride solution. At 140° acetylene slowly evolved as evidenced by the slight formation of cuprous acetylide. Evolution of acetylene became very rapid at 160°. The temperature was maintained at 160–170° for 3 hr. The resulting black oil was distilled from the reaction flask at 0.1 mm. to separate the product from starting material and tar. The amount of acetylene evolved was determined by decomposing the filtered and washed cuprous acetylide with 10% hydrochloric acid, passing in hydrogen sulfide, and weighing the filtered and dried cuprous sulfide.

Trimethyl 2,5-dimethylpyrrole-1,3,4-tricarboxylate: Five grams (0.03 mole) of methyl 2,5-dimethylpyrrole-1-carboxylate and 4.7 g. (0.03 mole) of dimethyl acetylenedicarboxylate gave a yellow waxy solid, b.p. *ca.* 150° (0.07 mm.). Recrystallization from carbon tetrachloride yielded 4.6 g. (51%) of colorless crystals, m.p. 94°; ultraviolet spectrum (methanol): λ_{max} 265 mμ (5990); NMR spectrum: τ = 6.15 (1), 6.35 (2), 7.57 (2).

Anal. Calcd. for $C_{12}H_{15}NO_6$ (269.25): C, 52.53; H, 5.62; N, 5.20. Found: C, 52.58; H, 5.71; N, 5.07.

The cuprous sulfide obtained corresponded to 30.3% yield of acetylene.

Trimethyl pyrrole-1,3,4-tricarboxylate. Methyl pyrrole-1-carboxylate (2.5 g., 0.02 mole) and 2.9 g. (.02 mole) of dimethyl acetylenedicarboxylate gave a crystalline waxy solid, b.p. *ca.* 140° (0.25 mm.). Recrystallization from carbon tetrachloride yielded 2.1 g. (43.5%) of colorless crystals, m.p. 67° (reported m.p. 69°)[5]; ultraviolet spectrum (methanol): λ_{max} 251 mμ (9700); NMR spectrum: τ = 3.10 (2), 6.31 (6), 6.38 (3).

Anal. Calcd. for $C_{10}H_{11}NO_6$ (241.20): C, 49.79; H, 4.60; N, 5.81; Found: C, 49.88; H, 4.69; N, 5.69.

The cuprous sulfide obtained corresponded to 25.0% yield of acetylene.

Trimethyl 2-methylpyrrole-1,3,4-tricarboxylate. Methyl 2-methyl-1,3,4-tricarboxylate (2.8 g., 0.02 mole) and 2.9 g. (0.02 mole) of dimethyl acetylenedicarboxylate yielded a crystalline waxy solid, b.p. *ca.* 160° (0.25 mm.). Recrystallization from carbon tetrachloride gave 1.6 g. (31.0%) of colorless crystals, m.p. 64°; ultraviolet spectrum (methanol): λ_{max} 260 mμ (6700); NMR spectrum: τ = 2.45 (1), 6.06 (3), 6.27 (6), 7.45 (3).

Anal. Calcd. for $C_{11}H_{13}NO_6$ (255.22): C, 51.76; H, 5.13; N, 5.49. Found: C, 51.77; H, 5.09; N, 5.43.

The cuprous sulfide obtained corresponded to 19.0% yield of acetylene.

Pyrrole-3,4-dicarboxylic acids. The trimethyl pyrrole-1,3,4-tricarboxylates were refluxed for 2 hr. in 25 ml. of 50% methanol containing 2.0 g. of sodium hydroxide. At the end of this period 50 ml. of water was added; the solutions were filtered and acidified with concentrated hydrochloric acid. The precipitated acids were collected by filtration and air dried. The diethyl and dimethyl esters were obtained by treatment at room temperature with excess ethereal diazoethane and diazomethane respectively. The excess reagent and solvent were evaporated at reduced pressure and the esters were either recrystallized from benzene or sublimed.

2,5-Dimethylpyrrole-3,4-dicarboxylic acid. Two grams (0.0075 mole) of trimethyl 2,5-dimethylpyrrole-1,3,4-tricarboxylate yielded 0.9 g. (65%) of a grey powder, recrystallized from 50% methanol, m.p. 260–265° dec. (reported m.p. 250–251)[10]; ultraviolet spectrum (methanol): λ_{max} 270 mμ (7370), 207 mμ (9950).

The diethyl ester had a m.p. of 94–97° (reported m.p.

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96–97°)[10]; ultraviolet spectrum (methanol): λ_{max} 266 mμ (8030), 212 mμ (9450).

The dimethyl ester had a m.p. of 118–119°.

Anal. Calcd. for $C_{10}H_{13}NO_4$ (211.21): C, 56.86; H, 6.20; N, 6.63. Found: C, 56.65; H, 6.26; N, 6.59.

2-Methylpyrrole-3,4-dicarboxylic acid. Trimethyl 2-methylpyrrole-1,3,4-tricarboxylate (1.3 g., 0.0051 mole) yielded 0.7 g. (81%) of a light grey powder, m.p. 230–234° dec. (reported m.p. 236–237° dec.)[11]; ultraviolet spectrum (methanol): λ_{max} 261 mμ (6730), 242 mμ (5300), 208 mμ (9820).

The diethyl ester had a m.p. of 121° (reported m.p. 124–125°)[11]; ultraviolet spectrum (methanol): λ_{max} 260 mμ (7240), 212 mμ (9450).

The dimethyl ester had a m.p. of 159°.

Anal. Calcd. for $C_9H_{11}NO_4$ (197.19): C, 54.82; H, 5.62; N, 7.10. Found: C, 54.75; H, 5.58; N, 7.13.

Pyrrole-3,4-dicarboxylic acid. Trimethylpyrrole-1,3,4-tricarboxylate (2.1 g., 0.0087 mole) yielded 1.1 g. (80%) of a light-gray powder m.p. 290–297° dec. (reported m.p. 290–292° dec.)[11]; ultraviolet spectrum (methanol): λ_{max} 258 mμ (5610), 244 mμ (5800), 210 mμ (7480).

The diethyl ester had a m.p. of 151–152° (reported m.p. 153–155°)[11]; ultraviolet spectrum (methanol): λ_{max} 253 mμ (7550), 206 mμ (10,350).

The dimethyl ester had a m.p. of 241–242° (reported m.p. 244°).[5]

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The Reaction of Dihalonortricyclenes with Magnesium, Lithium, and Phenyllithium

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Elimination-rearrangement reactions have been reported by Schubert[1] with open chain dihalides and 1,1-bishalomethyl cyclic compounds and iodide. Applequist[2,3] found somewhat similar reactions in the reactions of 9-bromoanthracene photodimer. Wiberg[4] used a ring-bridging dehydrohalogenation in the cyclobutane series (though it is probably best considered an active methylene displacement type reaction). The present note reports the formation of bicycloheptadiene from the reaction of 3,5-dibromo- and diiodonortricyclenes with magnesium, lithium and phenyllithium; the reaction involves 1,4 elimination of halogen with cleavage of the cyclopropane ring.

The preparation of 3,5-dibromonortricyclene[5,6] and 3,5-diiodonortricyclene[7] was accomplished in the usual manner by reaction of bicycloheptadiene with halogen. Olefinic products which accompany the nortricyclenes were removed by reaction with permanganate.[8] Winstein has shown that the dibromonortricyclene produced in this manner is a mixture of *cis-* and trans isomers.[8] The diiodonortricyclene was shown to have the indicated ring structure by hydrogenation over platinum in alcoholic potassium hydroxide to yield nortricyclene. It was presumed that the diiodonortricyclene was also a mixture of *cis* and *trans* isomers, but no separation was attempted.

Reaction of diiodonortricyclene with magnesium in ether gave 75% of bicycloheptadiene which was identified by vapor phase chromatography and infrared spectrum. One g.-atom of magnesium was required per mole of dihalide. The reaction of diiodonortricyclene with lithium in ether or with phenyllithium in ether also led to bicycloheptadiene in 70% and 73% yields, respectively. Iodobenzene was present in the reaction mixture from phenyllithium. Reaction of dibromonortricyclene with magnesium or lithium in ether also gave bicycloheptadiene, though in somewhat lower yields (49% and 43% respectively).

The mechanism of the elimination appears to involve attack at one halogen by the metal (or phenyllithium) to yield the product directly or else to yield a monometallated product which subsequently loses halide. Applequist[2] found that monometallated compound with an appreciable lifetime appeared to form from 9-bromoanthracene photodimer, since the intermediate apparently could be partitioned to form mixtures of three products.

In view of the report of Winstein[8] concerning the possible toxicity of this series of compounds, work has been discontinued with them. Contact of diiodonortricyclene with the hands led to severe, though painless, blistering.

EXPERIMENTAL

Diiodonortricyclene.[7] A solution of 127 g. of iodine (0.5 mole) in 500 ml. of ether was added to a solution of 46 g. of bicycloheptadiene[9] (0.5 mole) in ether with stirring. The color of iodine persisted after addition of 460 ml. of the iodine solution, and addition was stopped. The ether solution was washed with 20% sodium bisulfite solution (3 × 100 ml.) and water, and the solvent was evaporated at reduced pressure. The residue was treated with saturated potassium permanganate solution until the violet color

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