Tetrahedron Letters No.40, pp. 2919-2923, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE "HOMOLOGISATION" OF PHENANTHRENE BY DIAZOMETHANE

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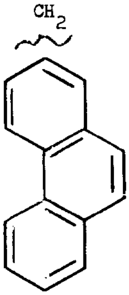
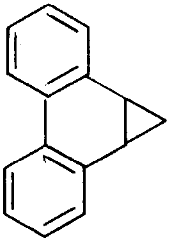
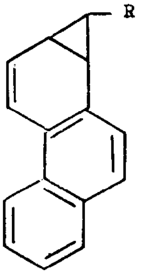
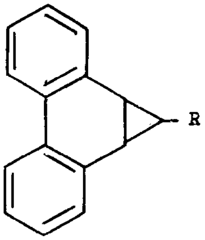
(Received 10 July 1964)

In a recent publication Müller, Fricke and Kessler (1) discuss the reaction between diazomethane and phenanthrene and assign structures I and II to two of their products. It has previously been demonstrated (3) that ethyl diazoacetate affords IIIa and IVa and although the 9,10-bond has been considered the most reactive in phenanthrene (2) it would not be surprising to find diazomethane (or methylene) likewise attacking the terminal as well as the central ring.


I


II


III a R = CO_2Et
b R = CO_2H


IV a R = CO_2Et
b R = CO_2H
c R = $CONMe_2$
d R = $CH_2NMe_2.HCl$

The similarity of the UV-light absorption data, quoted by Müller, for compounds I and II is surprising and one might expect these structures to have absorption spectra which resemble respectively a vinylnaphthalene and 9,10-dihydrophenanthrene. Alternatively it must be concluded that the cyclopropane ring in these structures can extend conjugative effects such that the energy of electronic transitions associated with UV-light absorption is unaffected. That the latter is not the case is demonstrated by the acids IIIb and IVb which have considerably different UV-spectra (3). The UV-spectrum of the acid IVb resembles that of 9,10-dihydrophenanthrene and differs in several important respects from the spectrum quoted for structure II, in particular the major long-wave absorption band occurs in the region 270-280 mμ and there are two less intense absorptions at 298 and 310 mμ. One would have expected the spectrum of II to resemble much more closely that of IVb. We have investigated the possibility that these differences are due to conjugation of the carboxylic grouping through cyclopropane to the aromatic chromophore in the excited state (4) and have compared the amine IVd with the amide IVc.

The acid IVb was converted into the acid chloride by heating with thionyl chloride in benzene and the addition of dimethylamine to the mixture afforded N,N-dimethyl-5,5a-dihydro-4bH-cyclopropa[l]phenanthrene-5-carboxamide (dimethyl dibenzonorcaradienecarboxamide) IVc which, after crystallisation from petroleum (b.p. 80-100°), was obtained as white needles, m.p. 177-179°.

Elemental analysis: Found: C, 82.2; H, 6.38; N, 5.35%.

$C_{18}H_{17}NO$ requires: C, 82.1; H, 6.51; N, 5.32%.

Reduction of the above amide with lithium aluminium hydride in boiling ether afforded 5-dimethylaminomethyl-5,5a-dihydro-4bH-cyclopropa[l]phenanthrene as an oil. This was converted into the hydrochloride IVd which, after crystallisation from ethanol-ether mixture, was obtained as white needles, m.p. 223-227.5°.

Elemental analysis: Found: C, 75.6; H, 7.15; N, 4.95%.

$C_{18}H_{19}N,HCl$ requires: C, 75.6; H, 7.05; N, 4.90%.

The UV-spectra of the amide IVc and the amine hydrochloride IVd are almost identical to that of the acid IVb and the data is presented in Table 1. We conclude that the cyclopropane ring does not transmit conjugation in this system and that the compound isolated by Müller cannot have structure II.

TABLE 1

UV-Spectra* in Ethanol

Compound	λ_{min} mμ (log ε)	λ_{max} mμ (log ε)
IVb	247 (3.64)	271 (4.18), 278-81 (4.15), 298 (3.72), 310 (3.76)
IVc	250 (3.72)	272 (4.14), 279-82 (4.09), 299 (3.69), 311 (3.73)
IVd	248 (3.56)	271 (4.14), 279-83 (4.09), 300 (3.69), 310 (3.74)

It is possible that Müller's product is 9-methylphenanthrene; the quoted m.p. and UV-spectrum are almost identical to that of 9-methylphenanthrene (6), as shown in Table 2, except that the low intensity absorptions of the α-band (5) at 317-349 mμ have not been mentioned.

TABLE 2

Compound	m.p.	λ_{max} mμ (log ε)	Ref.
9-methylphenanthrene	92°	252 (4.79), 277 (4.13), 284 (4.00), 297 (4.07)	6
"II"	89°	253 (4.75), 276 (sh), 284 (sh), 296 (4.03)	1

The lack of discrimination of diazomethane in its reactions with olefins

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* The compounds were also investigated in concentrated solution in the region 320-360 mμ but no absorptions having a log ε > 1.0 were detected. This clearly distinguishes the ring system from phenanthrene.

via photolytic or thermal decomposition is well established (7, 8) and the insertion of methylene into a C-H bond competes favourably with its addition to a double bond. In the presence of copper salts, however, the decomposition has been reported (8) to produce a selective form of methylene which does not give rise to insertion products. Müller and co-workers have shown (9) that methylene generated in this way reacts via a copper complex with aromatic compounds to give addition products only. It is possible that phenanthrene is exceptional or that there is sufficient thermal decomposition of diazomethane at 160° (under the experimental conditions) to generate the "less-selective" methylene. Alternatively 9-methylphenanthrene could arise by isomerisation of the product II.

The author thanks Miss E. V. Eggington of these laboratories for spectral measurements.

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ADDENDUM

Professor Müller (personal communication) has re-examined the reaction of diazomethane with phenanthrene and has found no evidence (from NMR spectra) for the presence of methylphenanthrenes in the crude reaction product. On the other hand, the fractions obtained after gas chromatography did show NMR absorptions compatible with methyl groups. He concludes that a mixture of methylphenanthrenes has been produced by rearrangement during the gas chromatographic separation (T > 200°) and is currently investigating this reaction in more detail.