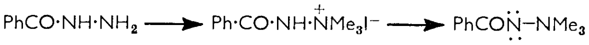
160. *The Thermolysis of Trimethylamine–benzimide; A New Rearrangement of the Curtius–Hofmann Type.*

By M. S. Gibson and A. W. Murray.

In the range 185—200°, trimethylamine–benzimide decomposes, with rearrangement, to trimethylamine and phenyl isocyanate, the latter trimerising to triphenyl isocyanurate. In the presence of *p*-bromoaniline, the phenyl isocyanate formed is trapped as *NN'*-di-*p*-bromophenylurea.

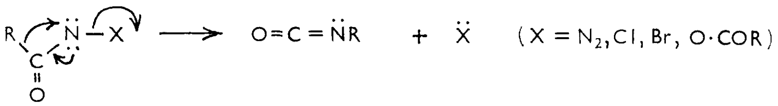
Attention is directed to the reversibility of diarylurea formation from aromatic amines and isocyanates at high temperatures.

Alkylation of acylhydrazides in a polar solvent has been shown to occur on the basic nitrogen atom. In the presence of an added proton acceptor, quaternary salt formation becomes possible. Thus, treatment of benzoylhydrazide with an excess of methyl iodide and ethanolic sodium ethoxide (2 equiv.) affords 1-benzoyl-2,2,2-trimethylhydrazinium iodide; the use of a larger proportion of sodium ethoxide results in the formation of the parent compound, trimethylamine-benzimide: [1]



$$\mathrm{PhCO{\cdot}NH{\cdot}NH_2} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}NH{\cdot}\overset{+}{N}Me_3I^-} \longrightarrow \mathrm{PhCO\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}{-}\overset{+}{N}Me_3}$$

The last compound is of particular interest because of its formal similarity to the type of compound or charged intermediate involved in the Curtius, Schmidt, Hofmann, and Lossen rearrangements, for which the currently accepted mechanism [2] may be generalised:



Trimethylamine-benzimide might be expected to undergo similar rearrangement, under appropriate conditions, yielding phenyl isocyanate and trimethylamine.

In the event, the compound proved to be relatively stable, no observable change occurring below its melting-point (169—170°); decomposition took place at slightly higher temperatures with evolution of trimethylamine and, at least initially, the residue appeared to contain phenyl isocyanate (doublet near 2200 cm.$^{-1}$).[3] Generally, thermolysis was carried out under dry nitrogen until no more basic gas was evolved. Such decompositions gave trimethylamine (*ca.* 45%, isolated as the dichloroiodide), but no phenyl isocyanate; the other major product was triphenyl isocyanurate (*ca.* 45%). The isolation of this compound demonstrates that the expected migration of the phenyl group from carbon to nitrogen has occurred, and is consistent with the view that phenyl isocyanate is formed but trimerises under the somewhat basic reaction conditions.[4]

Thermolysis of trimethylamine-benzimide was next carried out in the presence of *p*-bromoaniline (1 equiv.), chosen as a selective trapping agent for phenyl isocyanate. Trimethylamine was again evolved, and the residue provided the " trapped " phenyl isocyanate in the form of *NN'*-di-*p*-bromophenylurea; no triphenyl isocyanurate was isolated, showing it to be an artefact in the previous decompositions.

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[1] Hinman and Flores, *J. Org. Chem.*, 1959, **24**, 660.

[2] Gould, " Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1959, p. 621 *et seq.*; and refs. cited.

[3] Cf. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 267.

[4] Jones and Savill, *J.*, 1957, 4392.

The isolation of *NN'*-di-*p*-bromophenylurea requires special comment. Phenyl isocyanate and *p*-bromoaniline react normally at room temperature to give *N*-*p*-bromophenyl-*N'*-phenylurea;[5] however, from a control experiment at elevated temperatures, *NN'*-di-*p*-bromophenylurea was isolated. These apparently anomalous results can be rationalised in terms of the following equilibria:

$$\mathrm{PhN{=}C{=}O + BrC_6H_4{\cdot}NH_2 \rightleftharpoons PhNH{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br \rightleftharpoons PhNH_2 + O{=}C{=}N{\cdot}C_6H_4Br} \tag{1}$$

$$\mathrm{BrC_6H_4{\cdot}NH_2 + O{=}N{=}C{\cdot}C_6H_4Br \rightleftharpoons Br{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br} \tag{2}$$

$$\mathrm{PhNH_2 + O{=}C{=}N{\cdot}Ph \rightleftharpoons PhNH{\cdot}CO{\cdot}NHPh} \tag{3}$$

Thermolysis of trimethylamine-benzimide occurs under conditions in which the high-melting, sparingly soluble *NN'*-di-*p*-bromophenylurea separates as a solid phase, disturbing the set of equilibria in favour of the diarylureas in (2) and consequently (3). The thermal dissociation of monoarylureas and the frequent discrepancies in reported melting points of unsymmetrically substituted ureas have been the subject of previous comment;[6] there seems little doubt that the variation in melting points reported[5] for *N*-*p*-bromophenyl-*N'*-phenylurea stem from the involvement of equilibria (1)—(3) above.

The parent peak for trimethylamine-benzimide was not discernible in its mass spectrum but intense peaks of mass 119 and 59, corresponding to the breakdown pattern of the parent compound to phenyl isocyanate and trimethylamine, were present.

EXPERIMENTAL

Microanalyses were carried out by Mr. V. Manohin and by Drs. F. and E. Pascher. Infrared spectra are for mulls in Nujol and hexachlorobutadiene.

Trimethylamine–benzimide.—1-Benzoyl-2,2,2-trimethylhydrazinium iodide was prepared by the literature method; an analytical sample crystallised from n-propanol as colourless plates, m. p. 174—176° (not 194—196° as reported [1]) (Found: C, 39·4; H, 5·1; N, 9·3. Calc. for $C_{10}H_{15}IN_2O$: C, 39·2; H, 4·9; N, 9·0%); $\nu_{max.}$ 3350 (NH), 1675 cm.$^{-1}$ (C=O).

1-Benzoyl-2,2,2-trimethylhydrazinium iodide (5·4 g.) was basified with sodium hydroxide solution (2·5 g. in 7·5 ml. water) and the mixture extracted with chloroform (7 × 10 ml.). The extract was dried (Na_2SO_4), evaporated, and, and the crude product (2·6 g.) crystallised from n-propyl bromide (plates, m. p. 169—170°; lit.,[1] 168—169°); $\nu_{max.}$ 1600 cm.$^{-1}$ (C=O).

Pyrolysis of Trimethylamine–benzimide.—Trimethylamine–benzimide (2·05 g.) was heated (reflux condenser) in a stream of dry nitrogen at 185—200° (bath-temperature) for 45 min., and the effluent gases passed through concentrated hydrochloric acid (5 ml.).

(*a*) *Identification of trimethylamine.* The acid solution was evaporated to dryness yielding a hygroscopic, off-white hydrochloride (0·8 g.). This was dissolved in warm concentrated hydrochloric acid (10 ml.) containing powdered iodine (1·1 g.) and chlorine passed through the suspension until the iodine had just disappeared. The deep yellow precipitate (1·89 g.) was crystallised from concentrated hydrochloric acid yielding trimethylammonium dichloroiodide as canary-yellow plates, m. p. 120—121°, identical (mixed m. p. and infrared spectrum) with the dichloroiodide (6 g.) similarly obtained from trimethylamine hydrochloride (2·8 g.) (Found: N, 5·2. Calc. for $C_3H_{10}Cl_2NI$: N, 5·0%). Under these conditions, the tetrachloroiodide[7] of Chattaway and Garton was not obtained.

(*b*) *Triphenyl isocyanurate.* During the pyrolysis, a colourless solid (0·375 g.) collected in the condenser and on the cool parts of the flask. Crystallisation from ethanol gave flat plates, which sublimed as irregular plates from 200° and finally had m. p. 281—283°. This compound was identical (mixed m. p. and infrared spectrum) with an authentic sample of triphenyl isocyanurate (lit.,[4] m. p. 285°).

The oily residue in the flask was refluxed with water (2 × 14 ml.) for 45 min. to remove any undecomposed trimethylamine–benzimide, and the aqueous solution separated. On cooling, this deposited plates (45 mg.), m. p. 124—144° (m. p. 144—152° after crystallisation from

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[5] Goldschmidt and Molinari, *Ber.*, 1888, **21**, 2557; Hantzsch and Perkin, *ibid.*, 1897, **30**, 1394; Ingold, *J.*, 1924, **125**, 87.

[6] Kurzer, *J.*, 1949, 2292.

[7] Chattaway and Garton, *J.*, 1924, **125**, 183.

aqueous ethanol; $\nu_{max.}$ 3300, 1650, 1600, 1440, 1320, 752, 712, and 692 cm.$^{-1}$). This product was not obtained in a pure condition, and was not identified.

The insoluble residue from aqueous extraction (0·75 g.) on sublimation *in vacuo* (200—230°/15 mm.) yielded a further quantity (0·31 g.) of slightly impure triphenyl isocyanurate.

Thermolysis of Trimethylamine-benzimide in the Presence of p-*Bromoaniline.*—Trimethylamine–benzimide (0·6 g.) and crystallised *p*-bromoaniline (0·58 g.) were intimately mixed and heated to 200° (bath temp.) in a stream of dry nitrogen. The melt evolved trimethylamine and solidified after 10 min. The temperature was maintained at 200° for a further 15 min. and the mixture then cooled in a stream of nitrogen. Trituration of the residue with cold ethanol (6 ml.) yielded a solid (0·47 g.) which crystallised from acetic acid as plates, m. p. (sealed capillary, fast heating) 315° (decomp.) [lit.,[6] 314—316° (decomp.) for *NN'*-di-*p*-bromophenylurea] (Found: C, 42·3; H, 2·7; Br, 43·05. Calc. for $C_{13}H_{10}Br_2N_2O$: C, 42·2; H, 2·7; Br, 43·2%).

NN'-*Di*-p-*bromophenylurea.*—Phenyl isocyanate (1·2 g.) was added to molten *p*-bromoaniline (1·8 g.); a solid was immediately formed. The mixture was heated at 140° for 30 min., then cooled, and the product collected by using cold ethanol (10—15 ml.). Crystallisation from acetic acid gave *NN'*-di-*p*-bromophenylurea as plates, mixed m. p. (sealed capillary) with the product from the previous reaction, 314—316° (decomp.). Infrared spectra of both samples were identical.

Triphenyl isocyanurate with *p*-bromoaniline did not yield any detectable amount of *NN'*-di-*p*-bromophenylurea after being heated at 160—200° for 20 min.

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