38. *The Structure of the “Nitrenes.”*

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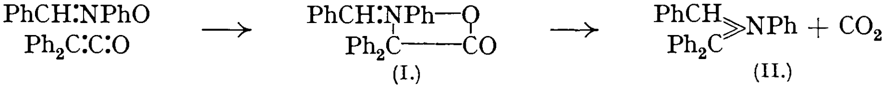
The “nitrenes” are a group of compounds first prepared by Staudinger and Miescher; they have been allotted a structure which involves a pentacovalent nitrogen atom. The experiments described here indicate that this structure is erroneous and that they are ethyleneimine derivatives. Hence these compounds do not form an exception to the general rule that the maximum covalency of nitrogen in its compounds is four.

It is now generally accepted that in its compounds nitrogen shows a maximum covalency of four and that the “pentavalent” nitrogen compounds are either of the type $[NR_4]^+X^-$, where the fifth group is an anion and the fifth valency an electrovalency, or of the type $R_3N \rightarrow O$, in which the bond between nitrogen and oxygen is not a true double bond of four electrons, but a co-ordinate link (semipolar double bond) of two electrons, so that the number of valency electrons held by the nitrogen atom is eight and not ten. There remain, however, in the literature a few compounds for which structures involving pentacovalent nitrogen have been proposed, and where the evidence as stated indicates that they may form exceptions to this generalisation. Such a class is the “nitrenes” of Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 554; Thesis, Zurich, 1918), but the observations recorded in this paper suggest that they do not possess the constitution which Staudinger and Miescher postulated.

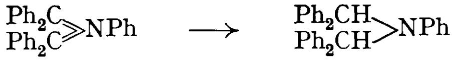
The “nitrenes” are formed by heating the addition compounds of a keten and the *N*-ether of an oxime (a nitrone in Staudinger's nomenclature), and the only ones that can be prepared contain a phenyl group attached to the nitrogen atom and phenyl groups attached to the carbon atoms. An example is “triphenyl-*N*-phenylnitrene” (Staudinger and Miescher, *loc. cit.*); diphenylketen and *N*-phenylbenzaldoxime give an addition compound, which they formulate as (I), and this loses carbon dioxide at 215° to give the nitrene, which they show as (II).



$$\begin{array}{c}PhCH{:}NPhO\\ Ph_2C{:}C{:}O\end{array} \longrightarrow \begin{array}{c}PhCH{:}NPh{-}O\\ Ph_2C{-}{-}{-}CO\end{array} \longrightarrow \begin{array}{c}PhCH\\ Ph_2C\end{array}\!\!>\!NPh + CO_2$$

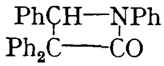
(I.) (II.)

Both the addition compound and the final product were given formulæ which involve pentacovalent nitrogen, but no evidence was advanced in favour of structure (I). As to the structure of the nitrene, Staudinger and Miescher admit the possibility of the ethyleneimine structure (III), but preferred (II) for two reasons. First, they state that the compounds are yellow, while nearly all ethyleneimines are colourless, and secondly, reduction of “tetraphenyl-*N*-phenylnitrene” gave an amine which, it was stated, would not form a nitrosoamine and hence was tertiary; they also state that this amine is identical with dibenzhydrylaniline, although they had difficulty in synthesising this amine and give no analytical data for their synthetic product.



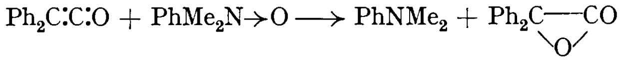
$$\begin{array}{l}Ph_2C\\Ph_2C\end{array}\!\!\gg NPh \longrightarrow \begin{array}{l}Ph_2CH\\Ph_2CH\end{array}\!\!> NPh$$

Apart from the valency difficulty implicit in the structures (I) and (II), the formula (I) for the addition compound seems highly improbable. It is known that a keten will add to a true double bond, but not to the semipolar double bond of an amine oxide; thus Staudinger has shown (*Ber.*, 1907, **40**, 1147) that diphenylketen gives an addition compound with benzylideneaniline and has proved that it has the structure (IV), while he has also shown that with dimethylaniline oxide there is no addition and that diphenylketen oxide is the product.



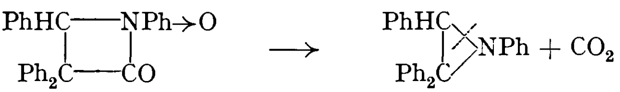
$$\begin{array}{l}PhCH—NPh\\ Ph_2C——CO\end{array}$$

(IV.)



$$Ph_2C{:}C{:}O + PhMe_2N{\to}O \longrightarrow PhNMe_2 + \underset{\diagdown O \diagup}{Ph_2C——CO}$$

Hence the addition of a keten to an *N*-phenyl oxime is much more likely to give the trimethyleneimine derivative (V). In such a compound a bond has been established between two carbon atoms, and when carbon dioxide is lost on heating, it is improbable that this bond will disappear. Consequently the "nitrene" is almost certain to contain this bond intact and to be the ethyleneimine (III).



(V.) (III.)

This view, which removes the valency anomalies in (I) and (II), finds support in the following observations. " Triphenyl-*N*-phenylnitrene " has been prepared and its properties are found to correspond with those given by Staudinger and Miescher with two exceptions. It is a colourless compound when pure and, contrary to their statement, it can be easily reduced to an amine. This is undoubtedly a secondary amine, because its *nitroso*-derivative has been obtained and analysed. Hence there is little doubt that the " nitrene " is in reality 1 : 2 : 3 : 3-tetraphenylethyleneimine and that the reaction has proceeded as is shown above. Reduction of the " nitrene " gives only one product, although the two C–N bonds are not identical and their opening should give two different amines. It would be expected that the bond which is less sterically hindered would be attacked the more readily (as shown in the dotted line in III) and the product should be 1-*anilino*-1 : 1 : 2-*triphenylethane,* $NHPh{\cdot}CPh_2{\cdot}CH_2Ph$. This prediction seems to be verified by the fact that Bergmann and Rosenthal (*J. pr. Chem.*, 1932, **135**, 267) have prepared the isomeric 1-anilino-1 : 2 : 2-triphenylethane, $NHPh{\cdot}CHPh{\cdot}CHPh_2$, and find that it melts at 164—166°, whereas our amine melts at 152—153°.

The structure of this " nitrene " would be best established by an independent synthesis, but our many attempts to achieve this have been unsuccessful. 1-*Chloro*-2-*anilino*-1 : 1 : 2-*triphenylethane,* $CPh_2Cl{\cdot}CHPh{\cdot}NHPh$, has been obtained, but no conditions could be found under which the ethyleneimine ring would close; the chlorine atom resembles that in triphenylmethyl chloride and is extremely readily hydrolysed. The failure to effect ring closure is due to the presence of the two phenyl groups on the carbon atom which carries the chlorine, because we find that 1-*chloro*-2-*anilino*-1 : 2-*diphenylethane* gives 1 : 2 : 3-*triphenylethyleneimine* when heated with alcoholic potash. A similar difficulty is recorded recently by Mannich and Baumgarten (*Ber.*, 1937, **70**, 210) in the closure of the trimethyleneimine ring. Attempts were made to prepare this ethyleneimine by the " nitrene " method from phenylketen and *N*-phenylbenzaldoxime; this would settle the point by showing that a " nitrene " obtained by Staudinger's method was really an ethyleneimine; they were, however, unsuccessful. The formation of ethyleneimines by the thermal decomposition of these addition compounds seems to be conditioned in some unknown way by the presence of several phenyl groups. A further example of this fact was found in the behaviour of the addition *compound* of diphenylketen and *N*-methylbenzophenoneoxime, which Staudinger was unable to prepare; when heated, this compound does not decompose smoothly to give an ethyleneimine, as the corresponding *N*-phenyl compound does, but only yields an intractable tar.

EXPERIMENTAL.

N-Phenylbenzaldoxime was obtained from *N*-phenylhydroxylamine and benzaldehyde (Bamberger, *Ber.*, 1894, **27**, 1556), and diphenylketen by the thermal decomposition of benzoylphenyldiazomethane (Schroeter, *Ber.*, 1909, **42**, 2346), prepared by the oxidation of benzilmonohydrazone (Curtius and Thun, *J. pr. Chem.*, 1891, **44**, 182). (The oxidation proceeds very much more readily if the yellow mercuric oxide is exposed to the moist air of the laboratory for 24 hours before use.) The decomposition of the diazo-compound was carried out in benzene solution in an atmosphere of carbon dioxide at 50—55°; after 1 hour evolution of nitrogen ceased; the benzene was removed at 60°, and the keten distilled in carbon dioxide; b. p. 146°/12 mm. *N*-Methylbenzophenoneoxime was obtained by methylation of the oxime and separation of the *O*- and the *N*-ether with light petroleum (Semper and Lichtenstadt, *Ber.*, 1918, **51**, 933).

Addition of Diphenylketen to N-*Methylbenzophenoneoxime : 2-Keto-3 : 3 : 4 : 4-tetraphenyl-1-methyltrimethyleneimine Oxide.*—The oxime-ether in benzene was added to a benzene solution of its equivalent of the keten in an atmosphere of carbon dioxide; addition of light petroleum precipitated a colourless *compound* which, after several recrystallisations from ligroin–benzene, melted at 164° (Found : C, 82·9; H, 5·8. $C_{28}H_{23}O_2N$ requires C, 83·0; H, 5·7%). The compound decomposed vigorously at 180° and evolved carbon dioxide, leaving a dark tar.

Addition of Diphenylketen to N-*Phenylbenzaldoxime : 2-Keto-1 : 3 : 3 : 4-tetraphenyltrimethyleneimine Oxide.*—The reaction was carried out as described by Staudinger and Miescher (*loc. cit.*); the product purified by washing with ether, light petroleum, and benzene melted at 199—200°; Staudinger and Miescher give m. p. 186—190°. Heating this compound gave " triphenyl-*N*-phenylnitrene " (1 : 2 : 2 : 3-tetraphenylethyleneimine), which after four recrystallisations from alcohol and one from light petroleum with 5% of benzene formed colourless needles, m. p. 107·5°; Miescher described this compound as pale yellow, m. p. 105—106° (Found : C, 89·6; H, 6·05. Calc. for $C_{26}H_{21}N$: C, 89·9; H, 6·05%).

Reduction of 1 : 2 : 2 : 3-Tetraphenylethyleneimine.—The imine (8 g.) in ether with 1 c.c. of water was treated with freshly prepared aluminium amalgam (5 g.). After 12 hours removal of the ether from the filtered solutions gave 1-*anilino*-1 : 1 : 2-*triphenylethane*, which was recrystallised from aqueous alcohol and ligroin–benzene; yield 7 g., m. p. 152—153° (Found : C, 89·7; H, 6·6. $C_{26}H_{23}N$ requires C, 89·4; H, 6·6%). This amine (1·5 g.) was dissolved in 15 c.c. of alcohol and 5 c.c. of concentrated hydrochloric acid, and a slight excess of saturated aqueous potassium nitrite added at 0°. After 3 hours the sticky solid which separated was collected and recrystallised, first from aqueous alcohol and then from ligroin–benzene; 1 g. of the *nitrosoamine* was obtained, m. p. 114—115° (Found : C, 82·7, H, 6·0; N, 7·3. $C_{26}H_{22}ON_2$ requires C, 82·5; H, 5·8; N, 7·4%).

2-*Anilino*-1 : 1 : 2-*triphenylethyl Alcohol.*—Desylaniline (27 g.) (Cameron, *Trans. Roy. Soc. Canada*, 1929, **23**, 53) in 100 c.c. of ether was added to a solution of phenylmagnesium bromide made from 64 g. of bromobenzene. After 30 minutes on the steam-bath, the mixture was cooled, and ice and concentrated aqueous ammonium chloride added. The ethereal layer gave 17 g. of the *product*, which was recrystallised from alcohol; m. p. 173° (Found : C, 85·3; H, 6·3; N, 3·9. $C_{26}H_{23}ON$ requires C, 85·5; H, 6·3; N, 3·8%).

Replacement of the hydroxyl group by chlorine offered great difficulty; this was traced to the solubility of the hydrochloride of the chloro-compound in chloroform and the extreme ease with which the chloro-compound is hydrolysed to the alcohol. 1-*Chloroanilino*-1 : 1 : 2-*triphenylethane* was eventually obtained by treating the alcohol (15 g.), dissolved in the minimum of ethylene dibromide, with phosphorus pentachloride (9 g.). A white precipitate of the hydrochloride of the compound slowly separated; it was removed and washed with dry ether; yield 8 g.; no definite m. p. Treatment of this hydrochloride with any aqueous reagent or with alcoholic potash regenerated the alcohol. The free base could, however, be obtained by rubbing the hydrochloride with cold dry pyridine; the base was recrystallised from chloroform–light petroleum; m. p. 196° (Found : Cl, 9·5. $C_{26}H_{22}NCl$ requires Cl, 9·3%). Attempts to bring about ring closure with pyridine, quinoline or dimethylaniline were unsuccessful; the product obtained under any conditions gave the alcohol when treated with water, which showed that the chloro-compound was unchanged. Ring closure of the alcohol to the ethyleneimine by heating with phosphoric oxide in boiling xylene was also tried; the only product isolated was ωω-diphenylacetophenone (m. p. 136°). This would be expected as the hydrolysis product of the anil formed by loss of water from the alcohol :

$$HO{\cdot}CPh_2{\cdot}CHPh{\cdot}NHPh \longrightarrow CPh_2{:}CPh{\cdot}NHPh \longrightarrow CHPh_2{\cdot}CPh{:}NPh \longrightarrow CHPh_2{\cdot}COPh$$

1 : 2 : 3-*Triphenylethyleneimine*.—Desylaniline was reduced to 2-anilino-1 : 2-diphenylethyl alcohol (Voigt, *J. pr. Chem.*, 1886, **34**, 13). This alcohol (3 g.) was treated in 10 c.c. of dry chloroform with phosphorus pentachloride (2·5 g.) and cooled; a hydrochloride (2·8 g.) separated on standing and was treated with excess of cold alcoholic potash. Addition of water precipitated 1-*chloro*-2-*anilino*-1 : 2-*diphenylethane*, which was recrystallised from methyl alcohol; m. p. 126° (Found : Cl, 11·5. $C_{20}H_{18}NCl$ requires Cl, 11·5%). When this compound was boiled with an excess of alcoholic potash for 1 hour, the solution turned yellow and potassium chloride separated. Addition of water gave a sticky solid, which was extracted with ether. From this solution a yellow gum was obtained which on recrystallisation gave the *triphenylethyleneimine* in colourless needles, m. p. 99° (Found : N, 5·1. $C_{20}H_{17}N$ requires N, 5·2%).

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