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THE FORMATION OF A NITRENE INTERMEDIATE IN THE REACTION OF NITRO COMPOUNDS WITH FERROUS OXALATE

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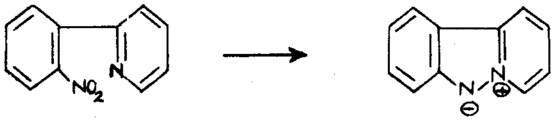
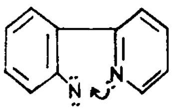
THE reaction of ferrous oxalate with certain aromatic nitro-compounds gives rise to a number of interesting cyclization reactions. For example, 2-nitrodiphenyl gives carbazole[1] whereas 2-nitrodiphenylamines give rise to phenazines[2]. The cyclization of 2-*o*-nitrophenylpyridine (I) with ferrous oxalate at 300° took place not onto a pyridine nuclear carbon but onto the pyridine nitrogen atom to give pyrido[1,2-*b*]indazole (II)[3]. (II) was also obtained in good yield by heating



I II



III

2-*o*-azidophenylpyridine in decalin. The formation of a nitrene intermediate (III) was suggested[3] for the ferrous oxalate reaction, though a

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[1] H. C. Waterman and D. L. Vivian, *J. Org. Chem.* **14**, 289 (1949).

[2] D. L. Vivian, G. Y. Greenberg and J. L. Hartwell, *J. Org. Chem.* **16**, 1 (1951).

[3] R. A. Abramovitch and K. A. H. Adams, *Can. J. Chem.* in the press.

concerted, or perhaps two-stage, cyclization and nitrogen elimination was also a strong possibility in the azide cyclization. Formation of a nitrene intermediate in the thermal decomposition of azides has been suggested[4, 5]; a concerted mechanism was not eliminated as a possible alternative in some instances. A nitrene $-\ddot{\underset{\cdot\cdot}{\mathrm{N}}}$ would be isoelectronic with a carbene and could be either strongly electrophilic (if the valence electrons are paired) or behave as a biradical in the triplet state (both types of behaviour are known for carbenes which can either add to olefinic double bonds[6] or abstract aliphatic hydrogen atoms[7]). Arguments in favour of the triplet state for nitrenes from azides have recently been put forward by Smolinsky[8]. Some of his arguments may become untenable in the light of the formation of (III) (but no δ-carboline or primary amine) from the thermal decomposition of 2-*o*-azidophenylpyridine which, however, is unaffected by ultraviolet light. It is clear that in the ferrous oxalate reaction leading to (II) the nitrene intermediate, if it is formed, must be strongly electrophilic (singlet state) since attack takes place exclusively at the pyridine nitrogen electron pair.

A number of reactions have now been carried out with nitro-compounds and ferrous oxalate to establish whether a nitrene is indeed formed, and if it is, whether it behaves as a singlet electrophilic reagent or as a biradical in the triplet state. It was hoped to trap a

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[4] G. Smolinsky, *J. Amer. Chem. Soc.* **82**, 4717 (1960).

[5] E. Wenkert and B. F. Barnett, *J. Amer. Chem. Soc.* **82**, 4671 (1960).

[6] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.* **81**, 4996 (1959).

[7] W. R. Moore, H. R. Ward and R. F. Merritt, *J. Amer. Chem. Soc.* **83**, 2019 (1961).

[8] G. Smolinsky, *J. Amer. Chem. Soc.* **83**, 2489 (1961).

nitrene intermediate by building an olefinic double bond into the nitro-compound. Unfortunately, o-nitrostyrene underwent extensive polymerization on being heated with ferrous oxalate and no product could be isolated from this reaction. The crude product did, however, give a positive Erhlich test for indoles. The reaction of o-nitrocinnamic acid with ferrous oxalate at 270-280° was more successful and indole-2-carboxylic acid as well as indole could be isolated in low yield (ferrous oxalate is known[9] to catalyze decarboxylations). Here again, the formation of a nitrene in the singlet state is indicated.

From the decomposition of 2'-azido-2,4,6-trimethylbiphenyl Smolinsky[4] obtained 8,10-dimethylphenanthridine (IV) as the major product, some amine (V) (arising from hydrogen abstraction from the solvent and the dihydrophenanthridine initially formed) and a small amount of 2,4,9-trimethylcarbazole. The action of ferrous oxalate dihydrate on 2'-nitro-2,4,6-trimethylbiphenyl (VI) at 300° in the absence of a solvent gave (V) (27.4%) and (IV) (22.6%). (V) cannot, therefore, arise from the dihydrophenanthridine exclusively. The possibility that the hydrogens could have been abstracted from the water of hydration of the oxalate by the nitrene intermediate was eliminated by the use of anhydrous ferrous oxalate: the proportion of (V) : (IV) was practically unchanged. Hydrogen abstraction by the nitrene must, therefore, be taking place from methyl groups in another molecule (alot of intractable tars were formed in most of the reactions reported here and yields were consequently low) somewhat more readily than intramolecularly. This can be rationalized if it is assumed that (i) the reaction is taking place at the surface of the ferrous oxalate (or its decomposition products

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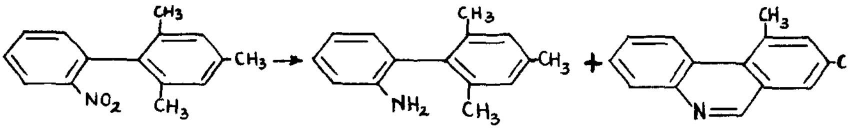
[9] F. Klingstedt, Swensk Papperstidn. **50**, 127 (1947).

e.g. FeO), and (ii) that the molecules, the two rings of which are non-coplanar, tend to orient themselves at the oxalate surface such that the nitro group of one molecule may be close in space to the methyl group of another. Some evidence in support of the first assumption was obtained as follows: anhydrous ferrous oxalate was first boiled under reflux with hexadecane (internal temperature 290°); very little decomposition of the ferrous oxalate occurred, even after prolonged heating. On the other hand, when (VI) was added brisk decomposition of the oxalate occurred at about 240°. It therefore seems as though the decomposition of the ferrous oxalate is catalyzed by the nitro-compound adsorbed on its surface and in turn this causes the nitrene to be formed. When a solution of (VI) in hexadecane was heated with anhydrous ferrous oxalate (V) (42.1%) and (IV) (14.8%) were obtained. No other products could be identified or isolated. In this case, hydrogen abstraction from the solvent is also possible.



VI V IV

o-Nitrophenylcyclohexane was heated with anhydrous ferrous oxalate and gave *o*-aminophenylcyclohexane (51.7%) and carbazole (40%). This reaction and probably also the previous one, undoubtedly involves a nitrene in the triplet state. The formation of carbazole rather than its tetrahydro-derivatives[8] is ascribed to the vigorous conditions of the reaction which can easily lead to dehydrogenation. On the other hand, heating *o*-nitroethylbenzene (VII) with anhydrous ferrous oxalate gave *cis*-*o*-ethylazobenzene (VIII) (15.6%) (comparison of UV and IR with authentic[10] *trans*-isomer) together with *o*-aminoethylbenzene (IX) (4.5%). A very small amount of an amine with a boiling point close to (IX) was detected by gas chromatography. This was not indoline and could perhaps be the benzazetine, arising through hydrogen abstraction from the α-CH_2-, followed by radical coupling. A trace of indole was also detected but no indoline. That the *cis*-azobenzene did not arise through isomerization of the *trans*-form was shown by heating the latter with anhydrous ferrous oxalate. Mainly unchanged *trans*-*o*-ethylazobenzene was recovered, together with a trace of amine (IX) and a small amount of a colourless base, b.p. 144-146°/0.5 mm. Formation of the *cis*-azo-compound is interesting in that it confirms that the molecules tend to be oriented in a preferred fashion on the oxalate surface. Formation of an azo-compound is not unprecedented; 2,2'-dinitrobiphenyl gives 3,4-benzocinnoline[1] and 2-nitrodiphenylsulphide gives 2,2'-bis(phenylmercapto)azobenzene[11] on being heated with ferrous oxalate.

Finally, the action of ferrous oxalate upon a hot solution of nitrobenzene and 1-hexadecene in hexadecane was examined. A small amount of basic material was isolated and distilled to give a fraction b.p. 83-120°/0.17 mm. consisting mainly of aniline (vapour phase chromatography) and a fraction b.p. 180°/0.11 mm. The latter was shown to be homogeneous by chromatography and analyzed for $C_{22}H_{37}N$. Its infrared spectrum showed bands at 3420 cm^{-1} (-NH-) and 970 cm^{-1} (*trans*-CH= CH-) but no $-CH=CH_2$ band. It took up 1 mole of H_2 on catalytic hydrogenation (no band at 970 cm^{-1}). Structure (X) is suggested for this amine and would arise from a triplet nitrene as follows:

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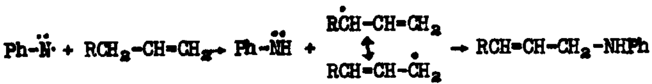
[10] E. Schultz, *Ber.*, **17**, 463 (1884).

[11] D. L. Vivian and H. C. Waterman, *J. Org. Chem.*, **21**, 914 (1956).



$$\mathrm{Ph\text{-}\ddot{N}\cdot + RCH_2\text{-}CH{=}CH_2 \rightarrow Ph\text{-}\ddot{N}H + \begin{matrix} R\dot{C}H\text{-}CH{=}CH_2 \\ \updownarrow \\ RCH{=}CH\text{-}\dot{C}H_2 \end{matrix} \rightarrow RCH{=}CH\text{-}CH_2\text{-}NHPh}$$

$\mathrm{R{=}\ CH_3\text{-}(CH_2)_{12}\text{-}}$

(I)

It would seem, therefore, as though the nitrene intermediate could either behave as a triplet biradical or as a singlet electrophilic reagent; it is probably generated in the triplet state, but could quickly undergo triplet to singlet transition at the surface of the strongly paramagnetic ion.

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