527. *Addition Reactions of Heterocyclic Compounds. Part III.* 2 : 3-Benzacridine and Some Dienophils.*

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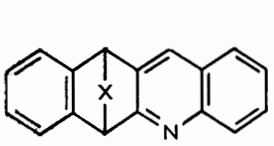
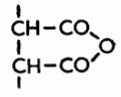
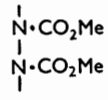
2 : 3-Benzacridine combined, like anthracene, with maleic anhydride and methyl azodicarboxylate to give the corresponding adducts. With methyl acetylenedicarboxylate in methanol, however, the product was the *N*-substituted benzacridinium methoxide or the conjugate methoxyacridan.

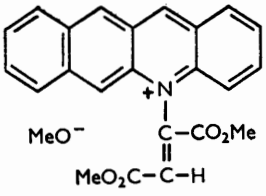
Acridine and anthracene undergo a number of addition reactions with the same reagents under similar conditions to give products differing widely in type. Acridine, for example, with bromine [1] and with methyl acetylenedicarboxylate in methanol [2] gives *N*-substituted acridinium derivatives while with anthracene under similar conditions the 9 : 10-dibromide [3] and an adduct across the 9 : 10-positions [2] are respectively obtained. In the case of 2 : 3-benzacridine addition of such reagents might take place to either of the central rings which would be competing for the reagent.

In order to investigate this, 2 : 3-benzacridine was treated with several dienophils. With *p*-benzoquinone in boiling toluene it gave only amorphous products, but with maleic anhydride a crystalline adduct was obtained. This has almost certainly the bridged structure (I), as acridine itself is reported [4] not to react with maleic anhydride and the structure is consistent with the spectral data. In a similar addition 2 : 3-benzacridine gave the adduct (II) with methyl azodicarboxylate. Treatment with acid gave a rearrangement product, the ultraviolet absorption spectrum (Fig. 4) of which shows additional conjugation suggesting the return of the fully aromatic system. This product may be 1- or 4-(*NN'*-dimethoxycarbonylhydrazino)-2 : 3-benzacridine, by analogy with the corresponding reactions in the anthracene series.[5]

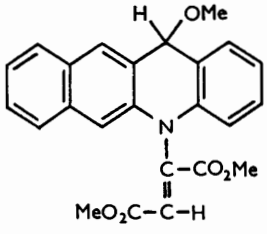


(I) X = 

(II) X = 



(III)



(IV)

In connexion with this a number of attempts were made to combine methyl azodicarboxylate with acridine in the presence or absence of acid catalysts but no reaction could be detected. Treatment of the ester with acridan gave only acridine and methyl hydrazodicarboxylate; this ester also dehydrogenates quinol to *p*-benzoquinone.[6] 5-Hydrazinoacridine was obtained from 5-chloroacridine and hydrazine hydrate in phenol [7,8] and was

* Part II, *J.*, 1956, 246.

[1] Acheson, Hoult, and Barnard, *J.*, 1954, 4142.
[2] Acheson and Burstall, *J.*, 1954, 3240.
[3] Perkin, *Bull. Soc. chim. France*, 1877, **27**, 464.
[4] Barnett, Goodway, Higgins, and Lawrence, *J.*, 1934, 1224.
[5] Alder and Niklas, *Annalen*, 1954, **585**, 81.
[6] Diels and Fritzsche, *Ber.*, 1911, **44**, 3018.
[7] Meister, Lucius, and Brüning, D.R.-P. 364031; *Friedlander*, **14**, 802.
[8] Cf. Jelinek and Boxer, *J. Biol. Chem.*, 1947, **170**, 491.

the only product isolable in a number of attempts to condense 5-chloro- and 5-phenoxyacridine with methyl hydrazodicarboxylate; the product was acridone when 5-methoxyacridine was used. However, 5-phenoxyacridine and methyl hydrazomonocarboxylate did give 5-(*N'*-methoxycarbonylhydrazino)acridine.

FIG. 1. FIG. 2.

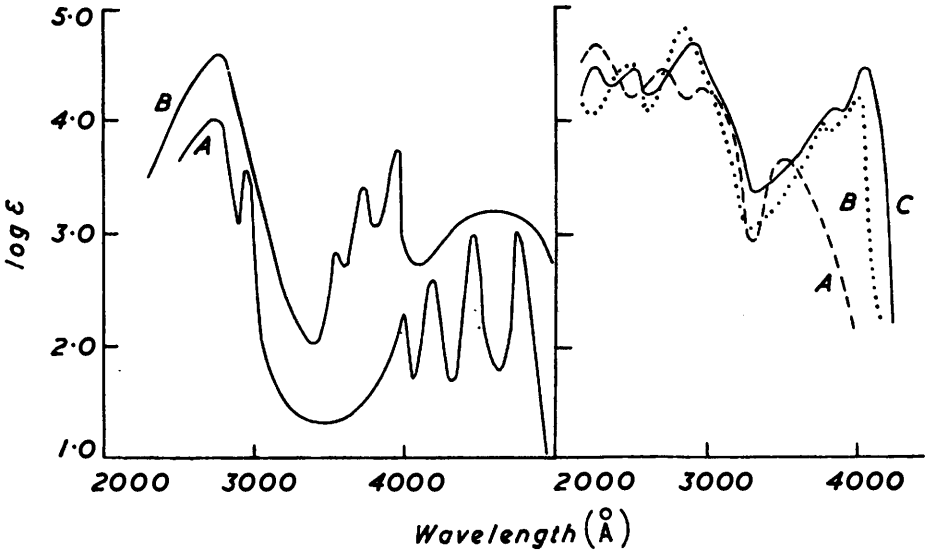


FIG. 1. *A, Naphthacene.*[12] *B,* 2 : 3-*Benzacridine.*

FIG. 2. *A, The benzacridan* (IV). *B,* 2 : 3-*Benzacridine hydrochloride. C, The benzacridinium chloride from* (III).

FIG. 3. FIG. 4.

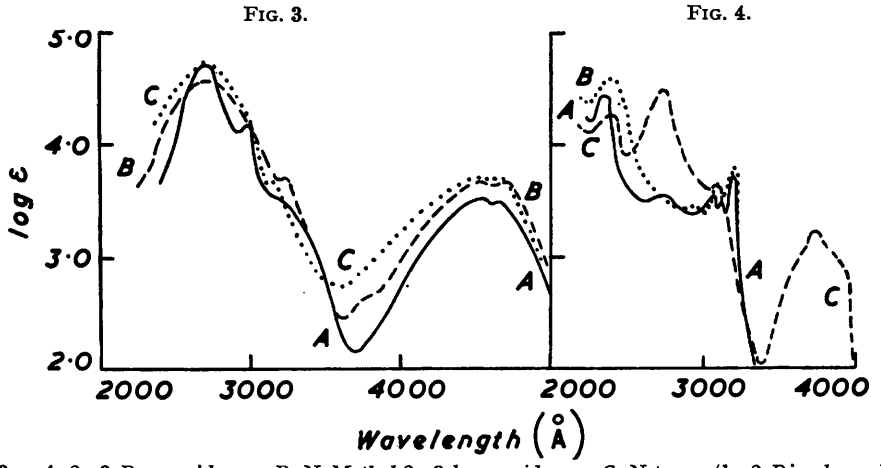


FIG. 3. *A,* 2 : 3-*Benzacridone. B,* N-*Methyl*-2 : 3-*benzacridone. C,* N-trans-(1 : 2-*Dicarboxyvinyl*)-2 : 3-*benzacridone.*

FIG. 4. *A,* 2 : 3-*Benzacridine–maleic anhydride adduct* (I). *B,* 2 : 3-*Benzacridine–methyl azodicarboxylate adduct* (II). *C, Acid-rearrangement product of adduct* (II).

2 : 3-Benzacridine and methyl acetylenedicarboxylate in benzene gave a low yield of a product containing 1 mol. of the acridine and 2 mols. of the ester. It may be analogous to the corresponding products from quinoline and phenanthridine [9] and is under investigation. In methanol solution, however, addition of both the ester and the solvent took place, giving

[9] A. W. Johnson, " Acetylenic Acids," Arnold and Co., London, 1950.

N-(*trans*-1 : 2-dimethoxycarbonylvinyl)-2 : 3-benzacridinium methoxide (III), in equilibrium with the conjugate acridan (IV). The stereochemistry is presumed by analogy with the similar *trans*-additions to acridine [2] and phenanthridine.[10] The ultraviolet absorption spectrum of the benzacridine (III or IV) in acidified methanol was very similar to that of 2 : 3-benzacridinium chloride (Fig. 2), but in neutral methanol the molecule is clearly much less conjugated and must be in the benzacridan form (IV). The long-wavelength bands of *N*-*trans*-(1 : 2-dimethoxycarbonylvinyl)acridinium salts and the corresponding methoxyacridan are [2] also separated by 600—700 Å. Oxidation of the benzacridine (III) with alkaline potassium ferricyanide gave *N*-(*trans*-1 : 2-dicarboxyvinyl)-2 : 3-benzacridone which had a similar ultraviolet absorption to that of *N*-methyl-2 : 3-benzacridone and 2 : 3-benzacridone (Fig. 3). This last close similarity suggests that the keto-form of 2 : 3-benzacridine is present to the virtual exclusion of the enolic tautomer, as in the case of acridone,[11] under these conditions. The ultraviolet absorption of 2 : 3-benzacridine (Fig. 1) broadly resembles that of naphthacene,[12] but the extinction maxima are greater and the long wavelength band has much less fine structure in agreement with other observations [13] on this type of comparison.

Experimental

Infrared absorption measurements were done in paraffin paste, and the ultraviolet measurements in methanol.

2 : 3-*Benzacridine and Maleic Anhydride*.—The acridine (0·5 g.) and maleic anhydride (0·22 g.) were refluxed (6 hr.) in dry toluene (5 ml.). Cooling the filtered and somewhat concentrated solution gave the *adduct* (I) which separated from toluene in colourless prisms, m. p. 304° (decomp.) (Found : C, 77·3; H, 4·1; N, 4·1. $C_{21}H_{13}O_3N$ requires C, 77·1; H, 4·0; N, 4·3%). Infrared absorption maxima were at 5·39, 5·45, 5·63, 6·14, 6·36, 6·67, 6·88, 7·10, 7·27, 7·42, 7·53, 7·65, 7·76, 7·95, 8·05, 8·15, and 9·3 μ. Infrared maxima of 2 : 3-benzacridine were at 6·14, 6·20, 6·27, 6·54, 6·73, 6·86, 7·28, 7·71, 8·39, 8·63, 8·91, 10·09, 10·48, 10·74, 10·92, 11·20, and 11·51 μ.

2 : 3-*Benzacridine and Methyl Azodicarboxylate*.—The acridine (2·0 g.), the ester (1·28 g.) and *p*-xylene (12 ml.) were refluxed for 7 hr., then filtered from some purple solid, and some of the solvent was evaporated. Cooling in ice–salt precipitated the *adduct* (II) (2·6 g.) which after successive crystallisation from *p*-xylene and methanol (charcoal) separated in colourless prisms, m. p. 225—226° (decomp., softens at 224°) (Found : C, 67·2; H, 4·6; N, 11·4. $C_{21}H_{17}O_4N_3$ requires C, 67·2; H, 4·5; N, 11·2%). The infrared maxima were at 5·75, 6·14, 6·36, 6·67, 6·81, 6·99, 7·10, 7·28, 7·50, 7·66, and 7·89 μ.

The colourless solution of the adduct in acetic acid was treated with a few drops of concentrated sulphuric acid and warmed slightly. A purple colour developed and on basification an orange solid was precipitated. Purification was effected by precipitation from glacial acetic acid by aqueous ammonia, an orange solid being obtained having m. p. 218° (Found : C, 67·0; H, 4·7; N, 11·6. $C_{21}H_{17}O_4N_3$ requires C, 67·2; H, 4·5; N, 11·2%). Infrared absorption maxima were at 5·73, 5·82, 6·15, 6·18, 6·28, 6·56, 6·68, 6·88, 6·95, 7·10, 7·48, 7·66, and 7·90 μ.

Acridan and Methyl Azodicarboxylate.—Acridan (0·5 g.) was mixed with the ester (2·0 g.) : much heat was evolved. After 3 hr. at 120° and crystallisation from toluene–light petroleum acridine, m. p. and mixed m. p. 108°, was obtained.

5-*Hydrazinoacridine*.—5-Chloroacridine (1·0 g.) and 100% hydrazine hydrate (3 ml.) were heated for 1·5 hr. in phenol (2·0 g.) at 130°. The red gum obtained on pouring the melt into 2N-sodium hydroxide (25 ml.) solidified on trituration with more alkali. Chromatographic purification on alumina from methanol, followed by crystallisation from warm (not boiling) methanol gave the product as pale red prisms, m. p. 265° (Found : C, 74·5; H, 5·6. Calc. for $C_{13}H_{11}N_3$: C, 74·6; H, 5·3%). The literature [7] gives m. p. 169°. In alkaline methanol the ultraviolet absorption spectrum showed the following maxima : 2300 Å (log ε 4·67), 3600 (3·62), 3800 (3·62), and 4600 (3·79).

5-N′-*Methoxycarbonylhydrazinoacridine*.—5-Phenoxyacridine (1·5 g.), methyl hydrazinecarboxylate hydrochloride (0·7 g.) and phenol (5·0 g.) were heated for 3½ hr. at 120—125° and poured into 2N-sodium hydroxide (25 ml.). The precipitate was ground with N-sodium hydroxide and washed with water, and crystallisation from methanol gave the *acridine* (0·6 g.)

[10] Acheson and Bond, *J.*, 1956, 246.
[11] Acheson, Burstall, Jefford, and Sansom, *J.*, 1954, 3742.
[12] Rădulescu and Bărbulescu, *Ber.*, 1931, **64**, 2225; cf. Clar, *ibid.*, 1936, **69**, 608.
[13] Badger, Pearce, and Pettit, *J.*, 1951, 3199.

as orange-red prisms, m. p. 229° (Found : C, 67·4; H, 4·9; N, 15·4. $C_{15}H_{13}O_2N_3$ requires C, 67·4; H, 4·9; N, 15·7%). The ultraviolet absorption spectrum showed maxima at 2350 Å (log ε 4·51), 2900 (3·91), and 4000 (3·97).

N-(trans-1 : 2-*Dimethoxycarbonylvinyl*)-2 : 3-*benzacridinium Methoxide* (III).—2 : 3-Benzacridine (0·4 g.) and methyl acetylenedicarboxylate (0·28 g.) were refluxed for 1½ hr. in methanol (3 ml.). The *product* (0·58 g.) separated on cooling and crystallised from methanol as orange prisms, m. p. 128° (Found : C, 71·3; H, 5·3; N, 3·3; OMe, 21·9. $C_{24}H_{21}O_5N$ requires C, 71·5; H, 5·2; N, 3·5; 3OMe, 23·1%). Infrared maxima were at 5·81, 6·13, 6·26, 6·64, 6·73, 6·86, 6·99, 7·40, 7·70, 7·85, and 8·00 μ.

N-(trans-1 : 2-*Dicarboxyvinyl*)-2 : 3-*benzacridone*.—The above adduct (0·11 g.) was dissolved in hot 10% aqueous potassium hydroxide (1·1 ml.), potassium ferricyanide (0·28 g.) in hot water (0·55 ml.) was added, and the mixture left on a steam-bath for 3 hr. Filtration and acidification precipitated the buff *acid*, m. p. 184° (Found, after drying over P_2O_5 *in vacuo* at 15° : C, 66·7; H, 4·2; N, 4·0. $C_{21}H_{13}O_5N,H_2O$ requires C, 66·8; H, 4·0; N, 3·7. Found, after similar drying at 116° : C, 70·0; H, 3·7; N, 4·2. $C_{21}H_{13}O_5N$ requires C, 70·2; H, 3·6; N, 3·9%). Infrared absorption maxima were at 5·80, 6·10, 6·25, 6·78, 7·30, and 7·90 μ.

2 : 3-*Benzacridone*.—Crystallisation from ethanol–dioxan gave golden-yellow prisms, m. p. 304° (Found : C, 83·0; H, 4·5. Calc. for $C_{17}H_{11}ON$: C, 83·3; H, 4·5%). Infrared absorption maxima were at 3·15 (broad, hydrogen bonding), 6·10, 6·14, 6·20, 6·29, 6·39, 6·54, 6·65, 6·78, 7·10, 7·30, 7·36, 7·50, 7·63, 7·75, 7·90, and 7·98 μ.

N-*Methyl*-2 : 3-*benzacridone*.—2 : 3-Benzacridone (0·4 g.) and potassium hydroxide (1·2 g.) were ground with a little ethanol and dried (oven). The purple product was powdered, heated with methyl sulphate to 100° (20 min.), and poured into aqueous ammonia. The precipitate after crystallisation from methanol (charcoal) gave the *methylbenzacridone* as pale yellow needles, m. p. 215° (Found : C, 83·6; H, 5·1. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0%). Infrared maxima were at 6·10, 6·18, 6·23, 6·29, 6·73, 6·91, 7·30, 7·44, 7·57, and 7·74 μ.

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