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ON THE HOMOLOGATION OF STABLE CARBONIUM IONS

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THE nucleophilic character of diazomethane suggests that it should react with carbonium ions as shown in the following generalized equation.

$$\underset{\text{I}}{R_3C^+} \longrightarrow R_3C\text{-}CH_2N_2^+ \longrightarrow \underset{\text{II}}{R_3C\text{-}CH_2^+} \longrightarrow \text{Products}$$

From this equation one might anticipate that the carbonium ion I must be of more than transitory existence, i.e. a "stable" carbonium ion, and that since one is generating a primary carbonium ion of the type II, Wagner-Meerwein rearrangements will ensue. To test the feasibility of this reaction[1] we have examined the reaction of diazomethane with three stable carbonium ions, xanthylium (IIIa), thiaxanthylium (IIIb), and N-methylacridinium (IIIc) ions These were chosen since the homologated carbonium ions IV if formed should rearrange to the corresponding dibenz [b,f] oxepin (Va),[5] dibenzo [b',f]

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[1] The formation of aziridinium salts from the reaction of iminium salts with diazomethane[2] may be considered to be an example of this reaction

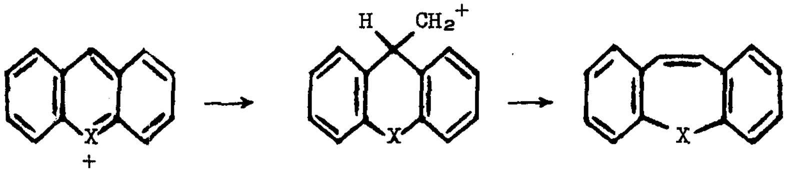
[2] N.J. Leonard and K. Jann, J.Amer.Chem.Soc. 82, 6418 (1960).

[3] E.D. Bergmann and M. Rabinovitz, J.Org.Chem. 25, 827 (1960).

[4] E.D. Bergmann and M. Rabinovitz, J.Org.Chem. 25, 828 (1960).

[5] ~~F.L. Anet and P.M.G. Bavin, Canad.J.Chem. 35, 1084 (1957).~~

thiepin (Vb)[4] and N-methyldibenzo [b,f] azepin (Vc).[6]



III a) X = O
b) X = S
c) $X = NCH_3$

IV a) X = O
b) X = S
c) $X = NCH_3$

V a) X = O
b) X = S
c) $X = NCH_3$

The reaction of xanthylium perchlorate (IIIa) with ethereal diazomethane proceeded briskly at 0°, accompanied by nitrogen evolution and the dissolving of the salt, affording after chromatography a 61% yield of the expected dibenz [b,f] oxepin (Va), m.p. 108-109° (Found: C, 86.49; H, 5.21), reported,[7] m.p. 111°, possessing the appropriate U.V.[5] and I.R. spectra.

Similarly, the reaction of thiaxanthylium perchlorate (IIIb) with diazomethane at 0° afforded after chromatography a 22% yield of dibenzo [b,f] thiepin (vb), m.p. 86-87° (Found: C, 79.80; H, 4.88, S, 15.25), reported,[4] m.p. 89-90°, possessing the correct U.V. and I.R. spectra.[4]

Since the very insoluble N-methyl acridinium perchlorate failed to react with ethereal diazomethane, the reaction of N-methyl acridinium iodide (IIIc) with diazomethane was investigated, a slow (12 hr) reaction occurring which afforded a low yield (less than 10%) of N-methyldibenzo [b,f] azepin (Vc), bright yellow needles, m.p. 142-143° (Found: C, 86.82; H, 6.49; N, 6.80), reported,[6] m.p. 143-144°. The main product from this reaction was a colorless compound, needles, m.p. 115° (d), isolated in 50% yield, whose structure is assigned as VI (Found: C, 54.05; H, 4.11; N, 3.88; I, 38.26. Calc. for $C_{15}H_{14}NI$: C, 53.75; H, 4.21; N, 4.18; I, 37.87). On heating to its

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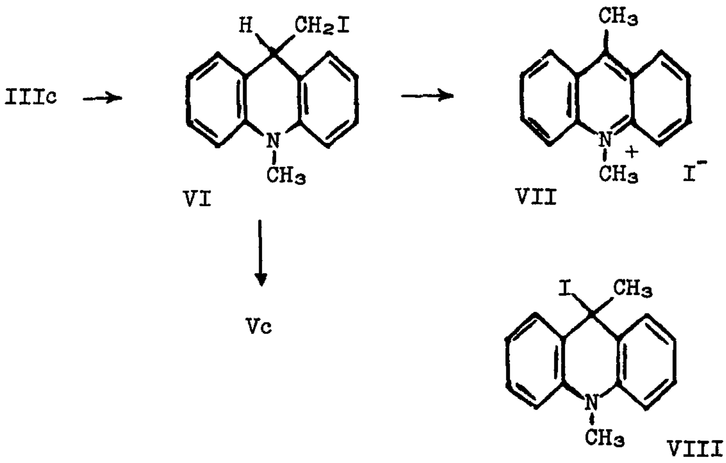
[6] R. Huisgen, E. Laschtuvka, and F. Bayerlein, Chem.Ber. 93, 392 (1960).

[7] R.H.F. Manske and A.E. Ledingham, J.Amer.Chem.Soc. 72, 4799 (1950).



melting point or on merely standing at room temperature in methanol VI rearranged by a 1-2 hydrogen shift to form 9,10-dimethyl acridinium iodide (VII), m.p. 255° (d) (Found: C, 53.66; H, 4.17; N, 4.03; I, 37.98), identified by comparison with an authentic sample. In contrast VI reacted with silver perchlorate in ether to afford by an aryl shift N-methyl dibenzo [b,f] azepin (Vc) (29%) together with a 9% yield of VII, the isolation of the azepin eliminating the alternative structure VIII.

The formation of VI in the reaction of acridine methiodide with diazomethane may be interpreted as an initial attack by diazomethane, affording the ion IVc which is largely captured by the nucleophilic iodide ion to afford VI, a small percentage of IVc rearranging via an aryl shift to afford the azepin Vc. On the other hand the perchlorates of IIIa and IIIb react with diazomethane forming, respectively, IVa and IVb which in the absence of a nucleophilic ion rearrange to the corresponding oxepin (Va) and thiepin (Vb). On reflection one may envisage a number of interesting aspects of this reaction, the more titillating of which are being actively pursued.