carbon atoms (2.52 kX.) expressed as a fraction of d_{100}. For $h = 80$, the denominator of (1) becomes zero at $\alpha = 18.3°$, and F_{h00} attains its maximum value. The direction of maximum polarizability of the crystal, $''\eta_\gamma$, should lie approximately in the direction of the dimers and thus affords another measure of the angle of tilt. η_γ makes an angle of 17° 23′ with $[d_{100}]$, in good agreement with the value of 18.3° derived from the diffraction data. The conventional "angle of tilt," which is the angle of the dimers with respect to the plane of the carboxyl groups, is $90° - \alpha$, or about 72°.

Acknowledgment.—The authors express their thanks to S. F. Herb for preparing the linoleic acid isomer used.

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RECEIVED JANUARY 26, 1950

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[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

NEW COMPOUNDS

Preparation of 2-Bromo-4-nitroethylbenzene and α,α-Dibromo-4-nitroethylbenzene

2-Bromo-4-nitroethylbenzene.—*p*-Nitroethylbenzene,[1] 75.5 g. (0.5 mole) was brominated in the presence of 2.3 g. of iron powder.[2] After the gentle application of heat to start the reaction, a total of 81.6 g. (0.51 mole) of bromine was added at such a rate as to maintain the temperature at 60–70°. After standing over-night the mixture was heated, first on a steam-bath, and finally to 150° until the evolution of hydrogen bromide ceased. The product was washed with dilute sodium bisulfite and water, dissolved in ethyl alcohol, decolorized, dried and concentrated. The residue was distilled under diminished pressure to yield 64 g. (55%), b. p. 155–179° (37 mm.). The distillate partially solidified when cooled to −6°, and the crystalline material was recrystallized repeatedly from ethyl alcohol, and together with some further material from the supernatant liquid, yielded 38.5 g. (34%) of pale yellow prisms, m. p. 31–32°.[3] The material so purified boils at 155–157° (20 mm.).

Anal. Calcd. for $C_8H_8O_2NBr$: C, 41.76; H, 3.50; N, 6.09; Br, 34.73. Found: C, 41.96; H, 3.51; N, 6.2; Br, 34.7.

It was characterized by permanganate oxidation to 2-bromo-4-nitrobenzoic acid, m. p. 170°,[4] which on tin-hydrochloric acid reduction yields *m*-bromoaniline, identified as its acetyl derivative.

α,α-Dibromo-4-nitroethylbenzene.—*p*-Nitroethylbenzene, 83.2 g. (0.55 mole), 2.5 g. of iron powder, 0.2 g. of 20-mesh iron filings, and a crystal of iodine was treated with 175 g. of bromine as above except at 90–100°. After washing the product was steam distilled which removed a much reduced quantity of 2-bromo-4-nitroethylbenzene. The residue, which solidified on cooling, was dissolved in ether, decolorized, dried and the solvent removed, then recrystallized from ethyl alcohol to yield 20.8 g. (12%) of α,α-dibromo-4-nitroethylbenzene as pale yellow needles, m. p. 76–78°.

Anal. Calcd. for $C_8H_7O_2NBr_2$: C, 31.09; H, 2.29; N, 4.53; Br, 51.73. Found: C, 31.35; H, 2.29; N, 4.5; Br, 52.0.

Its identity is tentatively assigned on the bases that permanganate oxidation produces *p*-nitrobenzoic acid which was identified by reduction to *p*-aminobenzoic acid, and while the compound does not produce a precipitate with alcoholic silver nitrate at room temperature, it does on the application of heat.

Attempts to convert 2-bromo-4-nitroethylbenzene into 4-nitro-1,2-diethylbenzene[5] with ethyl bromide and sodium in anhydrous ether were unsuccessful.

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[1] Cline and Reid, This Journal, **49**, 3150 (1927).

[2] Ferrum reductum or "iron by hydrogen" was used.

[3] Thermometers calibrated against U. S. P. Melting Point Standards.

[4] Scheufelen, *Ann.*, **231**, 172 (1885).

[5] Lambooy, This Journal, **71**, 3756 (1949).

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Substituted α-(4-Morpholinyl)-acetonitriles and Related Compounds

The nitriles listed in the table were prepared by one or more of the following methods, adapted from reported procedures: (1) from morpholine and the cyanohydrin in the presence of potassium cyanide,[1] (2) from morpholine, the aldehyde or ketone–sodium bisulfite complex, and potassium cyanide,[1,2] or (3) from morpholine hydrochloride, the carbonyl compound, and potassium cyanide.[3] The recovery and purification of the product was essentially the same for each method: If the product was solid, it was removed by filtration, washed with cold water, and recrystallized from aqueous ethyl alcohol. If the product was an oil, it was extracted with ethyl ether, dried over anhydrous sodium sulfate, and vacuum distilled. Mandelonitrile gave a 55% yield of α-phenyl-α-(4-morpholinyl)-acetonitrile by method 1, whereas 85 and 82% yields, respectively, of the same compound were obtained when benzaldehyde was used in methods 2 and 3. With acetone the yields of nitrile were only 20% by either methods 2 or 3; with formaldehyde the yield was 78% by method 3.

α-Phenyl-α-(4-morpholinyl)-acetamide. A.—A mixture of 3.3 g. of potassium cyanide and 8.1 g. of benzylidene dimorpholine[4] in 20 ml. of water was refluxed on the water-bath until homogeneous (about eleven hours); some ammonia was evolved. The solution was filtered hot after dilution with 20 ml. more of water. Rosettes of needles, m. p. 153.5–154.5,[5] crystallized on cooling; recrystallization from water raised the melting point to 157.5–158.5°. The yield was 4.8 g. or 70%.

Anal. Calcd. for $C_{12}H_{16}O_2N_2$: N, 12.73. Found: N, 12.82.

The compound was readily soluble in alcohol, hot water, and cold concentrated hydrochloric acid, but only slightly soluble in diethyl ether.

B.—Hydrolysis of α-phenyl-α-(4-morpholinyl)-acetonitrile in cold concentrated sulfuric acid gave a product melting at 156° after one recrystallization from water. A mixed melting point with a sample prepared by A was the same. The yield was 4.3 g. or 79% of theory.

α-Phenyl-α-(4-morpholinyl)-thioacetamide.—The crude product as obtained from phenyl morpholinylacetonitrile and hydrogen sulfide by the method of Gabriel and

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[1] Knoevenagel, *Ber.*, **37**, 4082 (1904).

[2] v. Braun, *ibid.*, **41**, 2118 (1908); Bucherer and Schwalbe, *ibid.*, **39**, 2796 (1906).

[3] Strecker, *Ann.*, **75**, 28 (1850); Zelinsky and Stadnikoff, *Ber.*, **39**, 1726 (1906); Marvel and Noyes, This Journal, **42**, 2264 (1920).

[4] Zief and Mason, *J. Org. Chem.*, **8**, 5 (1943).

[5] All melting points are corrected.