is obtained by taking the value in ether solution and correcting for the change in activity in passing to the gaseous state. Several assumptions were made and checked on nitrogen dioxide and formic acid. Inasmuch as an effort is being made to measure this reaction in the gaseous state and also the vapor pressure of hexaphenylethane, it is perhaps unnecessary to discuss the method further. Reaction 15, which is the sum of the above eight equations, gives the free energy change for concentrations of one atmosphere. However, since there is no change in entropy for such a gaseous reaction, the various species on both sides of the reaction having the same weight, this value may also be taken as ΔH for the reaction. Combining with Reaction 16 then gives the electron affinity of the free radical as 59 kilogram calories with a probable error of about five kilogram calories. The error in ΔF for Equation 8 is thought to be less than three kilogram calories and for all of the other reactions less than one kilogram calorie.

The author takes pleasure in expressing his appreciation of the interest and suggestions of Dr. W. H. Carothers.

Summary

The addition of sodium to triphenylmethyl has been found to be a reversible reaction. ΔF for this reaction has been determined and also for the dissociation of hexaphenylethane and sodium-triphenylmethyl. The electron affinity of triphenylmethyl in the gaseous state has been found to be 59 ± 5 kilogram calories.

Cambridge, Massachusetts

[Contribution from the Chemical Department, University of Bristol]

THE ACTION OF DIAZOMETHANE ON SOME AROMATIC ACYL CHLORIDES. V. THE MECHANISM OF THE REACTION

By T. Malkin and M. Nierenstein

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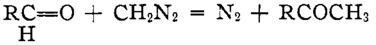
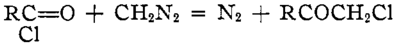
In Part III of this series[1] an attempt was made to coördinate the Schlotterbeck reaction[2] with what has now become known as the Nierenstein reaction.[3] It was suggested that the two reactions, where X = H (Schlotterbeck) and X = Cl or Br (Nierenstein) proceed as follows



$$\underset{\mathrm{H}}{\mathrm{RC}}{=}\mathrm{O} + \mathrm{CH_2N_2} = \mathrm{N_2} + \mathrm{RCOCH_3}$$



$$\underset{\mathrm{Cl}}{\mathrm{RC}}{=}\mathrm{O} + \mathrm{CH_2N_2} = \mathrm{N_2} + \mathrm{RCOCH_2Cl}$$

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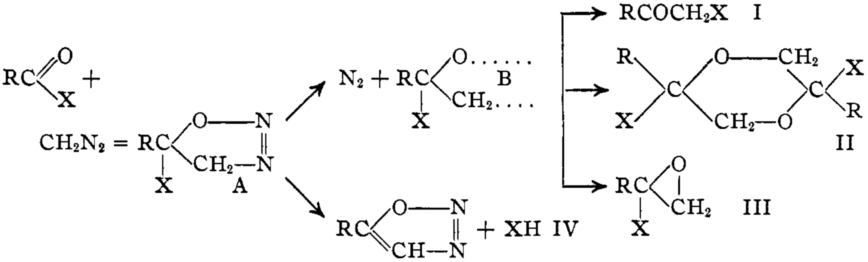
[1] Lewis, Nierenstein and Rich, This Journal, **47**, 1728 (1925).

[2] Schlotterbeck, *Ber.*, **40**, 479 (1907).

[3] (a) Clibbens and Nierenstein, *J. Chem. Soc.*, **107**, 1481 (1915); (b) Nierenstein, *ibid.*, **117**, 1153 (1920); (c) Nierenstein, Wang and Warr, This Journal, **46**, 2554 (1924); (d) Kahil and Nierenstein, *ibid.*, **46**, 2557 (1924); (e) Lewis, Nierenstein and Rich, *ibid.*, **47**, 1728 (1925); (f) Dale and Nierenstein, *Ber.*, **60**, 1026 (1927); (g) Malkin and Nierenstein, *ibid.*, **61**, 797 (1928).



This view was supported by the fact that not only ω-halogenated acetophenones (I) but that also dihalogenated dioxans (II) are produced under these conditions. Since the publication of this paper Arndt and his collaborators[4] have succeeded in obtaining compounds derived from Formula III, whereas Meerwein and Burneleit[5] have shown that acetone, where X = CH_3, yields with diazomethane products derived from both Formulas I and III.

A very interesting extension of the reaction was described by Arndt and his collaborators,[6] who succeeded in isolating products derived from Formula IV due to the elimination of XH (for example, HCl) in the intermediary substance A. Arndt's work thus completed the whole cycle of possibilities, indicated above, and it is to be regretted that he has unfortunately assigned to his products the general formula $RCOCHN_2$, although he finds that they do not give phenylhydrazones. It is evident from the literature[7] that it is quite an open question whether the products under consideration are to be regarded as true diazo compounds, as supposed by Arndt, or as cyclic diazo-anhydrides (IV), as suggested by Angeli,[8] and seriously considered by Staudinger[9] and Wieland.[10] The fact that these nitrogen-containing compounds are obtained under the above-mentioned conditions seems to indicate that they are diazo-anhydrides (IV), and not true diazo compounds, and this is confirmed by their resistance to iodine, as already pointed out by Wolff.[11] The statement that the

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[4] Arndt and Eistert, *Ber.*, **61**, 1118 (1928); Arndt, Eistert and Amende, *ibid.*, **61**, 1949 (1928).

[5] Meerwein and Burneleit, *ibid.*, **61**, 1840 (1928).

[6] Arndt, Eistert and Partale, *ibid.*, **60**, 1364 (1927); Arndt and Amende, *ibid.*, **61**, 1122 (1928).

[7] Meyer–Jacobson, "Lehrbuch der Organischen Chemie," **1920**, Vol. III, Pt. III, p. 624. Berlin and Leipzig.

[8] Angeli, *Ber.*, **26**, 1715 (1893).

[9] Staudinger, "Die Ketene," Stuttgart, **1912**, p. 30.

[10] Wieland, "Die Hydrazine," Stuttgart, **1913**, pp. 96, 103. The following quotation from Wieland (p. 103) summarizes his views: "Eine entscheidende Lostrennung der bisher als Diazoanhydride aufgefassten Verbindungen von den Diazokörpern wird voraussichtlich erst dann mit aller Sicherheit möglich sein, wenn man in einem Fall die beiden Isomeren erhalten hat."

[11] Wolff, *Ann.*, **325**, 142 (1902).

nitrogen-containing compound which Bradley and Robinson obtained by the interaction of diazomethane and benzoyl chloride is decomposed by iodine[12] "instantly in cold alcoholic solution with evolution of nitrogen" is clearly an error, since Wolff[11] emphasizes the fact that the reaction only takes place "in der Wärme." This is in agreement with our own observations, since we find that the decomposition of this substance begins only at 45°, being complete at 60°.

Quite a different interpretation of the reaction has been put forward by Robinson and his pupils,[13] who originally denied the production of any ω-chloro-acetophenone except "a trace detectable by the powerful lachrymatory properties and characteristic odor of this substance" when benzoyl chloride reacts with diazomethane. This trace has since been augmented by them to 9[13b] and 13%,[13c] as compared with the 72% obtained by Clibbens and Nierenstein.[3a]

According to the Robinson interpretation,[13b,c] the reaction proceeds in three stages, as follows

$$\text{RCOCl} + \text{CH}_2\text{N}_2 = \text{RCOCHN}_2 + \text{HCl} \qquad \text{(A)}$$

$$\text{CH}_2\text{N}_2 + \text{HCl} = \text{CH}_3\text{Cl} + \text{N}_2 \qquad \text{(B)}$$

$$\text{RCOCHN}_2 + \text{HCl} = \text{RCOCH}_2\text{Cl} + \text{N}_2 \qquad \text{(C)}$$

It will be realized that none of these stages accounts for the production of substances derived from Formula II. Furthermore, this interpretation assumes the formation of methyl chloride, a product identified qualitatively neither by us nor any other workers, nor even by Bradley and Robinson,[14] who state "the formation of methyl chloride . . . was not experimentally confirmed." In support of Robinson's views a series of quantitative experiments have been published by Bradley and Schwarzenbach.[15] Experiment V in their paper[16] claims that "the whole of the nitrogen and chlorine" has been "accounted for." An analysis of this experiment will thus serve best to show the inadequacy of the Robinson theory.

(1) According to the above-given equations, Reactions B and C depend on A for their HCl supply; therefore, using equimolecular quantities of benzoyl chloride and diazomethane, the *maximum* yield of methyl chloride is obviously 50%, diminishing in direct proportion as the production of RCOCH_2Cl (Equation B) increases. Experiment V records, however, 57% of methyl chloride and 13% of ω-chloro-acetophenone.

(2) Assuming that the Robinson scheme is correct, and methyl chloride is produced, then clearly the nitrogen evolution expresses quantitatively the ratio of B to C. Therefore, using diazomethane corresponding to 1772 cc.

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[12] Bradley and Robinson, *J. Chem. Soc.*, 1317 (1928).

[13] (a) Bradley and Robinson, *ibid.*, 1310 (1928); (b) Bradley and Robinson, *Nature*, **122**, 130 (1928); (c) Bradley and Schwarzenbach, *J. Chem. Soc.*, 2904 (1928).

[14] Ref. 13 a, p. 1317.

[15] Ref. 13 c, pp. 2909–2912.

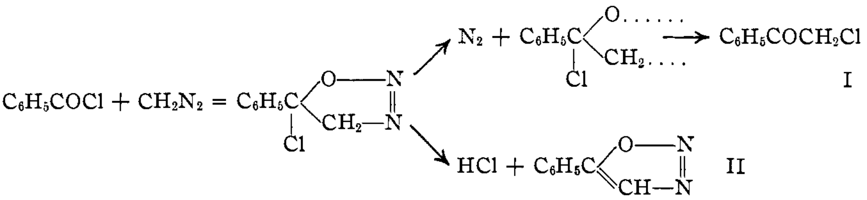
[16] Ref. 13 c, p. 2911.

of N_2,[16] an evolution of 886 cc. of N_2 corresponds to a yield of 31% of ω-chloro-acetophenone and not to 13% as recorded in Experiment V.

(3) If, however, one ignores the indirect determination of methyl chloride, then the nitrogen evolution and the amount of benzoyl chloride recovered unchanged, correspond to an approximate yield of 65%, and not 13% of ω-chloro-acetophenone.

In view of these considerations, and also in view of the fact that Experiment V is the *only* experiment which contains a complete analysis in support of Robinson's hypothesis, it seems to us that this hypothesis is quite unfounded, and requires further data, as well as the establishment of the production of large quantities of methyl chloride, before it can seriously be considered.

Although up to the present we have not succeeded in isolating the intermediary substance A, suggested by Lewis, Nierenstein and Rich,[3e] there is little reason to doubt that it forms the first stage in the reaction, and on decomposition subsequently leads to the production of Substances I (Schlotterbeck, Nierenstein, Arndt, Meerwein), II (Nierenstein), and III (Arndt, Meerwein). In the case of the Nierenstein reaction we find that higher temperatures favor the production of Substance I since, for example, 92% of ω-chloro-acetophenone is produced at 35°, 50% at 16°, and 32% at 0°. The production of Substance IV (Arndt, Robinson), takes place to any appreciable extent at low temperatures only,[17] and the formation of Substances I and II in the case of benzoyl chloride and diazomethane is thus shown as follows



The following apparatus has been in use in this Laboratory for the last ten years, when working with diazomethane prepared according to Pechmann, in flask A, ether being added through the funnel, D, and alkali through funnel E. The diazomethane produced is slowly distilled into flask B,[18] which contains the acyl chloride dissolved in dry ether (Grig-

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[17] It must be noted that the low temperatures used by Robinson and his collaborators are a fundamental variation of the original conditions laid down by Nierenstein and his collaborators, and it is, therefore, not surprising that no concordant yields of ω-chlorinated acetophenones have been obtained by these two sets of workers. See also Nierenstein, *Nature*, **122**, 313 (1928).

[18] Flask B is manufactured in England by Messrs. Plowden and Thompson, Ltd., Stourbridge, Birmingham, who list it as the "Nierenstein flask." This flask is extensively used in these Laboratories for the recovery of ether and other volatile solvents.

nard). The trap C leads into glacial acetic acid, in which manner diazomethane becomes a reagent which can safely be used without other special precautions.

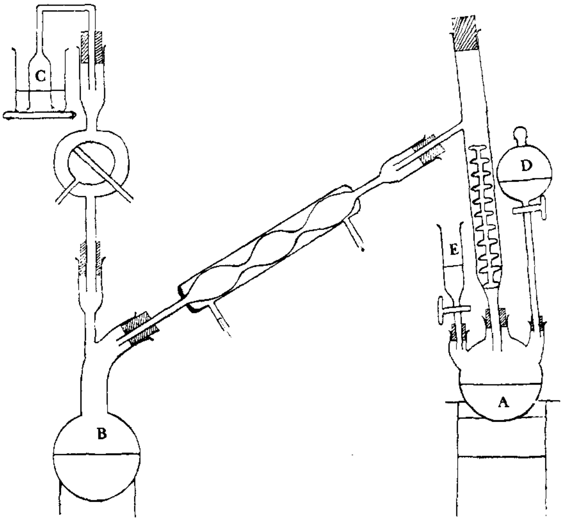

Fig. 1.

Summary

It is shown that the interaction of diazomethane with aromatic acyl chlorides proceeds on the same lines as the Schlotterbeck reaction, and requires no special interpretation, as suggested by Robinson.

BRISTOL, ENGLAND

[COMMUNICATION NO. 397 FROM THE KODAK RESEARCH LABORATORIES]

OPTICAL ROTATION OF CELLULOSIC MATERIALS. I. THE OPTICAL ROTATION OF SOLUBLE CELLULOSE IN ALKALI[1]

BY T. F. MURRAY, JR., C. J. STAUD AND H. LEB. GRAY

RECEIVED JULY 9, 1929 PUBLISHED APRIL 7, 1930

It appeared to the writers that a study of the optical rotation of the alkali-soluble portion of cellulose might help in determining the nature of the material dissolved and possibly the degradation which the cellulose has undergone.

Perhaps no reaction in cellulose chemistry has been more studied than the solubility of cellulose in alkali, almost continuously since the time of John Mercer.[2] A résumé has been published recently by G. Blanco.[3]

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[1] Presented before the Division of Cellulose Chemistry of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] John Mercer, English Patent 13,296 (1850).

[3] G. Blanco, *Ind. Eng. Chem.*, **20**, 926 (1928).