

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Nitriles. VII.¹ Decomposition Products from 2,2'-Azo-bis-2,3,3-trimethylbutyronitrile. Products Obtained from a Substituted Neopentyl Radical

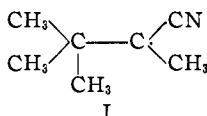
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2,2'-Azo-bis-2,3,3-trimethylbutyronitrile, a source of a substituted neopentyl radical, has been decomposed in benzene solution. No evidence of rearranged products was obtained. $(\text{CH}_3)_3\text{C}-\text{CH}(\text{CN})(\text{CH}_3)$ (IV) and $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}(\text{CN})$ (V) were isolated and their structures demonstrated. No evidence of $(\text{CH}_3)_2\text{CH}-\text{C}(\text{CN})(\text{CH}_3)_2$ (VI) and $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CN})(\text{CH}_3)_2$ (VII) was obtained. Derivatives of VI and VII were synthesized by unequivocal methods and shown to be different than those derived from IV and V.

Although the phenyl group in several neophyl radicals³ has recently been reported to rearrange, no case of a methyl group migrating in a neopentyl radical has been reported. Urry and Nicolaides^{3c} found no rearranged products when neohexyl chloride (1-chloro-2,2-dimethylbutane) was allowed to react with ethylmagnesium bromide and cobaltous chloride. Only neohexane and bineohexyl (3,3,6,6-tetramethyloctane) were obtained. In this reaction the neohexyl radical $(\text{CH}_3-\text{CH}_2)(\text{CH}_3)_2\text{C}-\text{CH}_2\cdot$ is probably formed as a reaction intermediate.

Since 2,2'-azo-bis-2,3,3-trimethylbutyronitrile was available to us from other work⁴ and since it is a convenient source of the substituted neopentyl radical (I), we have made a thorough product an-



alysis from its decomposition in benzene in order to determine if any rearrangement would take place. Although adverse resonance factors (see below) are probably present because of the substitution on the carbon atom containing an odd electron, there is a favorable polar factor.⁵

Discussion

The diastereomeric 2,2'-azo-bis-2,3,3-trimethylbutyronitrile was allowed to decompose in refluxing benzene solution for five days. The lower boiling products (mononitriles) were first removed by distillation. From the residue, by crystallization and distillation were isolated two dimeric products, most probably the two stereoisomers of

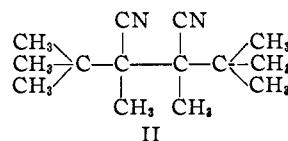
(1) For the preceding paper in this series, see C. G. Overberger, Thomas P. Gibb, Sheldon Chibnik, Pao-tung Huang and John J. Monagle, *THIS JOURNAL*, **74**, 3290 (1952). We are greatly indebted to the Research Corporation for the support of this work.

(2) The paper comprises a portion of a thesis presented by M. B. Berenbaum in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

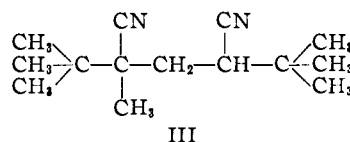
(3) (a) W. H. Urry and M. S. Kharasch, *THIS JOURNAL*, **66**, 1438 (1944); (b) S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947); (c) W. H. Urry and N. Nicolaides, Abstract of Papers, 118th Meeting of the A.C.S., Chicago, Illinois, September, 1950.

(4) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951).

(5) This polar factor in radical copolymerization may account for alternation. For an excellent review, see F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950). Here the nitrile group is electron withdrawing, and the methyl group is migrating from a carbon of relatively high electron density. Alternatively, it could be argued that rearrangement of this radical would not be favored due to the greater stability of the radical $(\text{CH}_3)_2\text{C}(\text{CN})(\text{CH}_3)$ over that of the rearranged radical $(\text{CH}_3)_3\text{C}-\text{C}(\text{CN})(\text{CH}_3)_2$.

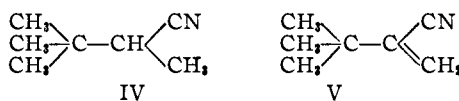


II (7%). These structures were demonstrated by analysis, by failure to react with bromine and phosphorus tribromide,⁶ and the absence of a C-methyl group.⁷ The possibility that one or both of these products is III, the product resulting from the addi-

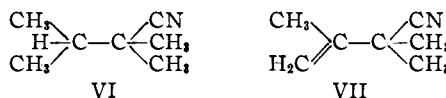


tion of the tertiary radical I to a disproportionated product $(\text{CH}_3)_3\text{C}-\text{C}(\text{CN})(=\text{CH}_2)$ followed by hydrogen abstraction is rendered unlikely since this product should react with bromine and phosphorus tribromide and should give some evidence of a C-methyl group.^{6c} Since no evidence of monomeric rearranged products was found it is very unlikely that these dimers are derived from rearranged radicals.

The mononitriles were fractionated through a fifty-plate center-tube column. Two products were isolated and their structures demonstrated (IV and V).



No evidence of the rearranged products VI and VII were obtained.



Derivatives of VI and VII were synthesized by unequivocal methods and shown to be different than those derived from IV and V. Dimethylisopropylacetic acid (structure VI) was prepared from dimethylisopropylcarbinol, formation of the chloride and Grignard reagent followed by carbonation by known general procedures. The ethyl ester of di-

(6) For a discussion of this reaction see (a) C. L. Stevens, *THIS JOURNAL*, **70**, 165 (1948); (b) C. L. Stevens and T. H. Coffield, *ibid.*, **73**, 103 (1951); (c) see also C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 4883 (1951).

(7) R. Kuhn and H. Roth, *Ber.*, **66**, 1274 (1933).

methylisopropenylacetic acid (structure VII) was prepared from ethyl α -bromoisobutyrate, zinc and acetone to give 3-hydroxy-2,2,3-trimethylbutyrate with subsequent dehydration by known procedures. Courtot⁸ had prepared the unsaturated ester (structure VII) by reaction of the hydroxy ester with phosphorus pentoxide, whereas Colonge and Dumont⁹ who used magnesium instead of zinc in the original condensation carried out the dehydration with iodine. Since 3-hydroxy-2,2,3-trimethylbutyrate can give rise to a neopentylcarbonium ion on dehydration, the acetate was prepared and cracked thermally¹⁰ to minimize this possibility of rearrangement during dehydration.

To further demonstrate structure VII, a quantitative hydrogenation of the amide of VII gave the amide of VI. The amide of VI was prepared by an unequivocal synthesis and shown to be identical with the hydrogenated product by a mixed melting point determination.

These facts confirm the structure proposed by Courtot who presented oxidation evidence to support his structure.

The structure of IV and V were determined independently by synthesis of their amides. The acid corresponding to IV was prepared by the procedure of Aston¹¹ and co-workers by a Favorski rearrangement of bromomethyl neopentyl ketone. We have found that considerable quantities of dibromide were also obtained by their procedure for the preparation of the monobromo ketone.

The structure of the rearranged product was demonstrated by Aston and co-workers by comparison with a known product. Further evidence for the structure of the nitrile (IV) was deduced by the formation of the bromo derivative with bromine and phosphorus tribromide. The structure of V was demonstrated by analysis, hydrolysis to the amide, and quantitative hydrogenation to give an amide identical with that obtained from IV. The ultraviolet absorption spectra of the amide of V is similar to that of methacrylamide.¹²

There can be little doubt that structures represented by formulas II, IV and V are those of the products reported here.

Experimental¹³

Decomposition of 2,2'-Azo-bis-2,3,3-trimethylbutyronitrile.—Decomposition of 192.5 g. (1.55 moles) of the equilibrium mixture of the diastereomeric azo nitriles derived from pinacolone⁴ was accomplished by refluxing in 1200 ml. of benzene for five days. After removing the solvent under vacuum, the lower molecular weight decomposition products (mononitriles) were collected in a single fraction totalling 133 g. (78%), b.p. 54–66° (35 mm.). The residual solid in the still pot was recrystallized from ether-petroleum ether to yield 7.2 g. (4.2%) of a dinitrile, m.p. 116.5–117.5°. After recrystallization from ether, the melting point of the long needle crystals was 117.5–118.5°.

(8) A. M. Courtot, *Bull. soc. chim.*, [3] **35**, 298 (1906).

(9) J. Colonge and P. Dumont, *ibid.*, **43**, 38 (1947).

(10) If the cyclic mechanism proposed by E. R. Alexander and A. Mudrak, *THIS JOURNAL*, **73**, 1810 (1950), is operative, no free carbonium ion is formed on thermal cracking of the acetate.

(11) J. G. Aston, J. T. Clarke, K. A. Burgess and R. B. Greenburg, *ibid.*, **64**, 300 (1942).

(12) Little or no data are recorded for the ultraviolet absorption spectrum of α,β -unsaturated amides. The maxima are below the range of the ordinary Beckman model DU spectrophotometer.

(13) All melting points are corrected.

*Anal.*¹⁴ Calcd. for C₁₄H₂₄N₂: N, 12.73. Found: N, 12.85.

The mother liquors from the above crystallization were concentrated and the material vacuum distilled. Two broad fractions were collected; 4.85 g. (2.8%) of a semi-solid product, b.p. 145–155° (6 mm.), and 6.50 g. (3.8%) of a glassy gel, b.p. 155–165° (6 mm.). These fractions appeared to be the diastereomeric dinitriles contaminated with a polymeric material. Recrystallization of the lower boiling fraction from petroleum ether (b.p. 28–36°) gave a crystalline product, m.p. 83–84°.

Anal. Calcd. for C₁₄H₂₄N₂: N, 12.73. Found: N, 12.61.

Trituration of the second fraction in petroleum ether (b.p. 28–36°) gave a white powder, m.p. 93–101°. Recrystallization from ether raised the melting point to 117–118° and gave no depression on mixed m.p. with the 117.5–118.5° melting dinitrile previously obtained from the original still-pot residue. Negative results were obtained in terminal methyl analyses on both of these dinitriles.

Prolonged treatment of these dinitriles with bromine and phosphorus tribromide according to the procedure of Stevens⁶ gave no indication of reaction. The starting compounds were almost quantitatively recovered by washing the reaction mixture and subliming the residue under vacuum.

Distillation of the Mononitrile Fraction.—A 28.0-g. portion of the low molecular weight nitrile mixture in which was dissolved 0.1 g. of picric acid as a polymerization inhibitor was distilled through a fifty-plate center-tube column. After collecting 9.8 g. of a homogeneous fraction, A, b.p. 75.0° (95 mm.), n_D^{20} 1.4204, and several intermediate fractions totalling 5.6 g., B, a solid product plugged the column head, m.p. 30–31°, b.p. 86° (95 mm.). An exact b.p. determination on the latter was difficult since an excessive boil-up rate was necessary to achieve equilibrium at the indicating thermocouple in the presence of the solid dinitrile. The remaining solid in the still pot was distilled through a small column at atmospheric pressure giving a total of 10.2 g. of the solid, C, m.p. 30–31°, b.p. 150.5–151.5°, n_D^{20} 1.4092 (on the super-cooled liquid).

Fraction A was identified as α -*t*-butylacrylonitrile (V).

Anal. Calcd. for C₇H₁₁N: C, 76.99; H, 10.16. Found: C, 76.77, 76.65; H, 9.86, 10.03.

Using the procedure of Mooradian and Cloke,¹⁵ treatment of 2.13 g. (0.019 mole) of the liquid nitrile with 30 ml. of 10% hydrogen peroxide and 4 ml. of 15% aqueous sodium hydroxide in 35 ml. of acetone yielded 2.03 g. (80%) of an oily solid after four days in the ice-chest. Recrystallization from petroleum ether (b.p. 60–68°) gave a crystalline amide, m.p. 107–108.5°.

Anal. Calcd. for C₇H₁₃NO: C, 66.01; H, 10.28; N, 11.01. Found: C, 65.83; H, 10.59; N, 10.96.

A mixed m.p. of this material with an authentic sample of dimethylisopropenylacetamide, structure VII, m.p. 106–107°, resulted in a depression to 85–91°. A mixture with an authentic sample of methyl-*t*-butylacetamide, structure IV, m.p. 107–108°, melted at 89–91°.

The ultraviolet absorption spectrum of the amide in 95% ethanol paralleled that for a known α,β -unsaturated acrylamide, methacrylamide.

Hydrogenation of 0.0724 g. of this material in 15 ml. of 99% ethanol in the presence of 0.0851 g. of pre-reduced platinum oxide required 96.5% of the one mole of hydrogen theoretically required. The hydrogenated product melted at 106–107.5°. There was no depression in the mixed melting point with authentic methyl-*t*-butylacetamide, m.p. 107.5–108.0°, mixed m.p. 107–107.5°.

Fraction B was redistilled through the 50-plate column yielding small additional amounts of material identical with fractions A and C, but did not reveal the presence of any other compound. Hydrolysis of 0.68 g. (0.0062 mole) of an intermediate cut from the redistillation with hydrogen peroxide and alkali in aqueous acetone yielded 0.45 g. (57%) of amide, m.p. 99–101.5°. Mixed melting points were run with methyl-*t*-butylacetamide, m.p. 107.5–108°, mixed m.p. 91–92°; with α -*t*-butylacrylamide, m.p. 107–108°, mixed m.p. 103–104°; and with dimethylisopropenyl-

(14) Analyses by Drs. Weiler and Strauss, Oxford, England, and Dr. F. Schwarzkopf, Long Island City, N. Y.

(15) A. Mooradian and J. B. Cloke, *THIS JOURNAL*, **68**, 785 (1946).

acetamide, m.p. 106–107°, mixed m.p. 86–91°. This amide derived from fraction B is apparently a mixture containing a large proportion of α -*t*-butylacrylamide. Fractional crystallization of the amides derived from the intermediate distillation fractions was unsuccessful.

Fraction C was identified as methyl-*t*-butylacetonitrile.

Anal. Calcd. for $C_7H_{13}N$: C, 75.60; H, 11.78; N, 12.61. Found: C, 75.34; H, 11.57; N, 12.54.

The nitrile was converted to the acid by refluxing a solution of 1.00 g. (0.0090 mole) of nitrile and 3 g. (0.046 mole) of potassium hydroxide in 5 ml. of diethylene glycol for 3 days. After separation of 0.44 g. of neutral material containing unreacted nitrile and amide, an almost quantitative yield (0.68 g.) of the acid was obtained, m.p. 52.8–54°. Aston, *et al.*,¹¹ report the melting point of methyl-*t*-butylacetic acid as 53.5°.

Using thionyl chloride and aniline a 0.20-g. (0.0015 mole) portion of this acid was converted to the anilide in 86% yield, m.p. 108.5–110.5°. Recrystallization from petroleum ether (b.p. 60–68°) brought the melting point to 111–112° (Aston, *et al.*,¹¹ 112°).

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.83. Found: C, 76.36; H, 9.44; N, 6.74.

A mixture with authentic methyl-*t*-butylacetanilide, m.p. 112–112.5°, melted at 111.5–112.2°. The nitrile was converted to the amide, m.p. 104.5–106°, in 59% yield by alkaline hydrogen peroxide in aqueous acetone.

Anal. Calcd. for $C_7H_{15}NO$: C, 65.08; H, 11.70; N, 10.83. Found: C, 65.23; H, 11.65; N, 10.90.

Mixed m.p. with an authentic sample of methyl-*t*-butylacetamide (m.p. 107.5–108°) was 105–106°.

Heating 2.22 g. (0.02 mole) of the nitrile with equimolar amounts of bromine and phosphorus tribromide for 7 hours at 90–100° yielded 2.40 g. (61%) of crude bromonitrile, m.p. 162–164°. Recrystallization from methanol raised the melting point of the waxy needles to 165–166°.

Anal. Calcd. for $C_7H_{12}NBr$: Br, 42.0. Found: Br, 41.7, 41.9.

Preparation of Methyl-*t*-butylacetic Acid Derivatives, Structure IV.—The methyl ester of methyl-*t*-butylacetic acid was prepared by a Favorski rearrangement of monobromomethyl neopentyl ketone according to the procedure of Aston, *et al.*¹¹

Bromination of methyl neopentyl ketone gave a variable yield of the monobromo ketone. About 20% of the starting ketone was recovered together with 25–40% of the desired compound, b.p. 83–87° (20 mm.), n_D^{25} 1.4602, d_4^{25} 1.215 (b.p. 106° (88 mm.)).¹¹

Anal. Calcd. for $C_7H_{13}OBr$: Br, 41.4. Found: Br, 41.1.

Approximately 20–40% of the product was the dibromo-methyl neopentyl ketone, b.p. 103–105° (10 mm.), n_D^{25} 1.5067, d_4^{25} 1.617.

Anal. Calcd. for $C_7H_{12}OBr_2$: Br, 58.7. Found: Br, 58.2.

Terminal methyl analyses on the bromoketones indicate that bromination occurred principally at the methylene rather than the methyl carbon.

Anal. Calcd. for $C_7H_{13}OBr$: $C(CH_3)$ for a *t*-butyl and a methyl ketone group, 8.4; $C(CH_3)$ for a *t*-butyl group (the brominated methyl group no longer furnishing acetic acid in the analysis), 1.8. Found: $C(CH_3)$, 6.54, 7.08.

Anal. Calcd. for $C_7H_{13}Br_2$: $C(CH_3)$ for a *t*-butyl and a methyl ketone group, 6.0; $C(CH_3)$ for a *t*-butyl group, 1.3. Found: $C(CH_3)$, 4.47.

A 49% yield of methyl methyl-*t*-butylacetate was obtained by rearrangement of the monobromo ketone with sodium methoxide, b.p. 143–144° at atmospheric pressure, n_D^{25} 1.4090 (71%, b.p. 95° (150 mm.)), n_D^{20} 1.4116.¹¹

Saponification of the ester was accomplished in 86% yield by prolonged reflux with 25% potassium hydroxide in diethylene glycol to give the acid, m.p. 48–51°, b.p. 110–112° (25 mm.) (m.p. 53.5°, b.p. 132° (55 mm.)).¹¹

The acid was converted to the acyl halide with thionyl chloride. A portion was treated with ammonia to give an 87% yield of the amide, m.p. 104–106°. Recrystallization from ether brought the melting point to 107.5–108°. A second portion of the acid chloride was treated with aniline

to give an almost quantitative yield of the anilide, m.p. 110–111°. Recrystallization from ether raised the melting point to 112–112.5° (112°).¹¹

Preparation of Dimethylisopropylacetic Acid Derivatives, Structure VI.—Dimethylisopropylacetic acid has been prepared by the carbonation of dimethylisopropylcarbinyl chloride by Whitmore and Laughlin¹⁶ and Ford, Jacobson and McGrew.¹⁷ However, experimental details were not given.

Dimethylisopropylcarbinol was obtained in 72% yield by reaction of methylmagnesium iodide with methyl isopropyl ketone, b.p. 63–66° (80 mm.), n_D^{25} 1.4155, d_4^{25} 0.8155 (b.p. 65° (80 mm.)), n_D^{25} 1.4151, d_4^{25} 0.8186.¹⁸

The corresponding chloride was obtained by the procedure of Brown and Fletcher.¹⁹ By shaking the carbinol with concentrated hydrochloric acid, a 69% yield of dimethylisopropylcarbinyl chloride was obtained, b.p. 46–48.5° (80 mm.), n_D^{25} 1.4172 (b.p. 67.6–70.0° (108 mm.)), n_D^{25} 1.4162.¹⁹

Carbonation of the Grignard reagent derived from the above gave a 25% yield of dimethylisopropylacetic acid, b.p. 103–105° (12 mm.), m.p. 49.5–50.5° (b.p. 100–101° (11 mm.)).¹⁷

The acid was converted to the acyl halide with thionyl chloride. Part of the acid chloride was converted to the anilide in almost quantitative yield. After recrystallization from petroleum ether (b.p. 30–60°) the product melted at 78.5–79.0°.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.83. Found: C, 75.81; H, 9.10; N, 6.94.

The remaining acid chloride was converted to the amide in 84% yield by treatment with ammonia in ether, m.p. 131.5–132.0° (129–130°).¹⁸

Preparation of Derivatives of Dimethylisopropenylacetic Acid, Structure VII.—Using the procedure of Courtot⁸ ethyl hydroxy-2,2,3-trimethylbutyrate was prepared in 50% yield, b.p. 92–94° (25 mm.), n_D^{25} 1.4358, d_4^{25} 0.969 (90%, b.p. 91° (17 mm.))⁸ (80%, 84–85° (13 mm.)), n_D^{14} 1.4341, d_4^{14} 0.980.⁹

The hydroxy ester was acetylated by refluxing a pyridine solution with excess acetyl chloride for 20 hours. The reaction products were separated by fractional distillation through an efficient column to yield a 48% recovery of starting material, b.p. 59–60° (1.5 mm.), n_D^{25} 1.4386, together with 53% (based on unrecovered starting material) of colorless ethyl 3-acetoxy-2,2,3-trimethylbutyrate, b.p. 71–72° (1.5 mm.), n_D^{25} 1.4288, d_4^{25} 1.004 (no yield, 119° (23 mm.)).⁸

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 60.93, 60.72; H, 9.19, 9.38.

The acetylated ester was then pyrolyzed to give ethyl dimethylisopropenylacetate by dropping 6.80 g. (0.031 mole) through an 8-inch length of 12-mm. tubing packed with $1/16$ inch glass helices and heated to 325°. The crude product was washed to removed acetic acid and saponified by prolonged reflux with 20% potassium hydroxide in diethylene glycol. The acid was then converted to the acyl halide with thionyl chloride. Treatment with ammonia in ether yielded 2.30 g. of amide (58% based on ethyl 3-acetoxy-2,2,3-trimethylbutyrate). After vacuum sublimation and recrystallization from petroleum ether (b.p. 60–90°), the dimethylisopropenylacetamide melted at 106.5–107.5° (107–108°).⁸ Catalytic hydrogenation of a portion of this material in ethanol using 10% palladium-on-charcoal as a catalyst yielded a product, m.p. 128–129°, shown to be identical with dimethylisopropylacetamide, m.p. 131.5–132.0°, mixed m.p. 130.5–131.0°.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman quartz ultraviolet spectrophotometer in 95% ethanol as solvent. The cell length used in all experiments was 1 cm.

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(16) F. C. Whitmore and K. C. Laughlin, *THIS JOURNAL*, **65**, 3732 (1933).

(17) T. A. Ford, H. W. Jacobson and F. C. McGrew, *ibid.*, **70**, 3793 (1948).

(18) F. Hovorka, H. P. Lankelma and J. W. Bishop, *ibid.*, **63**, 1097 (1941).

(19) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).