water, hot alcohol, hot butanol, hot carbon tetrachloride, but insoluble in paraffins and xylene.

Anal. Calcd. for $C_4H_6O_2Cl_2S$: Cl, 37.10. Found: Cl, 37.15, 37.07.

Attempts to chlorinate 3,4-dichlorotetramethylene sulfone at 190–200° gave no reaction, while at 225–240° the increase in weight was 20% to give a gel-like mass, which appeared to have carbon dispersed through it. Approximately 40% distilled at 55–170° at 2–4 mm. to give portions ranging from no sulfur and 68% chlorine to 23.7% sulfur and 12.6% chlorine. No definite compound was indicated.

CONTRIBUTION FROM THE
CHEMICAL RESEARCH LABORATORIES OF
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Orientation in Aromatic Compounds of Phosphorus. I. Nitration of Di-*n*-butyl Benzylphosphonate

BY GENNADY M. KOSOLAPOFF

Although nitration studies have been carried out with benzylphosphonic acid,[1] dibenzylphosphinic acid and tri-benzylphosphine oxide,[2] the chemical literature lacks an investigation of nitration of esters of phosphonic acids having the benzyl group.

Nitration of di-*n*-butyl benzylphosphonate, with fuming nitric acid or with mixed acid, was now found to give good yields of the *p*-nitro derivative. Other isomers, of which the ortho might have been expected, were formed in such small amounts as to avoid detection. The preparation of a *p*-nitrobenzylphosphonate is of interest because of the reported failure of an attempted direct preparation from trialkyl phosphites and *p*-nitrobenzyl chloride.[3]

Procedure

(a) Di-*n*-butyl benzylphosphonate (28.4 g.) was added over thirty minutes to a stirred mixture of 25 ml. of concentrated sulfuric acid and 25 ml. of concentrated nitric acid at 0–2°. The mixture was stirred at this temperature for one hour and was poured into one liter of ice water. The product was isolated by extraction with benzene (300 ml.), washing with cold water and sodium carbonate solution, and distillation.

(b) Di-*n*-butyl benzylphosphonate (20 g.) was added over thirty minutes with stirring to 100 ml. of fuming nitric acid (d. 1.5) at 0° and the solution was stirred for thirty minutes. The product was then isolated as described above.

Procedure (a) yielded 30.0 g. (91%) of the nitrated ester, while procedure (b) gave 20.0 g. (86%) of the same substance. This was a pale yellow liquid, b. p. 210–211° at 3 mm., n^{23}_D 1.5058; mol. wt. found, 326, 330; calcd., 329.

The identity of this material, as di-*n*-butyl *p*-nitrobenzylphosphonate, was shown by quantitative conversion to *p*-nitrobenzylphosphonic acid upon hydrolysis (six hours) with boiling concentrated hydrochloric acid. The resulting acid melted at 226° (recrystallized from water), which was above the previously reported figure (217°) for the acid obtained by nitration of the free phosphonic acid.[1] The equivalent weight of the acid, however, agreed well with the calculated value (found: 216; calcd. 217), and oxidation with alkaline permanganate gave only *p*-nitrobenzoic acid.

The distillation residues after the isolation of the nitrated ester (about 1 g. in both procedures) gave, upon hydrolysis, a further small amount of *p*-nitrobenzylphosphonic acid, while the residual mother liquors gave minute amounts of the same material, which, however, on treatment with alkaline permanganate gave *p*-nitrobenzoic acid with a somewhat low melting point (235–236°), which may indicate the presence of small amounts of isomers which were too minute for definite isolation.

Attempted reduction of di-*n*-butyl *p*-nitrobenzylphosphonate by potassium sulfide in water at 90° failed to take place and the product was recovered unchanged.

The reduction was accomplished satisfactorily, however, when ten grams of the ester was added over thirty minutes to a mixture of twenty grams of iron filings and 60 ml. of 10% acetic acid at 75–80°; the mixture was stirred for thirty minutes, cooled, mixed with 200 ml. of benzene and filtered after neutralization with sodium carbonate. The benzene extract was washed with water, dried and concentrated in vacuum (water pump). The residual di-*n*-butyl *p*-aminobenzylphosphonate was a deep yellow undistillable oil (9 g.), which could not be induced to crystallize. Its hydrochloride was similarly an uncrystallizable oil. Hydrolysis by boiling hydrochloric acid (seven hours) gave a 93% yield of the previously reported *p*-aminobenzylphosphonic acid[4]; m. p. 324–325° (with dec.).

The physiological action of these substances will be reported elsewhere.

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[1] Litthauer, *Ber.*, **22**, 2145 (1889).

[2] Challenger and Peters, *J. Chem. Soc.*, 2610 (1929).

[3] Lugovkin and Arbuzov, *Doklady Akad. Nauk. S. S. S. R.*, **59**, 1301 (1948).

[4] Kosolapoff, THIS JOURNAL, **69**, 2112 (1947).

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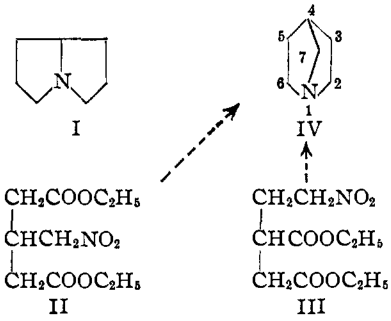
The Addition of Nitroparaffins to Diethyl Glutaconate and Diethyl Itaconate

BY NELSON J. LEONARD AND GRADUS L. SHOEMAKER[1]

The reductive cyclization of γ-nitropimelic esters has provided a convenient method for the synthesis of pyrrolizidine (I) and substituted pyrrolizidines.[2] In an effort to extend the reductive cyclization of nitro-diesters as a means of producing bicyclic compounds containing a bridgehead nitrogen, the addition of nitroparaffins to glutaconic and itaconic esters was studied. The adducts of nitromethane with diethyl glutaconate (II) and with diethyl itaconate (III) should produce the same bicyclic amine, 1-azabicyclo[2.2.



I

IV

$CH_2COOC_2H_5$—$CHCH_2NO_2$—$CH_2COOC_2H_5$

II

$CH_2CH_2NO_2$—$CHCOOC_2H_5$—$CH_2COOC_2H_5$

III

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[2] Leonard, Hruda and Long, THIS JOURNAL, **69**, 690 (1947); Leonard and Beck, *ibid.*, **70**, 2504 (1948).

1]heptane (IV),[3] if hydrogenation over copper chromite at high temperature and pressure were to convert II and III as it does the γ-nitropimelic esters.

Diethyl β-nitromethylglutarate (II) was obtained by the condensation of nitromethane with diethyl glutaconate in the presence of benzyltrimethylammonium hydroxide in 51% yield. Ethyl β-carbethoxy-δ-nitrovalerate (III) was obtained in lower yield by the condensation of nitromethane with diethyl itaconate in the presence of either diethylamine or diisopropylamine. Very little mono-condensation product could be isolated when benzyltrimethylammonium hydroxide was used as the condensing agent. Neither II nor III yielded any 1-azabicyclo[2.2.1]heptane (IV) when subjected to hydrogenation in dioxane over copper chromite at 350 atm. and 260°.[2]

In the condensation of nitroethane with diethyl itaconate in the presence of diisopropylamine to give ethyl β-carbethoxy-δ-nitrocaproate, a solid product was also isolated which was identified unequivocally as diisopropylamine nitrite. The nitrous acid salt of diisopropylamine was shown to be the result of a reaction between the amine and nitroethane alone, since an excess of the nitroethane converted diisopropylamine to the salt in excellent yield. The formation of *nitrite* ion during the reaction of nitroparaffins with strong alkali was observed by Dunstan and Dymond,[4] but Lippincott[5] has claimed that *nitrate* ion is produced in the self-condensation of nitroethane in the presence of diethylamine. The direct production of a readily isolable nitrite derivative during the nitrous acid elimination reaction of a simple nitroparaffin appears to be unique, and diisopropylamine should serve as a most useful base for the study of this reaction. Where the elimination of nitrous acid from an aliphatic nitro derivative has been described previously, the nitro group invariably was attached to the carbon *beta* to a strongly negative group.[6,7]

Experimental

Diethyl β-Nitromethylglutarate.—To a stirred solution of 31 g. (0.5 mole) of nitromethane and 10 g. of benzyltrimethylammonium hydroxide (40% aqueous)[8] in 75 ml. of dioxane was added 31 g. (0.17 mole) of diethyl glutaconate.[9] The solution was kept at 65° for sixty hours. It was then cooled and neutralized with 6 *N* hydrochloric acid, and an equal volume of ethylene dichloride was added. The ethylene dichloride layer was washed with water and the more volatile components were removed by distillation at atmospheric pressure. The residue was fractionated *in vacuo* and the diethyl β-nitromethylglutarate was collected at 118–120° (0.5 mm.); $n^{20}\text{D}$ 1.4482; $d^{20}{}_4$ 1.1492; yield, 21 g. (51%).

Anal. Calcd. for $C_{10}H_{17}NO_6$: N, 5.67; MR_D, 57.32. Found: N, 5.43; MR_D, 57.61.

Ethyl β-Carbethoxy-δ-nitrovalerate.—A solution of 50 g. (0.27 mole) of diethyl itaconate (prepared in 95% yield from itaconic acid, Chas. Pfizer Co., through the use of an ethyl ester column), 61 g. (1.0 mole) of nitromethane and 35 g. (0.34 mole) of diisopropylamine was allowed to stand at 25° for sixteen days. The solution was neutralized with 6 *N* hydrochloric acid, and 100 ml. of ethylene dichloride was added. The ethylene dichloride layer was washed twice with 150-ml. portions of water. The solvent was removed and the residue was fractionated *in vacuo.* Diethyl itaconate (23.5 g.), b. p. 79–82° (2 mm.), was recovered and 8.6 g. (25% yield on the basis of unrecovered itaconic ester) of ethyl β-carbethoxy-δ-nitrovalerate was obtained; b. p. 126–130° (1.5 mm); $n^{20}\text{D}$ 1.4472; $d^{20}{}_4$ 1.1394.

Anal. Calcd. for $C_{10}H_{17}NO_6$: N, 5.67; MR_D, 57.32. Found: N, 6.08; MR_D, 58.00.

Ethyl β-Carbethoxy-δ-nitrocaproate.—A solution of 93 g. (0.5 mole) of diethyl itaconate, 50 g. (0.66 mole) of nitroethane, and 50 g. (0.5 mole) of diisopropylamine was allowed to stand at 25°. After one week crystals appeared on the wall of the flask and continued to form for two weeks. After forty days the crystalline solid was collected, washed with ethylene dichloride and dried (28 g.). The solution and the ethylene dichloride washings were combined and an additional 200 ml. of ethylene dichloride was added. From this point, the product was worked up in the manner described for ethyl β-carbethoxy-δ-nitrovalerate. The ethyl β-carbethoxy-δ-nitrocaproate distilled at 138–142° (2 mm.); $n^{20}\text{D}$ 1.4455; $d^{20}{}_4$ 1.1123; yield, 31 g. (40% yield on the basis of unrecovered itaconic ester).

Anal. Calcd. for $C_{11}H_{19}NO_6$: N, 5.36; MR_D, 61.94. Found: N, 5.58; MR_D, 62.58.

The crystalline product which separated was recrystallized from acetone and was freed from final traces of moisture by boiling toluene over the colorless needles, m. p. 140°.

Anal. Calcd. for $C_6H_{16}N_2O_2$: C, 48.62; H, 10.63. Found: C, 48.45; H, 10.77.

The infrared spectrum indicated the presence of strong hydrogen bonding. Acidification of the needles caused the evolution of nitrous fumes. Alkali liberated a base which formed a picrate as needles, m. p. 145–146°, which caused no depression in the melting point (145–146°) of an authentic sample of diisopropylamine picrate. The nitrous acid salt of diisopropylamine has been reported as melting at 140°.[10] An authentic sample of this compound was prepared by passing nitrous acid fumes through a dry toluene solution of diisopropylamine. After recrystallization from acetone and drying under toluene, the diisopropylamine nitrite melted at 140° and gave no depression in melting point with the compound isolated from the original reaction mixture.

Diisopropylamine nitrite likewise was produced in over 80% yield when nitroethane and diisopropylamine, in 2:1 molar ratio, were allowed to stand at 25°. The reaction is being investigated further.

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[3] Prelog and Cerkovnikov, *Ann.*, **525**, 292 (1936); Prelog, Cerkovnikov and Ustriceo, *ibid.*, **535**, 37 (1938); Prelog, Heimbach and Rezek, *ibid.*, **545**, 231 (1940).

[4] Dunstan and Dymond, *J. Chem. Soc.*, **59**, 410 (1891).

[5] Lippincott, This Journal, **62**, 2604 (1940).

[6] Kloetzel, *ibid.*, **70**, 3571 (1948).

[7] van Tamelen and Van Zyl, *ibid.*, **71**, 835 (1949).

[8] Bruson, U. S. Patent 2,342,119 (February 22, 1944); U. S. Patent 2,390,918 (December 11, 1945).

[9] Lochte and Pickard, This Journal, **68**, 721 (1946).

[10] Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. 1, Eyre and Spottiswoode, London, 1943, p. 875.

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3-Methyl-3-ethyl-2-hexanone

By Chas. T. Lester and John R. Proffitt, Jr.[1]

Whitmore and Lewis[2] have reported that 3,3-diethyl-2-pentanone is the smallest aliphatic ke-

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[1] Community Trust Fellow, 1945-1946.

[2] Whitmore and Lewis, This Journal, **64**, 1618 (1942).