with stirring. The crude solid which separated was filtered, dissolved in benzene, and chromatographed on an alumina column. The eluted solid was recrystallized from a benzene–hexane mixture to yield 1.55 g (45%) of yellow needles, mp 161.5–163°. Sodium hydrosulfite reduction of the diazoamino compound yielded only aniline and 5-aminoquinoline as products. Analyses and melting points for the triazenes are in Table II.

Rearrangement of 1-Phenyl-3-(5-quinolyl)triazene in Hydrochloric Acid (Typical Procedure).—A solution of 2 g of the diazoamino compound in 40 ml of ethanol was added to 40 ml of 50% hydrochloric acid at 0°. The solution was maintained at the temperature for 3 hr with intermittent shaking and placed in a refrigerator for 3 days. The reaction mixture was poured on ice and neutralized with ammonium hydroxide. The solid which separated was dissolved in benzene and chromatographed on an alumina column to yield 5-amino-8-phenylazoquinoline as the only product.

Determination of the Diazo Compounds Formed in the Rearrangement of 1-Phenyl-3-(5-quinolyl)triazene (Typical Trapping Procedure).—A solution of 2 g of the diazoamino compound in 25 ml of concentrated hydrochloric acid was allowed to stand at 0° for 1 hr. The mixture was then poured on ice and run slowly into a cold solution of naphthol in dilute sodium hydroxide and stirred for 1 hr at 0°. The mixture was then acidified and the precipitate was filtered and dried. The acid-insoluble product was 1-phenylazo-2-hydroxynaphthalene. When the solution was basified with sodium hydroxide 5-aminoquinoline was recovered.

Registry No.—I, 7771-16-6; II, 7731-50-2; III, 7775-90-8; IV, 7731-51-3; V, 7731-52-4; VI, 7731-53-5; VII, 7775-86-2; 5-amino-8-phenylazoquinoline, 7731-54-6; 6-amino-5-phenylazoquinoline, 7731-55-7; 8-amino-5-phenylazoquinoline, 7771-17-7; 5-amino-6-methyl-8-phenylazoquinoline, 7731-56-8; 8-amino-7-methyl-5-phenylazoquinoline, 7731-57-9; 5-amino-8-methyl-6-phenylazoquinoline, 7731-58-0; 8-amino-5-phenylazolepidine, 7731-59-1; 8-amino-7-phenylazolepidine, 7731-60-4.

Diels–Alder Reactions of Indene

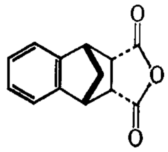
CHARLES F. HUEBNER,[1] PATRICIA L. STRACHAN,[1] ELLEN M. DONOGHUE,[1] NATALIE CAHOON,[1] LOUIS DORFMAN,[1] R. MARGERISON,[1] AND ERNEST WENKERT[2]

Chemical Research Division, CIBA Pharmaceutical Company, Summit, New Jersey, and Department of Chemistry, Indiana University, Bloomington, Indiana

Received September 8, 1966

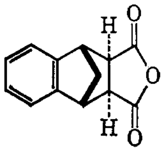
Details have been added to the indene–maleic anhydride reaction as well as a description of the *exo* adduct (II). The correct structure for the adduct with azodiformate is presented (VI). The reaction of indene with tetracyanoethylene leads to the cyclobutane (VIII) and pyrolysis of the latter is shown to lead, by a novel process, to the benzoquinoline (X). An interpretation of the reaction of indene and substituted indenes with two molecules of acetylene dicarboxylate is presented. The two different courses of the reaction are directed by a methyl substituent on the indene.

We have been interested for several years in the Diels–Alder reaction of indene. Our attention was drawn to this subject when it was found that the imide derived from the known maleic anhydride–indene adduct (I)[3] had strong sedative action of a unique kind.[4] The reactions of indene with maleic anhydride,[3] dimethyl acetylenedicarboxylate,[3] and diethyl azodiformate[5,6] appear in the voluminous catalog of examples studied by Diels and Alder. Having already shown the structure of the acetylenedicarboxylate adduct to be XIa,[7] we now wish to comment on its chemistry, to add some details to the indene maleic anhydride reaction, to present the correct structure of the azodiformate adduct, and to describe the reaction of indene with tetracyanoethylene.

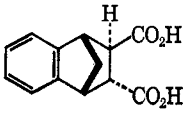


I

Alder and co-workers[3] have reported the preparation of both *endo* (I) and *exo* (II) isomers of the indene–maleic anhydride adduct. The former was prepared by a reaction of the olefin and the anhydride in benzene solution at 250°,[8] while the latter was obtained by esterification of I, alkaline epimerization to the *trans* diester, saponification, and pyrolysis of the resultant acid (III) at 260°. Repetition of these reactions indicated that the Alder *exo* compound (mp 159°) was a 1:1 mixture of I and II which could be separated by vapor phase chromatography. The actual *exo* isomer (until now not described) was shown to possess mp 252–253° and to be produced in small quantity in the preparation of the *endo* isomer. The formation of the *endo* compound (I) was improved in yield (42%) and in convenience by carrying out the Diels–Alder reaction in tetralin solution at 198° for 4.5 hr in the presence of a small amount of hydroquinone.



II



III

Resolution of the above problem of *endo–exo* isomerism was greatly aided by the use of proton magnetic resonance spectroscopy. In view of the difference of the magnetic environment of the hydrogens α to the carboxyl groups in *trans* diacid III, their pmr signals are distinct and characteristic of their stereochemical configuration. The spectrum of a solution of the acid in 1 *N* sodium deuterioxide in deuterium oxide revealed the *endo* hydrogen as a doublet of triplets at 3.03 ppm (from tetramethylsilane) and the

---

[1] CIBA Pharmaceutical Co., Summit, N. J.

[2] Indiana University, Bloomington, Ind.

[3] K. Alder, F. Pascher, and H. Vogt, *Ber.*, **75**, 1501 (1942).

[4] The report of a detailed investigation of a large number of congeners of this imide together with their pharmacology will be presented elsewhere. See C. F. Huebner, Belgian Patent 634,888 (1964).

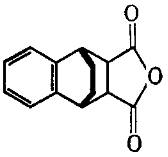
[5] O. Diels and K. Alder, *Ann.*, **450**, 237 (1926).

[6] K. Alder and H. Niklas, *ibid.*, **585**, 97 (1954).

[7] K. W. Muir, G. A. Sim, P. Strachan, and C. F. Huebner, *Chem. Ind.* (London), 1581 (1964).

[8] *Cf.* J. A. Berson and G. B. Aspelin, *Tetrahedron*, **20**, 2697 (1964).

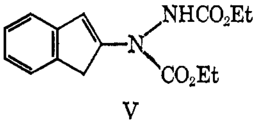
exo hydrogen as a triplet at 3.86 ppm. The pmr spectra of deuteriochloroform solutions of the anhydrides I and II exhibited α-hydrogen multiplets at 3.78 and 3.08 ppm, respectively. The spectra of a number of *exo*- and *endo*-benznorbornene (1,2,3,4-tetrahydro-1,4-methanonapthalene) derivatives based on I and II showed the difference of chemical shifts of α hydrogens of sets of stereoisomers to average a $\Delta\delta = 0.7$ ppm value. This appears to be approximately double the value found[9] and calculated[10] for homologous benzbicyclo[2.2.2]octene derivatives (*e.g.*, IV) as well as calculated for our benznorbornene derivatives.



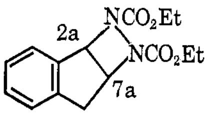
IV

Since the *exo* anhydride (II) had been obtained only in the Diels–Alder reaction carried out at 250° indicating a lower specificity at higher temperature, it became of interest to discover whether it was formed by isomerization of the *endo* anhydride (I). However, the Diels–Alder process could be shown to be irreversible, since heating either I or II under such drastic conditions as 280° for 3 days in sealed tubes left each anhydride unchanged (as indicated by vapor phase chromatographic analysis).

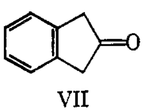
The adduct of indene and diethyl azodiformate described by Diels[5] had been assigned two possible structures, the indene V and the diazetidine VI. More recently Alder[6] showed preference to structure V because of the conversion of the adduct to 2-indanone (VII) and hydrazine on treatment with acid. However, spectral measurements now showed that the alternate structure VI is the correct one. No NH absorption band was evident in the infrared spectrum nor did the pmr spectrum show the vinyl proton demanded by V. Instead, the pmr spectrum in deuteriochloroform was fully consonant with structure VI. The 2a-hydrogen signal appeared as a doublet at 5.45 ppm ($J = 5.1$ cps), the hydrogen at 7a as a complex of ten lines centered at 5.01 ppm, and the two methylene hydrogens (ABX system) as a septet centered at 3.22 ppm. The hydrolytic transformation of VI to 2-indanone (VII) can be explained on the basis of a prior benzylic C–N bond rupture, reminiscent of the acid-catalyzed conversion of 1-indanylhydrazine to indene and hydrazine,[11] and hydrolysis of the intermediate enamine of type V.



V

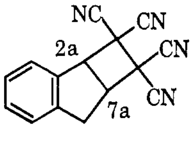


VI

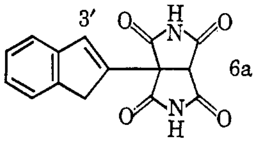


VII

The powerful dienophilic nature of tetracyanoethylene has been illustrated by the work of Middleton, *et al.*[12] Interaction of the cyanocarbon with indene yielded a 1:1 adduct whose pmr analysis permitted assignment of structure VIII. As in the case of the azodiformate adduct the pmr spectrum in acetone revealed four nonaromatic hydrogen signals in 1:1:2 ratio [a doublet at 5.05 ppm ($J = 7.6$ cps, hydrogen at 2a), a multiplet at 4.53 ppm (hydrogen at 7a), and a broad doublet at 3.66 ppm (methylene hydrogens), respectively].



VIII



IX

Treatment of VIII with formic and hydrochloric acids yielded the diimide IX involving acid-induced bond rupture at the site of the benzylic carbon instead of a hydrolysis product based on the tricarbocyclic structure type of the starting material. The ultraviolet [indene-type absorption maximum at 262 mμ (ε 23,700)] and pmr spectra in deuterated dimethyl sulfoxide [a multiplet of five hydrogens (inclusion of the vinyl hydrogen at 3′) at 7.58 to 7.08 ppm, a singlet at 4.60 ppm (hydrogen at 6a), and a narrow band at 3.62 ppm (half-height-width of 3.8 cps, methylene)] of the product were in agreement with structure IX. The presence of the neighboring imide units caused extraordinary rate enhancement of alkali-induced exchange of the cyclopentene hydrogens of IX. While indenes are known to undergo base-catalyzed hydrogen exchange,[13] mere dissolution of IX in a 1 *N* sodium deuterioxide solution in deuterium oxide led to instantaneous exchange of all but the four benzene hydrogens (as shown by pmr analysis). Recovery of starting compound by neutralization with deuterium chloride and mass spectral analysis thereof revealed a molecular ion peak at 288 = (IX + 6). The rapid indene hydrogen exchange must be a consequence of intramolecular exchange with the initially formed succinimide anions.

Another interesting reaction of VIII was its pyrolysis. On heating its diglyme solution for 2 hr at 150° it was converted into an isomeric product whose radically altered spectra bespoke a deep-seated change. The spectral properties of this new compound suggested its structure to be X. Its infrared spectrum showed NH bands at 3435, 3320, and 3203^{-1} cm and its complex ultraviolet spectrum (absorption maxima at 223, 236, 263, 315, 326, and 411 mμ) indicated a polynuclear aromatic chromophore and was reminiscent of the spectrum of benzo[*f*]quinoline, (maxima at 233, 267, 315, 329, and 344 mμ).[14] The pmr spectrum of a dimethyl sulfoxide solution of X revealed a two-proton signal at 6.75 ppm due to an amino group (exchangeable with deuterium oxide) and only aromatic hydrogen signals (see the Experimental Section). The

---

[9] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

[10] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

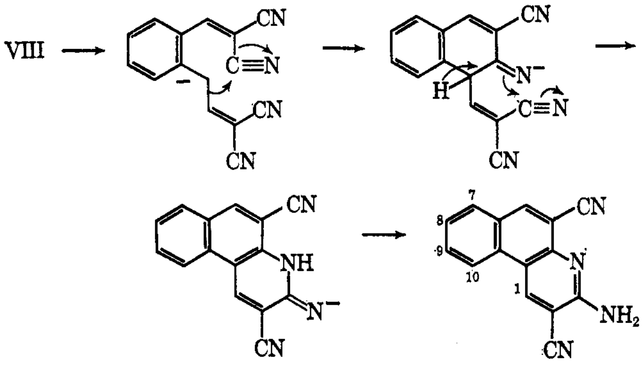
[11] C. F. Huebner, E. Donoghue, P. Strachan, P. Beak, and E. Wenkert, *J. Org. Chem.*, **27**, 4465 (1962).

[12] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

[13] *Cf.* G. Bergson, *Acta. Chem. Scand.*, **17**, 2691 (1963).

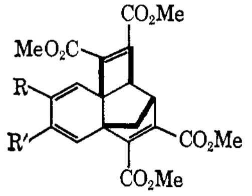
[14] W. S. Johnson, E. Woroch, and F. J. Mathews, *J. Am. Chem. Soc.*, **69**, 566 (1947).

unusual formation of X can be rationalized as follows: thermal cleavage of the cyclobutane ring, Thorpe condensation of the homocinnamonitrile moiety, followed by further ring closure of amine to nitrile function, and aromatization by tautomeric change. A trace of basic impurity of cyanide ion could bring about the reaction. Further, since X is basic the process would be autocatalytic.



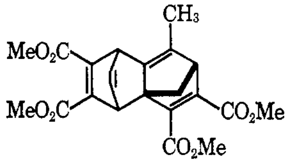
X

Interaction of indene and dimethyl acetylenedicarboxylate has yielded a 1:2 adduct, whose X-ray analysis (of the dibromide) revealed it to possess the unusual structure XIa.[7] Hydrogenation of the adduct gave an octahydro product while reduction with zinc in acetic acid yielded a dihydro product (XII). A stereochemical assignment cannot be made for XII, but a pmr analysis in deuteriochloroform of it revealed the presence of olefinic hydrogens (a four-proton multiplet at 6.45 to 5.75 ppm) indicating, as expected, that one of the maleic ester moieties had been reduced. A drastic change of the chemical shift of the methylene bridge [a two-proton near-doublet at 2.10 ppm in XIa to two one-proton multiplets at 2.78 ppm and 1.89 (for which the AB coupling of an ABC system is approximately 10 cps) in the dihydro product XII (both spectra in deuteriochloroform)] was noted. To account for the large downfield shift (0.89 ppm) of one of the methylene protons at least one ester function (preferably two) must be in the *exo* configuration. In a model norbornene, two groups which give an anisotropic effect (carboxyl and phenylsulfonyl) must be *exo* to obtain a downfield shift of the magnitude of 1 ppm.[15]

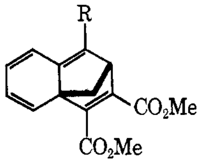


XIa, R = R′ = H
b, R = Me; R′ = H
c, R = H; R′ = Me
d, R = F; R′ = H

The reaction of dimethyl acetylenedicarboxylate with indenes is greatly susceptible to changes by structure factors. 5-Methyl-, 6-methyl-, and 5-fluoroindene underwent addition in a manner analogous to indene itself, yielding products XIb–d, respectively. It is worthy of note that in the pair, 5- and 6-methylindene, which are interconvertible by prototropic shift, each gives its own discrete acetylenedicarboxylate adduct. The compounds have very similar but not identical pmr spectra and show a mixture melting point depression. Neither 6-nitro- and 5-methoxy- nor 1-methyl- and 2-methylindene underwent any reaction while 3-methylindene gave an adduct of structure type different from XI. The presence of two vinyl protons and an olefinic methyl singlet as featured in the pmr spectrum (deuteriochloroform) of the adduct of 3-methylindene shows it to possess structure XIII. In more detail, a symmetrical multiplet of two vinyl hydrogens appears at 6.61 ppm and two allylic hydrogens appear at 4.81 and 4.53 ppm, each being a doublet of doublets in which the coupling constants are approximately 5.9 and 2.0 cps, respectively. These data best fit the system CHCH=CHCH. A tertiary hydrogen having the appearance of a narrow triplet or a quartet (half-height-width of 2.6 cps) is at 3.63 ppm and associated with this hydrogen is a methylene group (CH-CH_2) of which each hydrogen is a doublet of doublets centered at 2.32 and 1.91 ppm (J = 7.0 and 1.5 cps). The small coupling between the tertiary hydrogen and the methylene group indicates a norbornadiene arrangement. The methyl group attached to a double bond is a singlet at 1.92 ppm and the four methoxyl groups appear at 3.80 (one), 3.85 (one), and 3.88 ppm (two). These data, however, are insufficient to differentiate between the two possible stereoisomers of XIII.



XIII



XIV

If it be assumed that the first addition of dimethyl acetylenedicarboxylate to indenes proceeds in the way in which it does to styrenes[16] and hence the initial indene adduct is XIV[17] (R = H), the following suggestions can be made as possible interpretation of the above data. While polar factors inhibit the addition of acetylenedicarboxylic ester to the nitro and methoxy derivatives of indene, the lack of reactivity of 1- and 2-methylindene is probably due to steric reasons. The curious difference of chemical behavior of indene and 3-methylindene is associated with the addition of the acetylene derivative to the intermediate conjugated triene (XIV). On the assumption of the addition proceeding in two discrete steps, being perhaps of free-radical nature and leading to the least metastable, intermediate species, the difference between XV and

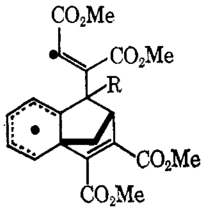
---

[15] H. Hogveen, G. Maccagnoni, F. Montanari, and F. Taddel, *J. Chem. Soc.*, 682 (1964).

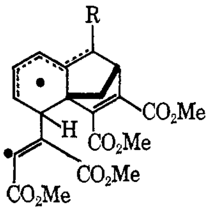
[16] B. F. J. Hudson and R. Robinson, *ibid.*, 715 (1941).

[17] It is noteworthy that the reaction of 1,2-dihydronaphthalene and dimethyl acetylenedicarboxylate must follow a similar path. The product, dimethyl 1,2-naphthalenedicarboxylate, would be expected from a thermal extrusion of ethylene from a homolog of XIV (R = H): F. Pascher, Thesis, University of Cologne, 1944.

XVI needs to be considered. If R = Me, the reaction would be expected to proceed *via* XVI.[18] However, in the case of R = H, the difference of XV and XVI is merely that of fixed "U" *vs.* "sickle" pentadienyl radicals. If the recent orbital treatment of pentadienyl anions[19] is also applicable to radicals the reaction should proceed *via* XV.



XV



XVI

While the adducts XI are still conjugated dienes, they do not undergo any further reaction with dimethyl acetylenedicarboxylate. This appears to be due not only to the presence of neighboring quaternary centers but also to skewness of the diene chromophore [anomalous absorption maximum at 238 mμ (ε 10,500)].

Experimental Section[20]

***endo*-1,2,3,4-Tetrahydro-1,4-methanonaphthalene-2,3-dicarboxylic Anhydride (I). Small-Scale Procedure.**—A mixture of 40.4 g of indene (0.347 mole), 24.12 g of maleic anhydride (0.246 mole), 35 ml of tetralin, and 1.5 g of hydroquinone was heated rapidly in a nitrogen atmosphere to 198° and held there for 4.5 hr. The solution was cooled to 120° and poured into 100 ml of ethyl acetate and this solution in turn was poured into 300 ml of toluene with stirring. The ethyl acetate was removed by distillation with additional toluene added to maintain the volume. The hot toluene mixture was filtered to remove polymer (26 g) and then cooled to −5 to −10°. The crystalline product was filtered and washed with a small amount of cold toluene, mp 181–185° (yield 18.5 g, 35.6%).

Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 73.21; H, 4.98.

A similar run using 6 g of hydroquinone gave a 65% yield of crude anhydride of lower purity which on recrystallization from toluene gave a yield in excess of 50%.

Large-Scale Procedure.—A mixture of 3.555 kg of indene, 2.120 kg of maleic anhydride, 12.2 g of hydroquinone, and 4.3 l. of benzene was heated at 250° in a glass-lined, 5-gal. autoclave for 5 hr. After cooling to 35°, the upper layer was decanted from the lower polymer layer into a bucket to solidify. The solid reaction mixture was refluxed for 5 hr with 65 l. of toluene and filtered hot, and the filtered solid was washed with 7 l. of toluene. The combined filtrates were cooled overnight to −10°, filtered, and washed with 2 l. of cold toluene to yield 1.416 kg of product. Concentration and cooling of the filtrate increased the yield to 1.755 kg (37.9%), mp 184–186°.

Concentration of toluene mother liquors gave second and third crops containing appreciable amounts of the *exo* as well as the *endo* isomer.

***exo*-1,2,3,4-Tetrahydro-1,4-methanonaphthalene-2,3-dicarboxylic Anhydride (II).**—The third crop of the above-described preparation which was shown by vapor phase chromatography to be 45% I and 55% II was subjected to preparative vapor phase chromatography using a Barber–Coleman gas chromatograph; column packings prepared from nitrile silicon gum XE-60 (10%) supported by Anakrom A.B.S. (50–60 mesh), column temperature 227° and a helium flow rate of 60 ml/min separated the pure *exo* anhydride (II), mp 252–253°. The relative retention times of *exo* and *endo* anhydride are 1.0 and 1.6, respectively.

Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.65; H, 4.45.

Ethyl 2,2a,7,7a-Tetrahydro-1H-indeno[1,2-*c*]diazete-1,2-dicarboxylate (VI).—A mixture of 1.68 g (0.0145 mole) of indene and 5.05 g (0.029 mole) of diethyl azodiformate in 2 ml of benzene was refluxed for 6 hr. Evaporation of the benzene left an oily residue which crystallized on standing in methanol. The product was recrystallized from methanol, mp 103–105°.

Anal. Calcd for $C_{15}H_{18}N_2O_4$: C, 62.05; H, 6.25; N, 9.65. Found: C, 61.56; H, 6.26; N, 9.34.

2,2a,7,7a-Tetrahydro-1H-cyclobut[*a*]indene-1,1,2,2-tetracarbonitrile (VIII).—A mixture of 10.0 g (0.078 mole) of tetracyanoethylene and 9.06 g (0.078 mole) of indene in 25 ml of dimethoxyethane was refluxed for 6 hr, then poured into water. The precipitate was collected, washed with diethyl ether, and recrystallized from tetrahydrofuran–water, mp 200–201°.

Anal. Calcd for $C_{15}H_8N_4$: C, 73.76; H, 3.30; N, 22.94. Found: C, 73.89; H, 3.52; N, 22.63.

2,3a,5,6a-Tetrahydro-3a-(2-indenyl)pyrrolo[3,4-*c*]pyrrole-1,3,-4,6-tetraone (IX).—A mixture of 1.0 g of VIII, 4 ml of concentrated hydrochloric acid, and 16 ml of 97% formic acid was refluxed for 5 hr, then cooled, and poured into water. The brown precipitate was decolorized with Norit and recrystallized from ethanol, mp 310–312°.

Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.93. Found: C, 63.99; H, 3.64; N, 9.89.

3-Amino-2,5-dicyanobenzo[*f*]quinoline (X).—A mixture of 1 g of VIII and 10 ml of diglyme was heated in a sealed tube at 150° for 2 hr. On cooling it was poured into water and olive-green precipitate was filtered and recrystallized three times from dimethylformamide, mp 312–315°. Pmr spectrum in deuteriodimethyl sulfoxide revealed a singlet at 9.40 (H at 1), a singlet at 8.69 (H at 6), a broad doublet at 8.61 ($J_{9,10} \cong 7.5$ cps, H at 10), a doublet of a doublet with additional splitting at 8.01 ($J_{7,8} = 7.0$ cps, $J_{7,9} = 2.0$ cps, H at 7), a multiplet at 7.71 (H at 8 and 9), and a broad singlet at 7.37 ppm (H of NH_2).

Anal. Calcd for $C_{15}H_8N_4$: C, 73.76; H, 3.30; N, 22.94. Found: C, 73.62; H, 3.51; N, 22.97.

Methyl 1,2,2a,3,4,5,6,7,8,9-Decahydro-3,5a-methano-5aH-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate.—A solution of 6.0 g of XIa (0.015 mole) in 150 ml of methanol was hydrogenated (Parr hydrogenation apparatus) over 1.0 g of 10% palladium on carbon at 40 psi at room temperature for 3 hr. The catalyst was filtered off and the methanol was evaporated. The solid residue was recrystallized from ethanol, mp 158–161°.

Anal. Calcd for $C_{21}H_{28}O_8$: C, 61.75; H, 6.91. Found: C, 61.90; H, 6.81.

Methyl 1,2,2a,3-Tetrahydro-3,5a-methano-5aH-cyclobuta[*d*]-naphthalene-1,2,4,5-tetracarboxylate (XII).—A mixture of 500 mg of XIa and 500 mg of zinc dust in 10–15 ml of glacial acetic acid was refluxed for 4 hr. After evaporation of the solvent the residue was diluted with water and neutralized with ammonium hydroxide. The organic material was extracted with ether, washed with water, dried over magnesium sulfate, and evaporated to dryness. The solid residue was recrystallized from ethyl acetate, mp 153–156°.

Anal. Calcd for $C_{21}H_{22}O_8$: C, 62.68; H, 5.51. Found: C, 62.79; H, 5.56.

Adducts of Dimethyl Acetylenedicarboxylate and Substituted Indenes XIa–d. General Procedure.—A mixture of 0.2 mole of dimethyl acetylenedicarboxylate and 0.1 mole of indene was heated on the steam bath for 5–6 hr. The product crystallized when triturated with methanol or ethanol and was recrystallized from ethanol.

Methyl 2a,3-tetrahydro-3,5a-methano-5aH-cyclobuta[*d*]naphthalenedicarboxylate (XIa) had mp 128–129°. *Anal.* Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 62.96; H, 5.19.

Methyl 2a,3-dihydro-8-methyl-3,5a-methano-5aH-cyclobuta-[*d*]naphthalenedicarboxylate (XIb) had mp 121–122°. *Anal.* Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.64; H, 5.25.

Methyl 2a,3-tetrahydro-7-methyl-3,5a-methano-5aH-cyclobuta[*d*]naphthalenedicarboxylate (XIc) had mp 126–128°. *Anal.* Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 64.18; H, 5.62. The mixture melting point of XIb and c is 107–111°.

Methyl 2a,3-tetrahydro-8-fluoro-3,5a-methano-5aH-cyclobuta-[*d*]naphthalenedicarboxylate (XId) had mp 128–129°. *Anal.*

---

[18] *Cf.* P. D. Bartlett and L. K. Montgomery, *J. Am. Chem. Soc.*, **86**, 616 (1964).

[19] R. Hoffmann and R. A. Olofson, *ibid.*, **88**, 943 (1966).

[20] Pmr spectra were recorded on a Varian A-60 instrument using tetramethylsilane as an internal standard. Melting points were determined with a Thomas–Hoover apparatus.

Calcd for $C_{21}H_{19}FO_8$: C, 60.03; H, 4.55. Found: C, 59.96; H, 4.65.

Methyl 4,7-tetrahydro-3-methyl-4,7-etheno-2aH-cyclopent-[*b,c*]indene-1,2,5,6-tetracarboxylate (XIII) was recrystallized from aqueous methanol, mp 106–107.5°. *Anal.* Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.96; H, 5.26.

Registry No.—Indene, 95-13-6; I, 7646-55-1; II, 7635-37-2; VI, 7635-30-3; VIII, 7646-56-2; IX, 7646-57-3; X, 7646-58-4; methyl 1,2,2a,3,4,5,6,7,8,9-decahydro-3,5a-methano-5aH-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate, 7635-39-4; XII, 7635-40-7; XIa, 7695-31-0; XIb, 7646-59-5; XIc, 7635-41-8; XId, 7646-60-8; XIII, 7706-43-6.

Acknowledgments.—We wish to express appreciation for the interest and help of Dr. E. Schlittler throughout this work. Mr. F. LeMunyon carried out the vapor phase chromatography and Dr. J. Marsh helped with nomenclature problems. Microanalyses were performed under the supervision of Mr. G. Robertson. The mass spectrum was run by Dr. H. Hürzeler, CIBA Ltd., Basle, Switzerland.

Synthesis of Azaindenes. The Benzo[*c*]pyrazolo[1,2-*a*]cinnolinium Cation, a Novel Heteroaromatic Cation[1]

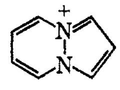
DONALD G. FARNUM,[2] ROBERT J. ALAIMO, AND JOYCE M. DUNSTON

Department of Chemistry, Cornell University, Ithaca, New York, 14850

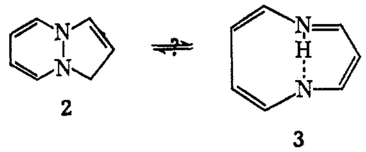
Received October 18, 1966

Investigation of possible synthetic routes to the pyrazolo[1,2-*a*]pyridazinium cation (**1**) and the potentially aromatic 1,5-diazonene (**3**) has led to the observation of a novel reaction of benzocinnoline and trimethylene dibromide, the preparation of a novel dibenzoderivative **7** of **1**, and the observation of a mild aromatization reaction involving loss of either hydrogen atoms or a methyl group. The 1,3-dipolar addition reaction has been applied to the synthesis of a number of azaindenes.

The work to be described was initially undertaken to examine the synthesis and the properties of derivatives of pyrazolo[1,2-*a*]pyridazinium cation (1) and its dihydro derivative (2). These systems were considered to be of interest because of their novelty, the unusual ten π-electron cationic system present in **1**, and the possibility of valence and prototropic tautomerism of **2** to the potentially aromatic ten π-electron monocyclic heterocycle 1,5-diazonene (**3**).[3] We report here some preliminary, and partially successful efforts to prepare derivatives of **1** and **2**.



1



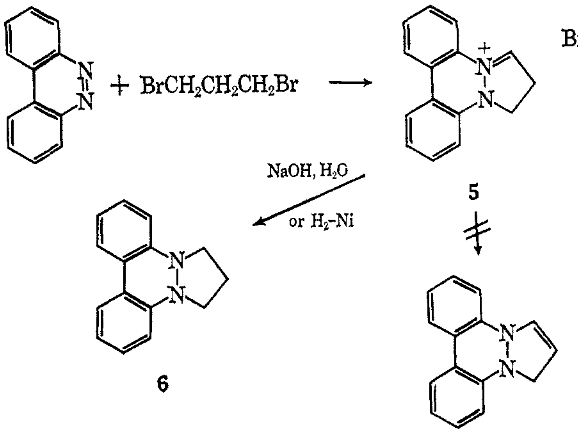
2 **3**

Our first goal was the dibenzo derivative (**4**) of **2**. Reaction of benzocinnoline with trimethylene dibromide in boiling ethanol gave a good yield of dark red, felted needles, no melting point below 290°, identified as the imminium bromide **5** (2,3-dihydrobenzo[*c*]-pyrazolo[1,2-*a*]cinnolinium bromide) on the basis of the following evidence. The ionic nature of the compound was evident by formation of blood-red solutions in water which gave an immediate precipitate with silver nitrate. Analysis was in accord with the structure. The infrared spectrum was completely free from N–H absorption from 2.5 to 4.0 μ. The ultraviolet-visible spectrum is compared with that of benzocinnoline N-oxide in Table I. It can be seen that the major regions of ultraviolet absorption overlap for these two related systems, although red bromide **5** has additional absorption in the visible. It was hoped that treatment of red bromide **5** with base would result in conversion to the desired eneamine (**4**). However, from the addition of aqueous sodium hydroxide to an

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA OF BENZOCINNOLINE AND SOME ANALOGS

$\lambda_{max}^{95\%\ EtOH}$, mμ (log ε)				
5	Benzo-cinnoline N-oxide	**7**	**6**	Benzo-cinnoline
222 (4.08)	245 (4.48)	218 (4.11)	253 (3.55)	251 (4.70)
259 (4.69)	253 (4.50)	259 (4.74)	317 (3.36)	308 (3.95)
295 (3.76)	265 (4.30)	293 (3.81)	392 (3.42)	372 (3.20)
320 (3.70)	285 (4.00)	319 (3.72)		
333 (3.72)	330 (3.95)	333 (3.72)		
373 (2.87)	365 (3.80)			
391 (3.11)			415 (2.54)	
487 (2.53)				
528 (2.53)			525 (1.54)	



---

[1] This investigation was supported by Public Health Service Research Grant GM 12383-02 from the Division of General Medical Sciences.

[2] Fellow of the Alfred P. Sloan Foundation, 1962–1965. Department of Chemistry, Michigan State University, East Lansing, Mich. 48823.

[3] Several recent examples of heterocyclic[4] and carbocyclic[5] relatives of **1** and **2** have appeared in the literature.

[4] (a) T. W. G. Solomons, F. W. Fowler, and J. Calderazzo, *J. Am. Chem. Soc.*, **87**, 528 (1965); (b) V. Boekelheide and N. A. Fedoruk, *Proc. Natl. Acad. Sci. U. S.*, **55**, 1385 (1966).

[5] (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).