phenylmalonic acid (2.5 g.), obtained as a reaction product, melted at 152–153° (dec.).[45]

Anal. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.47; neut. equiv., 90.08. Found: C, 60.10; H, 4.58; neut. equiv., 90.42.

When heated, the weight of the carbon dioxide evolved represented 24.21% of the weight of the phenylmalonic acid; calcd. 24.43%. The residue was phenylacetic acid; mixed m.p. 76–77°. When the phenylmalonic acid was treated with diazomethane, dimethyl phenylmalonate was obtained; m.p. 49.5–51°.[46]

1-Phenyl-2-butanone (0.5 g.), semicarbazone m.p. 152–153°,[47] and 0.8 g. of a substance which boiled above 157° (1 mm.) were isolated also.

Reaction of Diphenyl-β-dimethylaminoethylacetonitrile with Ethylmagnesium Bromide.—To the Grignard reagent, prepared from 27.2 g. of ethyl bromide, 6.0 g. of magnesium and 90 cc. of ether, a solution of 26.4 g. of diphenyl-β-dimethylaminoethylacetonitrile in 60 cc. of toluene was added. After removal of the ether, the mixture was refluxed for 8 hours and then carbonated with a stream of carbon dioxide. The reaction product was 4,4-diphenyl-6-dimethylamino-3-hexanone (27.4 g., 92.7%); b.p. 153.5–157° (1 mm.). The hydrochloride melted at 173–174.5°.[48]

Anal. Calcd. for $C_{20}H_{26}ONCl$: N, 4.22; Cl, 10.68. Found: N, 4.06; Cl, 10.62.

Reaction of Phenyl-β-dimethylaminoethylacetonitrile with Ethylmagnesium Bromide.—A solution of 18.8 g. of the nitrile in 60 cc. of toluene was added to the Grignard reagent prepared from 32.7 g. of ethyl bromide, 7.3 g. of magnesium and 100 cc. of ether. After removal of the ether, the mixture was refluxed for 8 hours. The 4-phenyl-6-dimethylamino-3-hexanone (11.2 g., 51.2%) obtained boiled at 90–92° (0.5 mm.). The hydrochloride melted at 139–140° after recrystallization from methyl ethyl ketone.

Anal. Calcd. for $C_{14}H_{22}ONCl$: N, 5.48; Cl, 13.86. Found: N, 5.59; Cl, 13.95.

The hydrochloride of the oxime of the amino ketone melted at 164–165.5° after recrystallization from isopropyl alcohol–ethyl acetate.

Anal. Calcd. for $C_{14}H_{23}ON_2Cl$: N, 10.35; Cl, 12.79. Found: N, 10.57; Cl, 13.01.

The phenyl-β-dimethylaminoethylacetic acid, which was obtained after hydrolysis, melted at 183–184° after recrystallization from ethanol.

Anal. Calcd. for $C_{12}H_{17}O_2N$: N, 6.76. Found: N, 6.88.

Reaction of Phenyldi-(β-diethylaminoethyl)-acetonitrile with Ethylmagnesium Bromide.—To the Grignard reagent, prepared from 27.2 g. of ethyl bromide, 6.0 g. of magnesium and 80 cc. of ether, a solution of 31.5 g. of the nitrile in 50 cc. of toluene was added. After removal of the ether, the mixture was refluxed for 7 hours, 150 cc. of toluene was added and the mixture was carbonated. The product was 1-phenyl-1,1-di-(β-diethylaminoethyl)-2-butanone; yield 24.7 g. (71.3%); b.p. 124–127° (0.03 mm.). The hydrochloride melted at 235–236° after recrystallization from methanol–ethyl acetate.

Anal. Calcd. for $C_{22}H_{40}ON_2Cl_2$: N, 6.68; Cl, 16.90. Found: N, 6.78; Cl, 17.06.

ANN ARBOR, MICHIGAN

[45] H. Scheibler, *Ber.*, **58**, 1205 (1925), reported 151.5°.

[46] M. Rising and J. Stieglitz, THIS JOURNAL, **40**, 723 (1918), found 50°.

[47] E. Fourneau, *Compt. rend.*, **146**, 699 (1908), found 153°.

[48] D. J. Dupre, J. Elks, B. A. Hems, K. N. Speyer and R. M. Evans, *J. Chem. Soc.*, 500 (1949), found 173.5–175°.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

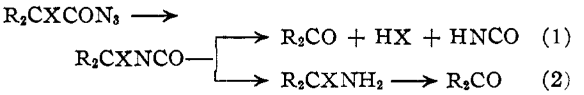
The Curtius Rearrangement of α-Bromodineopentylacetyl Azide

BY HARRY D. ZOOK, MYER REAM[1] AND EARSIE W. DELCHAMPS[1]

RECEIVED JULY 13, 1953

In the rearrangement and hydrolysis of α-bromodineopentylacetyl azide to dineopentyl ketone an intermediate compound, β-*t*-butyl-α-neopentylvinyl isocyanate, was isolated. A new route is proposed for this type of Curtius reaction; *viz*, α-halo azide → α-halo isocyanate → α,β-olefinic isocyanate → imine → carbonyl compound.

Pyrolysis and rearrangement of acyl azides usually lead to isocyanates (Curtius reaction). When the azide contains halogen or hydroxyl groups in the α-position or α,β-unsaturation, the product is an aldehyde or ketone. Two routes have been proposed for the conversion of α-halo azides to aldehydes and ketones.[2]

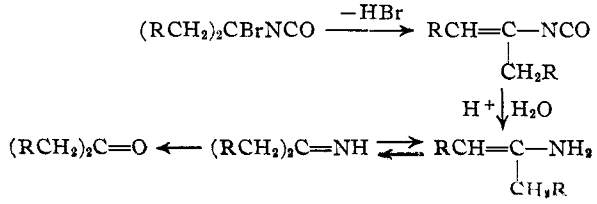


$$R_2CXCON_3 \longrightarrow R_2CXNCO{-}\left[\begin{array}{ll} \longrightarrow R_2CO + HX + HNCO & (1) \\ \longrightarrow R_2CXNH_2 \longrightarrow R_2CO & (2) \end{array}\right.$$

Little evidence for either course has been cited. Cyanic acid is a product in the conversion of α-hydroxy azides to carbonyl compounds.[3]

We have isolated a stable intermediate in the degradation of α-bromodineopentylacetyl azide to dineopentyl ketone. The compound distilled without decomposition at 86° at 8 mm. and gave positive tests for unsaturation. Acid-catalyzed hydrolysis gave dineopentyl ketone in 80% yield and equivalent amounts of ammonia and carbon dioxide. These facts are consistent with the formula, β-*t*-butyl-α-neopentylvinyl isocyanate. This formula was confirmed by analysis, ozonolysis, spectrophotometric measurements and the preparation of suitable derivatives.

Thus, dehydrohalogenation into a neopentyl group occurs rather than retention of the bromine atom or its replacement by a hydroxyl group. The dehydrohalogenation occurs after the rearrangement when the benzene solution is stirred with cold water, for if stirring is inadequate, the product contains bromine and decomposes to a gas and tarry residue upon distillation. The following course for the reaction is consistent with the facts in this case.



$$\begin{gathered} (RCH_2)_2CBrCON_3 \xrightarrow{-N_2} (RCH_2)_2CBrNCO \xrightarrow{-HBr} RCH{=}\underset{\underset{\displaystyle CH_2R}{|}}{C}{-}NCO \\ \Big\downarrow H^+ \, H_2O \\ (RCH_2)_2C{=}O \longleftarrow (RCH_2)_2C{=}NH \rightleftarrows RCH{=}\underset{\underset{\displaystyle CH_2R}{|}}{C}{-}NH_2 \end{gathered}$$

[1] This paper is based on M.S. theses submitted to The Pennsylvania State College by Myer Ream, 1947, and Earsie W. Delchamps, (1952).

[2] J. v. Braun, *Ber.*, **67**, 218 (1934); P. A. Smith in "Org. Reactions," **3**, 356 (1946).

[3] T. Curtius, *J. prakt. Chem.*, **94**, 273 (1916).

Attempts to isolate intermediates in the rearrangements of α-bromomethylethylacetyl azide and α-bromomethylneopentylacetyl azide were unsuccessful. Steric factors may play a part in the occurrence of dehydrohalogenation and the stability of the olefinic isocyanate.

Experimental

α-Bromodineopentylacetyl Azide.—Dineopentylacetyl chloride was made from 200 g. of Butlerow acid (mostly α)[4] and 238 g. of thionyl chloride. The product was fractionated through an 18-plate column to give twelve fractions, 131 g., boiling at 108° at 22 mm., n^{20}_D 1.4430–1.4436. Fifty-one grams (0.233 mole) of the acyl halide was treated with 1 ml. of phosphorus trichloride and 41 g. (0.256 mole) of bromine. The mixture was heated overnight on the steam-bath and excess bromine then removed through a water aspirator. The crude acyl halide was dissolved in 100 ml. of acetone and added over a period of two hours to a solution of 30 g. of sodium azide in 100 ml. of water. The temperature was maintained at 5–10° throughout the addition. Two liquid phases were formed. The upper layer contained most of the dineopentylacetyl azide.

Curtius Rearrangement.—The azide layer from the above preparation was added slowly to 300 ml. of boiling benzene, and the mixture was refluxed for two hours. Ninety per cent. of the calculated amount of nitrogen gas was evolved based on a theoretical yield of the acyl azide. The solution was cooled and stirred vigorously for 24 hours with 1 l. of cold water. Fractionation of the benzene layer through a 12-plate column gave six fractions, 13.9 g. (27% over-all) of olefinic isocyanate, b.p. 85–87° at 8 mm., n^{20}_D 1.4487–1.4490. After refractionation through a micro column, the product had n^{20}_D 1.4485–1.4487.

Anal. Calcd. for $C_{12}H_{21}ON$: C, 73.79; H, 10.84; N, 7.17. Found: C, 74.06; H, 10.90; N (Dumas), 7.14.

Five similar preparations were carried out. Inadequate stirring of the benzene layer with cold water gave the α-bromo isocyanate which decomposed to a gas and tar upon distillation. When isolation of the product was effected by steam distillation of the benzene solution from 400 ml. of 20% hydrochloric acid, the product was mixed with dineopentyl ketone from which it could be separated by fractionation through a 10-plate column. A 32% over-all yield of the intermediate isocyanate was isolated in one experiment.

Two drops of the compound decolorized more than 80 drops of 1% bromine in carbon tetrachloride and more than 40 drops of 1% aqueous potassium permanganate. α-Naphthyl isocyanate gave negative tests with these reagents.

The product exhibited continuous absorption of light with no maximum in the region 2200–3000 Å. The results are consistent with absorption characteristics of the isocyanate group[5] and a compound containing a double bond.

The compound reacted with phenylmagnesium bromide to give an amide, m.p. 145–146.5°.

Anal. Calcd. for $C_{18}H_{27}ON$: N, 5.13. Found: N (Kjeldahl), 4.98.

Before drying in a vacuum over phosphorus pentoxide, the m.p. was 139–140° and the nitrogen analysis indicated that a molecule of water of crystallization was present.

An N-phenylurea, m.p. 169°, was formed by heating the compound with a solution of aniline in methanol.

Ozonolysis of 1 g. of the product was carried out in methylene chloride. The ozonide was decomposed by boiling water followed by steam distillation. A 2,4-dinitrophenylhydrazone prepared on a drop of the distillate melted at 203°. Admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde gave no depression in melting point.

The olefinic isocyanate was unchanged when stored for three months in corked vials in the ice-box or in a sealed tube at room temperature. However, when stored in corked vials at room temperature, some of the fractions underwent an increase in refractive index and viscosity; others deposited crystals, m.p. 155–158° after recrystallization from ethanol. The crystals absorbed bromine in carbon tetrachloride and may be the corresponding olefinic symmetrical urea.

Hydrolysis to Dineopentyl Ketone.—A mixture of 30 g. of the olefinic isocyanate, 30 ml. of concentrated hydrochloric acid and 100 ml. of water was refluxed for two days. The product was isolated by steam distillation and dried by fractionation with 25 ml. of benzene through a 10-plate column. Dineopentyl ketone was obtained in six fractions, 20.6 g. (80%), b.p. 61° at 10 mm., n^{20}_D 1.4200, oxime, m.p. 76–78°.

As further proof that the compound was an isocyanate, an 0.80 millimole sample was hydrolyzed with 1:1 sulfuric acid in a modified Kjeldahl apparatus. Carbon dioxide was swept by nitrogen into standard barium hydroxide solution, and ammonia was determined in the residue by alkaline distillation according to the standard Kjeldahl procedure. Obtained were 0.15 millimole of carbon dioxide and 0.13 millimole of ammonia. Thus, although only about 20% of the compound was hydrolyzed during the heating period and much distilled unchanged with the nitrogen stream, equivalent quantities of ammonia and carbon dioxide were formed in the hydrolysis.

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[4] F. C. Whitmore and C. D. Wilson, THIS JOURNAL, **56**, 1397 (1934).

[5] S. Woo and T. Liu, *J. Chem. Phys.*, **3**, 544 (1935).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Kinetic Study of the Rearrangement of Some Benzoates of 9-Decalyl Hydroperoxide

BY PAUL D. BARTLETT AND JOHN L. KICE[1]

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The Criegee rearrangement of the benzoate of 9-decalyl hydroperoxide into 1-benzoyloxy-1,6-epoxycyclodecane has been followed kinetically by means of an iodometric titration of the perester. An unsaturated ether has been isolated as a by-product. The rearrangement is of the first order, shows only moderate acid catalysis, and is intramolecular in the sense that rearrangement in the presence of sodium *p*-bromobenzoate does not lead to bromine-containing product. The rates of rearrangement of the substituted benzoates bearing the nitro, bromo, methyl and methoxyl substituents in the para position fit the Hammett equation with a value of $\rho = 1.34$.

The benzoate of 9-decalyl hydroperoxide has the property, in common with camphene hydrochloride, of undergoing molecular rearrangement rapidly in solvents of high ionizing power and slowly in poorly ionizing solvents.[2] Criegee and Kaspar[2] have shown convincingly that this rearrangement involves an ionic fission of the oxygen–oxygen link and takes a course analogous to the Wagner–Meerwein rearrangement in which there is an ionic fission of a carbon–halogen or carbon–oxygen link. Recent progress in formulating the intermediates in the Wagner–Meerwein rearrangement[3-6] raises the

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[1] National Science Foundation Fellow, 1952–1953.

[2] R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

[3] S. Winstein and D. Trifan, THIS JOURNAL, **71**, 2953 (1949).

[4] D. J. Cram, *ibid.*, **71**, 3863 (1949).

[5] J. D. Roberts, *ibid.*, **73**, 3542 (1951).

[6] F. Brown, B. D. Hughes, C. K. Ingold and J. F. Smith, *Nature*, **168**, 65 (1951).