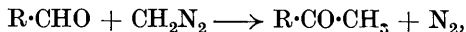


CLXXIV.—*The Interaction of Benzoyl Chloride and Diazomethane together with a Discussion of the Reactions of the Diazenes.*

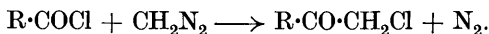
By WILLIAM BRADLEY and ROBERT ROBINSON.

MEYER (*Monatsh.*, 1905, **26**, 1300) and Schlotterbeck (*Ber.*, 1907, **40**, 479; 1909, **42**, 2559) observed that certain aldehydes react with diazomethane with formation of methyl ketones,



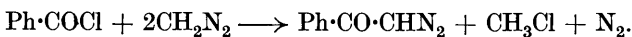
and Clibbens and Nierenstein (*J.*, 1915, **107**, 1491) stated that an

analogous reaction occurred to a predominating extent when certain acid chlorides were employed :



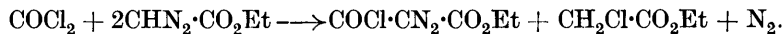
Subsequently Nierenstein and his co-workers greatly extended the scope of the reaction and favourable yields were said to be obtained in many cases (Nierenstein, J., 1920, **117**, 1153; Nierenstein, Wang, and Warr, *J. Amer. Chem. Soc.*, 1924, **46**, 2554; Kahil and Nierenstein, *ibid.*, p. 2557; Lewis, Nierenstein, and Rich, *ibid.*, 1925, **47**, 1728; Dale and Nierenstein, *Ber.*, 1927, **60**, 1026). This reaction of diazomethane has received very little attention from other workers, but a footnote in a paper by Staudinger and Mächling (*Ber.*, 1916, **49**, 1973) records the fact that only very small yields of $\alpha\alpha'$ -dichloro- and $\alpha\alpha'$ -dibromo-diacetyl were obtained from oxalyl chloride and bromide respectively by the action of diazomethane and the major products could not be purified or were not examined; the work is attributed to Dr. H. Schlubach.

In the course of some synthetical experiments we wished to make an application of Nierenstein's reaction, but in the rather complex case studied an excellent yield of a diazo-ketone was obtained and this served our purpose even better than a chloro-ketone would have done. We therefore turned to the typical case of benzoyl chloride and diazomethane and found exactly the same results, namely, the formation of diazoacetophenone in high yield :

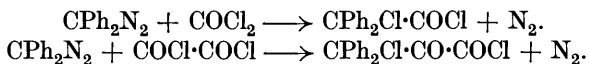


Clibbens and Nierenstein (*loc. cit.*) stated that benzoyl chloride (1 mol.) and diazomethane (1 mol.) gave a product from which a 72% yield of ω -chloroacetophenone was isolated by distillation. Under these conditions we think the residue after removal of the solvent would consist of diazoacetophenone (0.5 mol.) and benzoyl chloride (0.5 mol.) and if this mixture were distilled, especially in presence of water, it might give some ω -chloroacetophenone. In later work Nierenstein used diazomethane in excess, sometimes in great excess, and under these conditions the formation of the chloro-ketone would be minimal. It is well known that acids decompose diazomethane very much more rapidly than they decompose diazoacetophenone—we have confirmed this observation, working with hydrogen chloride in ethereal solution. In our experiments the recognition of traces of ω -chloroacetophenone in the actual reaction mixture was facilitated by the powerful lachrymatory properties and characteristic odour of the compound; it was not isolated in substance from the mother-liquors of the diazoacetophenone.

The formation of diazoacetophenone in this manner does not constitute a novel type of reaction, for Staudinger and Mächling (*loc. cit.*) and Staudinger, Becker, and Hirzel (*Ber.*, 1916, **49**, 1973) have shown that ethyl diazoacetate can be acylated in a similar manner and in accordance with the following example :



On the other hand, diphenyldiazomethane was found by Staudinger, Anthes, and Pfenninger (*Ber.*, 1916, **49**, 1941) to be inactive towards benzoyl chloride and to react with carbonyl chloride and oxalyl chloride in accordance with the scheme :



In these cases it is obvious that the formation of a diazo-ketone is not feasible.

Lewis, Nierenstein, and Rich (*loc. cit.*) state that benzoyl bromide, treated with diazomethane, gives rise to ω -bromoacetophenone in 28% yield and 3 : 6-dibromo-3 : 6-diphenyl-1 : 4-dioxan in 62% yield. The chemistry involved in the degradation of the latter substance is of an unconventional type. The dibromodiphenyldioxan contains two $\text{CPhBr} \cdot \text{O} \cdot$ groups, yet it is stable and crystallises from alcohol unchanged. It may be reduced by treatment with activated magnesium in dry ether and decomposition of the product (yield, 76%); the resulting 3 : 6-diphenyl-1 : 4-dioxan, a diphenyl derivative of ethylene ether, may then be hydrolysed to phenylethylene glycol, $\text{CHPh}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, in 3 hours by means of 10% aqueous potassium hydroxide on the steam-bath and in presence of benzene (yield, 62%). In our experiments benzoyl bromide and diazomethane yielded diazoacetophenone.

Mechanism of the Reactions of the Aliphatic Diazo-compounds.—On the basis of the electronic theory of valency the Angeli-Thiele formula for the diazenes becomes $\text{CR}_2 = \overset{+}{\text{N}} = \overset{-}{\text{N}}$ (each line representing two electrons), and we may assume that the driving force in the manifold reactions of these substances is the tendency to neutralise the charges associated with the nitrogen atoms.

An examination of these reactions reveals two striking and apparently anomalous circumstances. In the first place diazomethane, this example being used for convenience, is both anionoid and kationoid; it reacts vigorously with electron-seeking agents, for example, protons and halogen molecules, and with electron-donating agents, for example, organo-metallic compounds. It is true that different positions in the diazomethane molecule are involved, but the second apparent anomaly is that the carbon atom

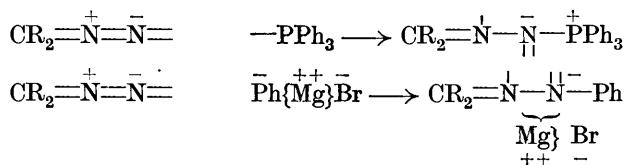
next to the positively charged nitrogen is the anionoid centre and the negatively charged nitrogen is the kationoid centre.

The indication is that the maintenance of atomic electron configurations is a far more urgent need than the neutralisation of charges and that in both cases, paradoxical though it seems at first sight, the electronic changes do ultimately lead to a more even distribution of the charge. The conjugative electron displacements which we postulate are represented in the annexed figures.



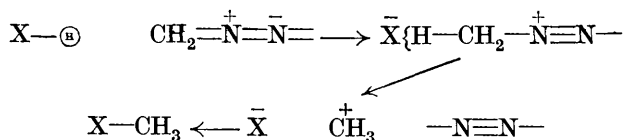
In (A) the charge on the central nitrogen remains unchanged but that on the terminal nitrogen is transferred in part to carbon. In (B) the charge on the central nitrogen is neutralised, but of course the terminal nitrogen receives electrons from outside and some other atom must acquire a positive charge.

Two simple examples of the operation of scheme B are the following :



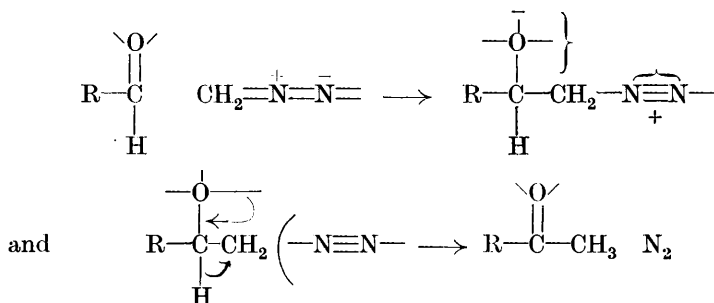
Behaviour towards cyanidion is regarded as one of the most searching tests for kationoid reactivity, and not only CN^- but also SO_3Na^- attach themselves to the terminal nitrogen atom of the diazenes.

In the action of acids on the diazenes we probably see scheme (A) at work, because the stronger acids, HX , in which the free electrons of X are least active, react most easily with the diazo-compounds.

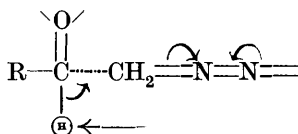


Here we assume the intermediate formation of a diazonium salt and a final decomposition along familiar lines. The reaction with the halogens is entirely analogous and may be summarised by the expressions : $\text{Br}_2 + \text{CH}_2\text{N}_2 \longrightarrow \text{Br}\cdot\text{CH}_2\cdot\text{N}_2\cdot\text{Br} \longrightarrow \text{Br}_2\text{CH}_2 + \text{N}_2$.

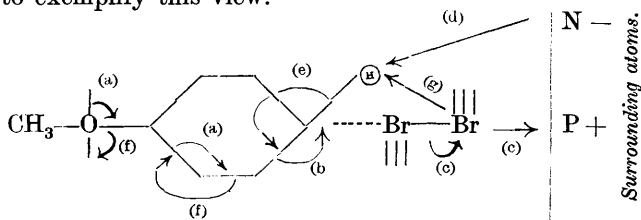
Schlotterbeck's reaction presents a more complex case :



Such recoil reactions are common in this group, but it is not necessary to assume a completed transfer of a charge as in the above representation. The first phase of the process may well proceed to a fractional extent only and once the carbon atoms are connected the main changes leading to the separation of nitrogen and the wandering of a proton will proceed by a more direct route as in the expression

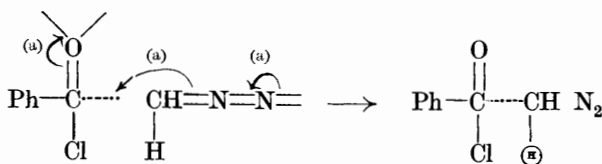


This conception of a reaction oriented or directed by a process involving fractional valencies and then carried to completion by a different and more direct mechanism was first suggested by one of us in 1920 (Robinson, *Mem. Manchester Phil. Soc.*, **54**, No. 4) and stated to be applicable to *m*-substitutions in benzene derivatives. Ingold and Ingold have since put forward a similar scheme in connexion with *o-p*-substitutions also (*J.*, 1926, 1313). An alternative hypothesis is that of vibrations of the electronic displacements (Robinson, B.A. Meeting, Southampton, 1925; *Chem. News*, 1926, **133**, 7). These may be rapid and of quite small amplitude and the substitution processes and other reactions would then be approximately continuous. The bromination of anisole may be used to exemplify this view.

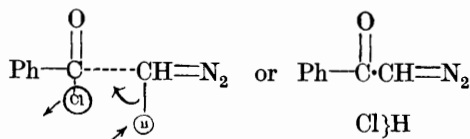


The substitution is supposed to be initiated by the tendency of bromine to acquire electrons. This can be satisfied in the *o-p*-positions (not in *m*-) and a bond is produced by the displacement (b) because the consequent displacements (a) are possible owing to the fact that the oxygen atom affords a resting place for the positive charge, where it is balanced by the surroundings (N). The partial formation of the C—Br bond (b) enables the second bromine atom to consummate to the same fractional extent (c) its tendency to become bromidion when it is electrovalently associated with surroundings (P). A circuit is thus completed and the movement of electrons in it has involved a tentative attachment of bromine to carbon and an equal separation of bromidion. The oxygen atom is not, however, in its most stable condition and reverts to this by an electron displacement (electrical current) in a different circuit, this time involving the hydrogen atom and not affecting (b) or (c). The lines of force between (N) and the oxygen atom are broken; then (f) reverses (a) and (e) and (d) are consequences. The partly liberated proton may seek the centres (N) or there may be any degree of short-circuiting up to the limit expressed by (g), which is an alternative or part alternative to (d). The first-mentioned set of displacements and processes (a), (b), (c) can then occur again and alternate with the recovery displacements (d), (e), (f) until the substitution is completed. It is possible to construct similar schemes for other reactions involving conjugated systems of various types.

We represent the formation of diazoacetphenone in the following manner :



At this stage the terminal nitrogen has succeeded in transferring a fraction of its negative charge to the oxygen atom and a bond between the carbon atoms has been initiated. The repulsion exerted by the central nitrogen on the proton indicated is now reinforced by that exerted by the oxygen and chlorine nuclei and the following changes may be almost synchronous :

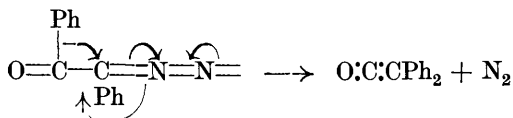


The initial electronic changes (a) may be to some extent permanent, since the oxygen atom can well hold a part of the negative charge, or, naturally, the strain may be completely or partly released by reversal of these displacements.

The reactions of the diazenes with unsaturated ethenoid substances seem to belong to both types (A) and (B) and in either case the mode of occurrence of these additive processes can be readily accommodated by the electronic theory. There is need of further work on the constitution of the primary additive products of aliphatic diazo-compounds and unsymmetrical unsaturated substances.

In the polymerisation of the diazo-compounds, for example, the formation of pseudodiazoacetic acid, the kationoid centre of one molecule evidently attacks the anionoid centre of another.

Finally the varied decompositions are readily interpreted, one of the most interesting being that discovered by Schröter (*Ber.*, 1909, **42**, 2346) :



EXPERIMENTAL.

Materials.—Diazomethane was prepared from nitrosomethylurethane and its ethereal solution was slowly distilled through a 45 cm. column. The volume of nitrosomethylurethane required was calculated from the normal yield under standard conditions (Houben-Weyl, "Die Methoden der Organischen Chemie," 1923, **3**, 124), that is, 0.18—0.20 g. of diazomethane from 1 c.c. of nitrosomethylurethane.

Ether was dried over phosphoric oxide and distilled through the apparatus immediately before an experiment.

A fresh specimen of benzoyl chloride from Kahlbaum was employed.

Diazoacetophenone.—(A). A solution of benzoyl chloride (2.5 g.; 1 mol.) in ether (5 c.c.) was added to an ethereal solution of diazomethane (1.25 mols.) maintained at -5° to 0° . A mild evolution of nitrogen occurred and continued for 1—1½ hours. The yellow solution was kept over-night, and the ether then evaporated in a rapid current of air. The residue consisted of a colourless oil (1.0—1.5 g.), easily soluble in 10 c.c. of cold light petroleum, together with a pale yellow, crystalline material (1.3 g.) which on recrystallisation from light petroleum afforded diazoacetophenone (1.10 g.), m. p. 47—49°.

(B). The above experiment was repeated with the addition of

tripropylamine (2.5 g.) and the result was a product containing unchanged benzoyl chloride, tripropylamine, a trace of ω -chloroacetophenone (recognised by odour only), and diazoacetophenone (1.2 g.). Evidently the tertiary base does not effectively de-activate the liberated hydrogen chloride.

(C). Benzoyl chloride (2.1 g.; 1 mol.) was treated as in (A) with diazomethane (2 mols.). After 24 hours the ether was evaporated, leaving a crystalline residue, which was washed with light petroleum (25 c.c.) and then weighed 1.8 g. The light petroleum deposited a further 0.05 g. of the substance and on evaporation left about 0.1 g. of a yellow oil containing benzoyl chloride, diazoacetophenone, and a mere trace of ω -chloroacetophenone (odour). The yield in this experiment amounted to 91% of that theoretically possible.

The solid products described above as consisting of diazoacetophenone exhibited identical behaviour and were free from ω -chloroacetophenone. The substance crystallised from light petroleum in pale yellow, flat needles, m. p. 48—48.5° (Wolff, *Annalen*, 1903, **326**, 142, gives m. p. 49—50°) (Found: C, 65.9; H, 4.1. Calc. for $C_8H_6ON_2$: C, 65.7; H, 4.1%).

The substance decomposed in contact with porous material at 116—118°. An alcoholic solution was coloured deep red on the addition of sodium hydroxide or alternatively by the addition of zinc dust and ammonia became purple or blue according to the conditions (Wolff, *Annalen*, 1902, **325**, 141).

The substance exhibited the characteristic reactions of an aliphatic diazo-compound. Iodine decomposed it instantly in cold alcoholic solution with evolution of nitrogen, and the action of dilute sulphuric acid gave nitrogen and a substance (benzoylcarbinol) that quickly reduced Fehling's solution in the cold.

Quantitative and smooth decomposition occurred on warming with glacial acetic acid. The product was isolated by means of ether and crystallised from light petroleum in large, colourless tablets, m. p. 48—49° (Zincke, *Annalen*, 1883, **216**, 308, gives m. p. 49—49.5°). The substance reduced Fehling's solution in the cold in the course of $\frac{1}{2}$ —1 minute and its m. p. was not depressed by admixture with an authentic specimen of ω -acetoxyacetophenone.

The formation of methyl chloride in the reaction between benzoyl chloride (1 mol.) and diazomethane (2 mols.) was not experimentally confirmed.

Interaction of Benzoyl Bromide and Diazomethane.—Benzoyl bromide (2.8 g.; 1 mol.) in ether (5 c.c.) was added to an ethereal solution of diazomethane (2 mols.) at -5° to 0° . The vigorous evolution of nitrogen, appeared to be complete in 5—10 minutes, but

the mixture was kept over-night. The semi-solid residue after removal of the ether was dissolved in boiling light petroleum and, on cooling, diazoacetophenone (1.25 g.), m. p. 45—47°, separated. A further quantity (0.4 g.), m. p. 44—46°, was obtained from the mother-liquor. The main fraction mixed with pure diazoacetophenone had m. p. 46—48°; on recrystallisation from light petroleum it was obtained in long, flat, pale yellow needles, m. p. 48—49°, exhibiting the characteristic reactions. The final mother-liquor contained benzoyl bromide and, apparently, a trace of ω -bromoacetophenone.

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