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THE REACTION OF DICHLOROCARBENE WITH ANTHRACENE

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THE reaction of dichlorocarbene with olefins has been demonstrated to provide a convenient route to cyclopropanes.[1] Although it has been demonstrated[2] that the Reimer - Tiemann reaction involves a dichlorocarbene intermediate, there have been no reports of dichlorocarbene reacting with unsubstituted aromatic hydrocarbons.

Chromatography on alumina of the crude product of the reaction of chloroform with a benzene slurry of anthracene and potassium t-butylate afforded a white crystalline compound, (I), (10%), m.p. 128 - 129°. Found: C, 76.0; H, 6.39; Cl, 11.8. Calc. for $C_{19}H_{19}ClO$: C, 76.4; H, 6.41; Cl, 11.9. The ultraviolet spectrum of I (λ_{max}^{EtOH} 282 mμ, log ε = 4.04) is in good agreement with that of dibenzo [a,e]- cycloheptatriene.[3]

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[1] W. von E. Doering and A.K. Hoffman, J. Amer. Chem. Soc. **76**, 6162 (1954); W. von E. Doering and W.A. Henderson, Jr., Ibid. **80**, 5274 (1958); W.E. Parham, H.E. Reiff and P. Swartzentruber, Ibid. **78**, 1437 (1956); S.M. McElvain and P.L. Weyna, Ibid. **81**, 2579 (1959).

[2] J. Hine and J.M. van der Veen, J. Amer. Chem. Soc. **81**, 6446 (1959).

[3] T.W. Campbell, R. Ginsig and H. Schmid, Helv. Chim. Acta **36**, 1489 (1953).

The absence of benzylic chlorine in I was demonstrated by its failure to react with alcoholic silver nitrate. The nuclear magnetic resonance spectrum (CCl_4) of I has aromatic peaks at 2.27 and 2.79, a methine peak at 5.08, and a methyl peak at 8.73.[4] The peak area ratios are approximately 9:1:9 for aromatic methine: methyl protons.

When I dissolved in concentrated sulfuric acid, a deep red solution of the 10-chlorodibenzotropylium ion, IV, was obtained. The ultraviolet and visible spectrum of this solution is in agreement with those of the dibenzo [a,e]tropylium cation, V, and the 5-phenyldibenzo[a,e]tropylium cation, VI,[5] with some shifts due to the presence of the chlorine substituent (Table 1). On the basis of the evidence given, I can reasonably be formulated as 10-chloro-5-t-butoxydibenzo[a,e]cycloheptatriene.

TABLE 1

Absorption Maxima in 98% Sulfuric Acid

Ion	λ log ε	λ log ε	λ log ε	λ log ε	λ log ε	λ log ε	λ log ε
IV	246 4.10	255 4.09	311 4.84	384 3.96	400 3.81	513 3.48	545 3.51
V	236 4.16	270 3.84	306 5.09	380 4.02	398 3.95	508 3.52	540 3.51
VI	240 4.26	268 4.10	312 5.01	384 3.76	414 3.70	528 3.65	564 3.69

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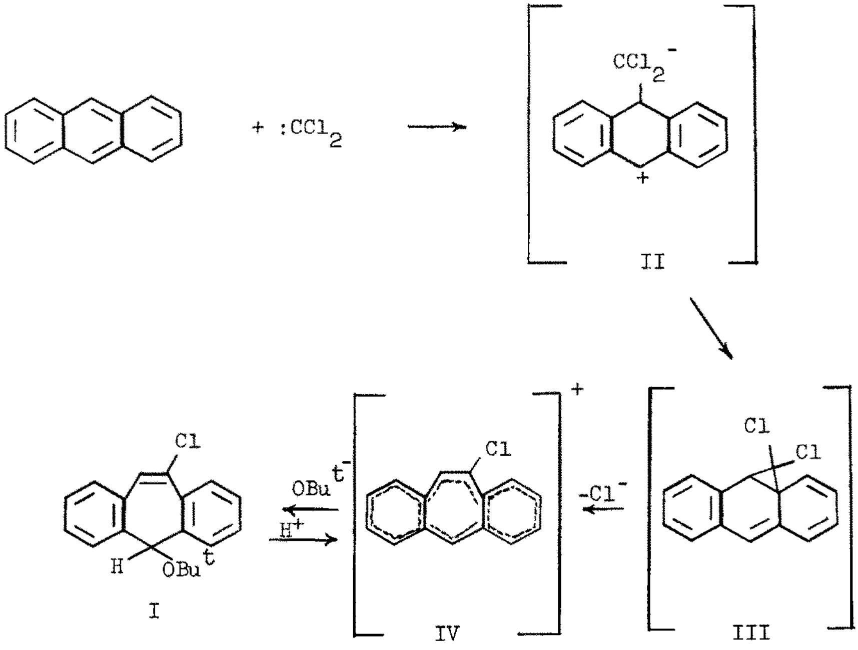
[4] Chemical shift values are in p.p.m. relative to tetramethylsilane standard = 10.0 p.p.m. NMR spectra are by Dr. M. Saunders, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

[5] G. Berti, J. Org. Chem. **22**, 230 (1957).

One possible mechanistic explanation for the formation of I involve the addition of dichlorocarbene to anthracene to give an intermediate zwitterion, II, which can close to the norcaradiene-type structure, III. This species would be expected to lose chloride ion to give the 10-chlorodibenzotropylium ion, IV, which in the presence of potassium t-butylate goes to the product, I.



The scope of this reaction with respect to other carbenes and other aromatic hydrocarbons is being investigated.