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
PUBLICKER INDUSTRIES, INC.
EDDINGTON, PA. RECEIVED JANUARY 13, 1949

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.

---

(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).

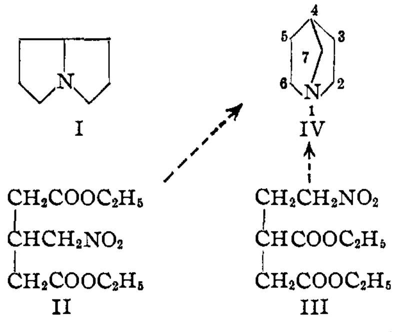
(4) Kosolapoff, THIS JOURNAL, **69**, 2112 (1947).

THE ROSS CHEMICAL LABORATORY
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA RECEIVED JANUARY 19, 1948

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.



$CH_2COOC_2H_5$–$CHCH_2NO_2$–$CH_2COOC_2H_5$ (II)

$CH_2CH_2NO_2$–$CHCOOC_2H_5$–$CH_2COOC_2H_5$ (III)

---

(1) Present address: Department of Chemistry, Rutgers University, New Brunswick, New Jersey.

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