P-(β,β′-ethyl ether) bis(t-butylaminodiphenylphosphonium)bromide was prepared. In this latter case benzene was used as solvent.

To ascertain whether the quaternization occurs on the phosphorus or on the nitrogen atom, P-benzyl(t-butylamino)diphenylphosphonium chloride was subjected to alkaline hydrolysis. Only t-butylamine and benzyldiphenylphosphine oxide were isolated from the hydrolysis product. It is thus evident that the quaternization occurs on the phosphorus atom.

The alkaline hydrolysis of mono- and diquaternary aminophosphonium halides offers a convenient method for the preparation of mono- and ditertiary phosphine oxides.

EXPERIMENTAL[5]

Materials. The preparation of t-butylaminodiphenylphosphine was carried out by the method previously described[6] except that dry benzene rather than ethyl ether was used as solvent. A yield of 80% is obtained by this procedure. The organic halides were used as received from the following sources: benzyl chloride and 2,4-dichlorobenzylchloride from Heyden Newport Chemical Corp., chlorodiphenylmethane from Distillation Products Industries, p-xylylene dichloride from Pennsalt Chemicals Corp., bis(chloromethyl)durene from Humble Oil and Refining Co., and β,β′-dibromodiethyl ether from Matheson, Coleman and Bell. Dimethylformamide (b.p. 152.6–153.5°) from Fischer Scientific Co. was used as received.

Procedure. As an example of the procedure used in the aralkylation of t-butylaminodiphenylphosphine the following description of the synthesis of P-(xylylene)bis(t-butylaminodiphenylphosphonium chloride) is given:

A solution of 8.8 g. (0.05 mole) of p-xylylene dichloride and 25.7 g. (0.10 mole) of t-butylaminodiphenylphosphine in 150 ml. of dimethylformamide was stirred at reflux for 4 hr. The mixture was then allowed to cool to room temperature and the colorless crystalline product was filtered, washed twice with ethyl ether and dried. The product weighed 28.0 g. (81% yield) and melted at 264° dec. An analytical sample was recrystallized from an ethyl ether-ethanol mixture to give colorless, salt-like crystals which melted at 269° dec. The compound is soluble in water. The use of ethyl ether and benzene for the reaction described lowers the yield considerably.

The diquaternary aminophosphonium salts tend to crystallize as hydrates as has been reported for the synthesis of diphosphonium salts.[4]

The physical properties, analytical data, and yields for the various aminophosphonium salts synthesized in this investigation are listed in Table I.

A characteristic of all the spectra of these aminophosphonium salts is an intense band at 1120 cm.$^{-1}$ and two moderately strong bands between 940 and 820 cm.$^{-1}$ A strong band also appears near 720 cm.$^{-1}$ in common with other aryl-substituted phosphonium compounds where the phosphorus atom is functioning as an electron donor.[7]

The alkaline hydrolysis of P-benzyl(t-butylamino)diphenylphosphonium chloride was carried out as follows:

A mixture of 3.8 g. (0.01 mole) of P-benzyl(t-butylamino)-diphenylphosphonium chloride and 2.0 g. of potassium hydroxide in 30 ml. of water was stirred at reflux for 1 hr. The amine was collected in a water trap. The crystalline residue was filtered and dried. It crystallized from aqueous ethanol as fine, colorless needles (m.p. 191–193°). The melting point agrees with that reported for benzyldiphenylphosphine oxide.[8] The product weighed 2.6 g. and represents a 86% yield based on the aminophosphonium chloride used.

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[5] All melting and boiling points are uncorrected. Microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

[6] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

[7] J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 2120 (1960).

[8] G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 116.

Reaction of Trinitromethyl Compounds with Potassium Iodide

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In a recent report from this laboratory the preparation of potassium 1,1,3-trinitropropane (I) by the reduction of 1,1,1,3-tetranitropropane with potassium iodide in methanol was described.[1] Since the product was important to a proof of structure, we wish now to establish that the preparative reaction was unambiguous and to record some further examples of this convenient method for the conversion of trinitromethyl compounds to salts of the corresponding 1,1-dinitro derivatives (1-nitroalkyl-1-nitronates).

$$RC(NO_2)_3 + 2\,KI \longrightarrow RC(NO_2)_2^-K^+ + KNO_2 + I_2$$

The closest reported analogies to these reactions of which we are aware involve the potassium iodide reductions of tetranitromethane to potassium nitroform[2] and of 1-bromo-1,1-dinitroalkanes to the corresponding 1-nitro-1-nitronate salts.[3]

Attempts to convert 2,2,2-trinitroethanol to potassium 2,2-dinitroethanol by this method were unsuccessful. The only product isolated under a variety of conditions was potassium nitroform,

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[1] M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *J. Org. Chem., in press.*

[2] C. Krauz and J. Stepanek, *Chem. Obzor.*, **12**, 81 (1937); *Chem. Abstr.*, **31**, 6138 (1937).

[3] K. Klager, *Anal. Chem.*, **23**, 534 (1951); J. Meisenheimer, *Ber.*, **36**, 434 (1903).

[4] S. S. Novikov, I. S. Korsakova, and N. N. Bulatova, *Zhur. Obshchei Khim.*, **29**, 3659 (1959).

TABLE I

POTASSIUM 1-NITROALKYL-1-NITRONATES

$RC(NO_2)_2^-K^+$	Yield,	Ultraviolet Spectrum	Carbon, %		Hydrogen, %		Nitrogen, %		Potassium, %	
R	%	λ_{max} (log ϵ)	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_2CH_2NO_2$ (I)[a]	33	373.5 (4.24)[b]	16.58	16.57	1.84	2.08	19.35	19.10	18.02	17.99
$CH_2CH_2COOCH_3$ (II)	77	379 (4.23)[c]	26.08	25.75	3.07	3.07	12.17	12.40	16.98	16.95
$CH_2CH_2COC_6H_5$ (III)	17	379 (4.21)[c]	50.40	50.46[d]	4.23	4.13[d]	11.76	11.52[d]	14.14	13.99
$CH_2CH_2COCH_3$ (IV)	40	379 (4.22)[c]	28.03	27.98	3.30	3.38	13.08	13.39	18.25	18.23
$CH_2CH_2CONH_2$ (V)	87	379 (4.21)[c]					19.50	19.68		
CH_3 (VI)	81	381.5 (4.23)[e]								

[a] Ref. (1). [b] Solvent, water. [c] Solvent, dilute potassium hydroxide. [d] Analyses for carbon, hydrogen, and nitrogen were on 4,4-dinitrobutyrophenone, m.p. 77.0–77.7°, obtained by acidification of an aqueous solution of the potassium salt and recrystallization of the precipitated product from methanol-water. The same product, m.p. 77–78° has been reported as a product of the Michael reaction of dinitromethane with acrylophenone.[4] [e] L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957) report 381 (4.21).

probably resulting from deformylation which took place more rapidly than reduction.

EXPERIMENTAL[5]

Methyl 4,4,4-trinitrobutyrate,[6] 5,5,5-trinitropentanone-2, and 4,4,4-trinitrobutyramide[1] were prepared by the reaction of nitroform with the appropriate conjugated olefins.

4,4,4-Trinitrobutyrophenone.[7] A solution of 24.2 g. of 4,4,4-trinitrobutyryl chloride in 200 ml. of dry benzene was stirred vigorously at 9° while 13.4 g. of anhydrous aluminum chloride was added portionwise. The mixture was refluxed for 1 hr., cooled to room temperature, and the aluminum halide complexes were destroyed by the careful addition of ice and 6*N* hydrochloric acid. The organic phase was separated, washed with 5% sodium bicarbonate and with water, dried over anhydrous magnesium sulfate, and the solvent removed *in vacuo*. Recrystallization of the residue from hexane gave 21.0 g. (79%) of tan needles, m.p. 78.8–79.3°. A further recrystallization from hexane (charcoal) gave 18.2 g. (64%) of white needles, m.p. 78.8–79.3°.

Anal. Calcd. for $C_{10}H_9N_3O_7$: C, 42.41; H, 3.20; N, 14.83. Found: C, 42.54, 42.74; H, 3.26, 3.14; N, 14.18, 14.42.

The same compound has been prepared by the Michael reaction of nitroform with acrylophenone and reported[4] to melt at 80–81°.

Typical reduction procedure. One hundredth mole of the trinitromethyl compound in 20 ml. of methanol was added to 0.022 mole of potassium iodide in 50 ml. of methanol and either refluxed for 1 hr. or stirred overnight at room temperature. The black mixture was concentrated and the precipitated yellow salt filtered, washed with ether and recrystallized from methanol-water. The yields recorded in Table I do not result from any attempt to arrive at optimal conditions.

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(5) *Caution:* The compounds herein described are explosive in nature. Appropriate precautions should be taken in their handling.

(6) K. Schimmelschmidt, *Hunter Report BIOS 1919;* 22/IG, July 3, 1946.

(7) We are indebted to Dr. Rip G. Rice who performed this synthesis.

Alkaline Cleavage of a Homolog of Ricinoleic Acid

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Cleavage of ricinoleic acid derivatives in the presence of strong alkali at above 240°, to give decanedioic acid and 2-octanol, is well known.[1,2] Related research has been carried out on other hydroxy and keto compounds, and mechanisms for the cleavage reaction have been proposed.[2,3]

The major fatty acid of *Lesquerella lasiocarpa* seed oil, named lesquerolic acid, has been characterized as (+)-14-hydroxy-*cis*-11-eicosenoic acid.[4] When lesquerolic acid (93% pure; *cf.* Table I) was heated at 270–300° with sodium hydroxide, the reaction yielded principally dodecanedioic acid (Table I) and 2-octanol $[\alpha]_D^{25}$ − 0.2°. Slight levorotation of the 2-octanol obtained by alkali cleavage of ricinoleic acid has also been reported.[2] These cleavage products confirm the structure reported for lesquerolic acid[4] and indicate a probable area of utility of the new acid for the preparation of chemical intermediates.

The two unknown alkali cleavage products detected by gas-liquid chromatography, Table I, were not identified, nor was the source of the tetradecanedioic acid elucidated. In addition to the gas-liquid chromatography evidence, the dodecanedioic acid was identified by melting point in admixture with authentic dodecanedioic acid.

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(1) R. Adams and C. S. Marvel, *Org. Syntheses*, **Coll. Vol. I**, 366 (1946).

(2) G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.*, **1947**, 753 and references therein.

(3) R. A. Dytham and B. C. L. Weedon, *Tetrahedron*, **8**, 246 (1960) and references therein.

(4) C. R. Smith, Jr., T. L. Wilson, T. K. Miwa, H. Zobel, R. L. Lohmar, and I. A. Wolff, *J. Org. Chem.*, **26**, 2903 (1961).