4. Mercury caused the formation of ethylbenzene and considerably reduced the amount of resin formed.

5. Certain physical and chemical properties of the resin have been studied.

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THE BECKMANN REARRANGEMENT IN THE PRESENCE OF FREE RADICALS

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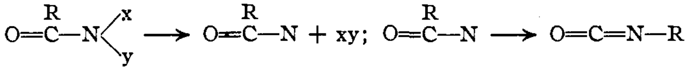
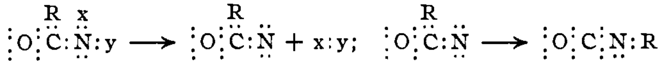
Of the several theories that have been advanced to explain the rearrangement of hydroxamic acids, halogen amides, acyl azides and other similar classes of compounds, the most successful has been the interpretation by Stieglitz.[2] Assuming the intermediate formation of a univalent nitrogen derivative, he proposed that all rearrangements of this character take place as follows



$$O{=}\overset{R}{C}{-}N\lt^{x}_{y} \longrightarrow O{=}\overset{R}{C}{-}N + xy;\quad O{=}\overset{R}{C}{-}N \longrightarrow O{=}C{=}N{-}R$$

Jones and Hurd,[3] suggesting an interpretation of the mechanism of these rearrangements based upon the modern conception of chemical bonds and electrons, formulated the rearrangement thus



$$\vdots O\vdots\overset{R}{C}:\overset{x}{\underset{..}{N}}:y \longrightarrow \vdots O\vdots\overset{R}{C}:\overset{..}{\underset{..}{N}} + x:y;\quad \vdots O\vdots\overset{R}{C}:\overset{..}{\underset{..}{N}} \longrightarrow \vdots O\vdots C\vdots\underset{..}{N}:R$$

Their interpretation, which excluded the oximes, assumed that the radical, R, in its wandering from the carbon atom to the nitrogen atom existed momentarily as a free radical, and that the relative ease of rearrangement of such types of compounds depended upon the tendency of the radical, R, in the univalent nitrogen derivative to exist as a free radical. This hypothesis was tested by studying the rearrangement of monophenyl-, diphenyl- and triphenylacethydroxamic acids and their derivatives.

Hurd[4] also found further evidence in support of this hypothesis in his study of certain derivatives of N-diphenylhydroxyurea, $(C_6H_5)_2N$-CO-NHOH.

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[1] Some of the preliminary experiments in this investigation, including the preparation of materials, etc., were carried out with the help of Mr. Howard W. Gilbert, a graduate assistant in the department.

[2] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); *ibid.*, **29**, 49 (1903); Stieglitz and Earle, *ibid.*, **30**, 349, 412 (1903); Stieglitz and Slossen, *Ber.*, **28**, 3265 (1895); **34**, 1613 (1901); Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914).

[3] Jones and Hurd, *ibid.*, **43**, 2422 (1921).

[4] Hurd, *ibid.*, **45**, 1472 (1923).

Continuing these investigations Jones and Wallis[5] studied the nature of the products formed by the rearrangement of certain acid azides and hydroxamic acids in which the group, R, is an optically active radical. *d*-Benzylmethylacetazide, $C_7H_7(CH_3)HCCON_3$, was found to give on rearrangement an optically active isocyanate, $C_7H_7(CH_3)HCNCO$, which could be converted into an optically active amine hydrochloride, and by treatment with aniline into an optically active monosubstituted urea. These experiments, together with certain other facts taken from a survey of the properties of optically active compounds described in the literature, led them to suggest that it was very probable that in the rearrangement of *d*-benzylmethylacetazide the optically active radical, R, if existing as a free radical, did so in such a way as to maintain a configuration required to produce an optically active rearrangement product; that is, it was, as originally supposed by Jones,[6] a positive radical which is of the nature of a carbonium ion, and that in its wandering from the carbon atom to the nitrogen atom it leaves behind the electron which it shared with the carbon atom.

The Rearrangement of Benzylmethylacetazide in the Presence of a Free Radical.—I have continued these investigations in order to determine the products formed by rearrangement when the rearrangement is carried out in the presence of a free radical; for I believed that such a determination would give further evidence in support of the hypothesis just outlined.

It has been known for some time that triphenylmethyl, because of its preëminent tendency to make addition compounds, is a good reagent for the detection of free radicals. Wieland,[7] for instance, used it in his study of tetraphenylhydrazine, and the assumption that the dehydrophenols[8] contain monovalent oxygen, and that the tetrazanes[9] are dissociable to form triarylhydrazils is based upon the fact that both classes of compounds readily combine with triphenylmethyl. It therefore seemed possible that this same interesting and very reactive compound might be used to advantage in a further study of those classes of compounds that undergo the Beckmann rearrangement. For this investigation benzylmethylacetazide was chosen as a compound typical of this group of substances. It was allowed to rearrange in the absence of air in a benzene solution of triphenylmethyl and the products of the rearrangement were determined. With no triphenylmethyl present the rearrangement has been formulated[5] as follows

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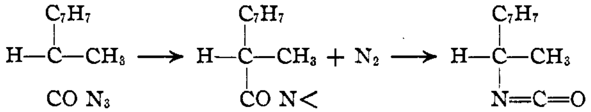
[5] Jones and Wallis, This Journal, **48**, 169 (1926).

[6] Jones, *Am. Chem. J.*, **50**, 441 (1913).

[7] H. Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart.

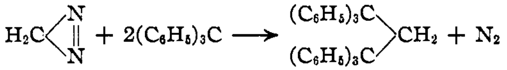
[8] S. Goldschmidt, *Ber.* **53**, 44 (1920); *ibid.*, **55**, 616, 628 (1922).

[9] S. Goldschmidt, *ibid.*, **55**, 3194, 3197 (1922).



$$\begin{array}{c}C_7H_7\\ |\\ H-C-CH_3\\ CO\ N_3\end{array} \longrightarrow \begin{array}{c}C_7H_7\\ |\\ H-C-CH_3\\ |\\ CO\ N<\end{array} + N_2 \longrightarrow \begin{array}{c}C_7H_7\\ |\\ H-C-CH_3\\ |\\ N=C=O\end{array}$$

However, a little reflection will show that when triphenylmethyl is present two different rearrangement products are possible. (1) If the radical, R, in the univalent nitrogen derivative, in its wandering from the carbon atom to the nitrogen atom exists momentarily as a true free radical, that is, does not leave behind on the carbon atom its electron and so become a positive ion, the formation of two different isocyanates is possible. The radical triphenylmethyl, can then compete with the radical, R, for the univalent nitrogen residue, and the quantity of triphenylmethyl isocyanate, $(C_6H_5)_3CNCO$, so formed would depend on well-known physical-chemical principles. An illustration of such a phenomenon is found in the reaction of diazomethane and triphenylmethyl. Investigations[10] have shown that these two substances react according to the equation



$$H_2C\left\langle\begin{array}{c}N\\ \|\\ N\end{array}\right. + 2(C_6H_5)_3C \longrightarrow \left.\begin{array}{c}(C_6H_5)_3C\\ (C_6H_5)_3C\end{array}\right\rangle CH_2 + N_2$$

Here, apparently, the free radical, triphenylmethyl, when in the proper concentration, is so successful in its competition with the methylene radical for union with another methylene radical that no ethylene seems to be formed in the reaction.

(2) However, if the radical, R, in its wandering from the carbon atom to the nitrogen atom, leaves behind its electron and becomes a positive ion as suggested by Jones and Wallis,[5] the chances of the formation of any triphenylmethyl isocyanate would be very slight. In fact the radical, R, would then be of an entirely different nature than the free radical, triphenylmethyl, and only the one isocyanate, $C_7H_7(CH_3)HCNCO$, would be expected.

The author's experiments on the rearrangement of benzylmethylacetazide in the presence of triphenylmethyl seem to give further evidence which tends to exclude the first possibility, and to show that the latter view of the rearrangement is the more probable. When a benzene solution of benzylmethylacetazide was added to a benzene solution of triphenylmethyl, and the rearrangement allowed to take place in the absence of air, a quantitative determination of the amount of oxygen absorbed by the free radical remaining after the rearrangement indicates that none of it took part in the reaction, and an analysis of the products of the rearrangement shows that only one isocyanate, $C_7H_7(CH_3)HC\text{-}NCO$, is formed in appreciable amounts.

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[10] Schmidlin, "Triphenylmethyl," Ferdinand Enke, Stuttgart (investigator, Schlenk).

Experimental Part

Materials.—The benzylmethylacetazide used in these investigations was prepared by the action of sodium azide on benzylmethylacetyl chloride dissolved in ether according to a method previously described.[5] The purity of the azide was determined by measuring quantitatively the amount of nitrogen evolved when the compound undergoes rearrangement. The solid triphenylmethyl used in these experiments was prepared and its purity determined according to the method of Gomberg.[11] The benzene used was of the purified variety that is commonly employed in investigations involving the use of free radicals.

Procedure.—A three-holed round-bottomed flask immersed in a thermostat was connected by means of glass tubing containing stopcocks to three azotometers[12] filled with benzene. After the air had been completely removed from the apparatus a known volume of benzene was run into the flask by means of a dropping funnel and a weighed portion of solid triphenylmethyl was introduced. When solution had taken place a weighed amount of benzylmethylacetazide dissolved in a small amount of benzene was added. The stopcocks in the azotometers were opened and the rearrangement was allowed to take place at a constant temperature. The volume of nitrogen evolved was measured and corrected to standard conditions of temperature and pressure. After the rearrangement was completed all stopcocks were closed and the azotometers were disconnected and filled with dry oxygen. After being again connected to the reaction flask, the stopcocks were opened and the oxygen was allowed to diffuse into the reaction chamber and be absorbed by the triphenylmethyl remaining in the solution. The flask was shaken vigorously from time to time and the volume of oxygen absorbed was measured and corrected to standard conditions of temperature and pressure. Several experiments were carried out varying the temperature at which the rearrangements took place and the concentrations of the benzylmethylacetazide and triphenylmethyl. In all cases the volume of oxygen absorbed after the rearrangement corresponded very closely to the theoretical amount of absorption expected if no triphenylmethyl had taken part in the reaction. The results are given in Table I.

TABLE I[a]

TABULATED RESULTS

Expt.	Rearrangement temp., °C.	Azide, g.	Triphenylmethyl g.	Soln., cc.	N_2 corr. to S.T.P., cc.	N_2, calcd., cc.	O_2 abs. corr. to S.T.P. cc.	Calcd. vol. of O_2 abs. assuming no triphenylmethyl reacted, cc.
1	35	1.023	...	60	118.3	121.2	...	...
2	35	...	1.192	60	...	...	53.9	55.0
3	35	0.887	1.203	60	103.0	105.2	56.1	55.5
4	50	1.097	1.314	60	127.2	130.1	59.2	60.6
5	35	1.147	2.864	60	133.3	137.0	129.8	132.1

[a] The vapor pressures of benzene used in these calculations were taken from tables published in Landolt and Börnstein. In Expt. 5 about two moles of triphenylmethyl were used for 1 mole of azide.

Analysis of the Products of Rearrangement.—An analysis was carried out of the products of rearrangement in Expt. 5. The benzene was partially removed by evaporation at room temperature in a vacuum desiccator. The triphenylmethyl peroxide,

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[11] Gomberg and Cone, *Ber.*, **37**, 2034, 3638 (1904).

[12] Three azotometers were necessary since in some of the experiments the amount of azide used gave more than 100 cc. of nitrogen on rearrangement.

formed by the action of the oxygen on the triphenylmethyl, was collected on a filter and washed with a small amount of benzene: 2.38 g. of dry product was obtained, melting point, 183°. One recrystallization from carbon disulfide gave a product melting at 185°. The recorded melting point of pure triphenylmethyl peroxide is 185–186°; yield of peroxide, 78%. The filtrate was analyzed for any isocyanates that might be present. Dry ammonia gas was passed through the solution and in a few minutes a white precipitate of the urea was obtained. This was collected on a filter, after 25 cc. of ligroin had been added to decrease its solubility in the benzene solution; 1.00 g. of dry product was obtained, melting point 146°. One recrystallization from alcohol and water gave a solid melting at 149°; yield assuming but the one isocyanate to have been formed, 97%.

The filtrate from the urea was concentrated and some oily products were obtained. Attempts to isolate any compounds of known constitution that might be expected to be formed failed. In all probability these oily products are produced by the decomposition of the triphenylmethyl peroxide. As has been already stated in the literature, although the absorption of oxygen by triphenylmethyl is nearly quantitative, the amount of triphenylmethyl peroxide obtained from a known weight of triphenylmethyl is not quantitative; other substances of unknown constitution are produced.

Summary

The Beckmann rearrangement of an acylazide in the presence of a free radical has been studied, and the products of the rearrangement have been determined. Benzylmethylacetazide was allowed to rearrange in the absence of air in a benzene solution of triphenylmethyl. Evidence is submitted in this paper to show that only one isocyanate, benzylmethylisocyanate, is formed. A discussion of this fact with reference to certain theories on the Beckmann rearrangement is given.

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A CLEAVAGE OF AZO DYES BY MEANS OF SULFITES*

BY KARL H. ENGEL

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Cleavage of azo dyes through the action of sulfurous acid or of acid sulfites has frequently been observed heretofore but, apparently, has not been investigated in detail. A few experiments of the writer, the interaction of 4-hydroxyazobenzene and sodium bisulfite, for example, indicated that a cleavage of the dye was apt to be complicated by various secondary changes, the rearrangement of primary reaction products sometimes, the formation of resinous by-products and a reduction of some of the azo nitrogen to ammonia. In short, such a reaction looked rather unpromising.

* The material here presented has been submitted as a thesis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Pennsylvania State College.