Aromatic Substitution by Alkyl Nitrenes

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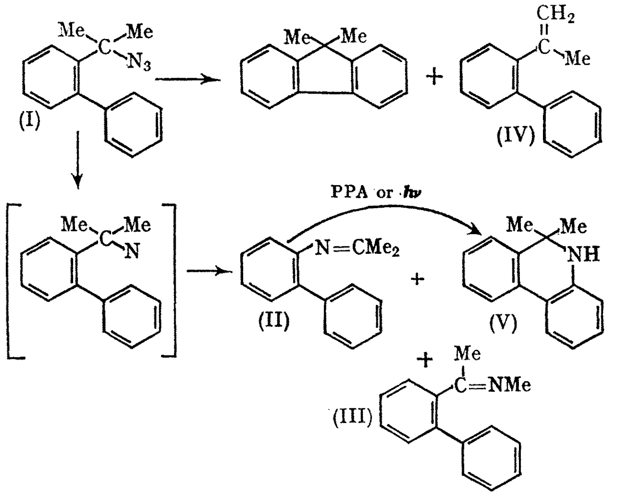
THE reactions of sulphonyl-, ethoxycarbonyl-, and cyanonitrenes with aromatic nuclei give either the substituted aniline or the substituted azepine.[1] Similarly, aryl[2] and arylsulphonyl nitrenes[3] can undergo intramolecular aromatic substitutions. There are, however, no authenticated examples of inter- or intra-molecular substitutions by alkyl nitrenes,[4] apparently because rearrangement of the nitrene by 1,2-hydrogen, -alkyl, or -aryl group migration to give the Schiff's base was much faster than attack on the aromatic nucleus. If the rates were made more nearly equal, aromatic substitution by alkyl nitrenes should be observed. We have achieved this with a suitable aromatic substituent on the nitrene and a tertiary alkyl azide.

Thermolysis of 1-biphenyl-2-yl-1-methylethyl azide [(I), b.p. 113—115°/0·22 mm.†] at 185—190° gave a mixture of the imines, (II) and (III), 9,9-dimethylfluorene, 2-biphenyl-2-ylpropene (IV) (hydrazoic acid was also formed), and the expected cyclisation product, 6,6-dimethyl-5,6-dihydrophenanthridine (V), m.p. 104—105°. Quantitative analysis was best effected after hydrolysis of the imines with dilute acid followed by gas chromatography [(II) was analysed as 2-aminobiphenyl and (III) as 2-acetylbiphenyl]. The structure of (V) was confirmed by its synthesis from (II)



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† Satisfactory analyses, i.r., n.m.r., and mass spectral data were obtained for all the new compounds reported.

with hot polyphosphoric acid (PPA). It was established that (II) was not converted into (V) either during the thermolysis or the gas chromatographic analysis. The main product from the thermolysis was the olefin (IV).

Thermolysis (*a*) *and photolysis* (*b*) *of* (I) *followed by hydrolysis: yields of products* (%)

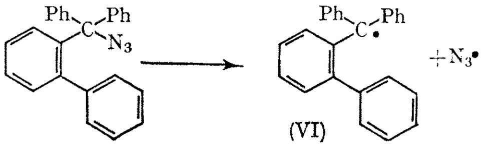
	(*a*)	(*b*)
2-Aminobiphenyl	7·4	8·0
2-Acetylbiphenyl	7·6	62·2
9,9-Dimethylfluorene	1·7	2·2
(IV)	62·0	—
(V)	6·5	2·5
Overall % yield	85·2	74·9
Biphenyl-2-yl:Me migratory aptitude (corrected statistically)	1·9	0·43*

* The yield of (V) has been added to that of 2-aminobiphenyl in the calculation of this ratio since (V) appears to be formed by photolysis of (II).

Although photolysis of (I) (Vycor filter) gave no olefin (IV), it did give the other products obtained in the thermolysis (Table). The dihydrophenanthridine (V) appears to be formed mainly from the subsequent photolysis of (II) produced initially, and not from the nitrene generated photolytically. Thus, (V) was detected gas chromatographically after 0·5 hr. of photolysis while (II) appeared shortly after photolysis was initiated. After *ca.* 1 hr. the yield of (II) dropped slightly while the yield of (V) slowly increased. After 2 hr., when no more azide remained in the irradiated mixture, (V) was still being produced, although in low yield. Irradiation of pure (II) under identical conditions produced (V).

The biphenyl-2-yl : methyl migratory aptitudes under the two different sets of conditions can be compared with the Ph : Me ratios of 4·05 and 0·96 for the thermal and photochemical processes, respectively.[5]

Intramolecular cyclisation of the alkyl nitrene also occurs, but in very low yields, in the thermolysis of biphenyl-2-yldiphenylmethyl azide, m.p. 116—118° (no olefin formation possible). The main products are the rearrangement products (imines), but some 9,9-diphenylfluorene, biphenyl-2-yldiphenylmethane, and 6,6-diphenyl-5,6-dihydrophenanthridine, m.p. 158—160° (identical with a sample prepared from 6-phenylphenanthridine with phenyl-lithium) were also formed. The low yield of cyclisation product was expected because of the greater migration aptitude of phenyl over methyl in the thermolyses. The formation of the above fluorene and methane derivatives strongly suggests the intermediate formation of biphenyl-2-yldiphenylmethyl radicals (VI) in this thermolysis, in competition with the cleavage leading to the nitrene and nitrogen.



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