ethylenes to yield ketones and ammines as shown in Table I. Nitrogen was also obtained in each instance.

Some olefins, such as styrene and indene, polymerize so rapidly in concentrated sulfuric acid, which was used as the reaction medium that they do not react with hydrazoic acid; others, such as stilbene and tetraphenylethylene are insoluble in concentrated sulfuric acid and for this reason do not react under our experimental conditions.

TABLE I

ACTION OF HYDRAZOIC ACID IN SULFURIC ACID SOLUTION

Reactant	Products and yields, %
1,1-Diphenylethylene	Aniline 40, acetophenone 30
Diphenylmethylcarbinol	Aniline 65, acetophenone 40
1,1-Diphenyl-1-butene	Aniline 57, butyrophenone 64
1-Anisyl-1-phenylethylene	*p*-Anisidine, acetophenone, aniline, *p*-methoxyacetophenone
Triphenylethylene	Aniline 30, phenylbenzylketone 25

The behavior of 1,1-diphenylethylene was typical of the compounds studied. It reacted smoothly at room temperature with the formation of 1 mole of nitrogen per mole of azide. Aniline and acetophenone were obtained from the reaction mixture. The plausible sequence of reactions suggested recently by McEwen, *et al.*,[2c] and which were arrived at independently by us accounts for the products obtained and illustrates the similarity of the reaction of carbonium ions with the reactivity of oxy- and oxocarbonium ions. The fact that the same products are obtained whether the starting material is diphenylmethylcarbinol or diphenylethylene indicates that each yields the same reactive intermediate, the diphenylmethylcarbonium ion. With unsymmetrical ethylenes such as anisylphenylethylene, two reactions are possible. The first involves the migration of the anisyl group to yield anisidine and acetophenone and the second involves the migration of the phenyl to yield aniline and *p*-methoxyacetophenone. We have found that the former reaction predominates since the ketone fraction of the products contains 75 ± 5% acetophenone and 25 ± 5% of the methoxy derivative. This is the same dependence of migrating aptitude upon electronic character as is shown in other rearrangements such as the pinacol rearrangement[3] which involves the migration of a group with its binding electrons.

Experimental

Two grams of each substance was added slowly with stirring to a 10% molar excess of sodium azide in concentrated sulfuric acid at room temperature. When gas evolution ceased the reaction mixture was poured into ice-water and extracted with ether. From the ether extract the ketone was isolated and identified as the semicarbazone by its melting point and mixed melting point with an authentic sample. It was further identified by a comparison of the infrared curve with that of an authentic sample. The aqueous portion after ether extraction was made alkaline and extracted with ether. From this extract the aniline was obtained and precipitated as the hydrochloride. Because sulfonation took place when 1-anisyl-1-phenylethylene was dissolved in concentrated sulfuric acid, its reaction with hydrazoic acid was run in 75% sulfuric. The ketone fraction, obtained in 80% yield, in this instance was not converted to the semicarbazone. An infrared curve of this material was the same as the curve of a synthetic mixture of 75% acetophenone and 25% *p*-methoxyacetophenone. After removal of the ether from the second extract of this experiment the residue was recrystallized from water to yield *p*-anisidine. The filtrate from the crystallization was extracted with ether and yielded aniline hydrochloride. Triphenylethylene is difficultly soluble in concentrated sulfuric acid and for this reason was run at 40°.

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[3] Bachmann and Moser, THIS JOURNAL, **54**, 1124 (1932); **56**, 2081 (1934); Pollak and Curtin, *ibid.*, **72**, 961 (1950).

Methyl Ester of Dehydroperillic Acid, an Odoriferous Constituent of Western Red Cedar (*Thuja plicata*)

BY E. F. KURTH

Anderson and Sherrard[1] isolated an acid, $C_{10}H_{12}O_2$, termed dehydroperillic acid and Erdtman and Gripenberg[2] found three additional isomerides, α-, β- and γ-thujaplicin, in the heartwood of *Thuja plicata* D. Don. During the past two years the author examined some highly fragrant crystals that were found in western red cedar sawlogs at Garibaldi, Oregon. The operator of a sawmill at this place reported observing the crystals occasionally in western red cedar logs.

The crystals were clear, water-white parallelepipeds, which melted at 34.5 to 35°. One large crystal had the dimensions 9 × 18 × 20 mm. Anderson and Sherrard prepared the methyl ester of their acid and found it had a pleasant odor and m. p. 34.5 to 35°. Erdtman and Gripenberg found α-thujaplicin, m. p. 34°, in Swedish grown *Thuja plicata* but not in American grown wood. An investigation of the crystals found in the American western red cedar sawlogs disclosed that they were the methyl ester of dehydroperillic acid. This compound is readily saponified with dilute alkalies to dehydroperillic acid. Inasmuch as the former workers used alkalies in their isolation of dehydroperillic acid and the thujaplicins, the methyl ester of dehydroperillic acid was not recognized as probably the chief odoriferous constituent of *Thuja plicata*.

Experimental

The crystals were readily soluble in ethyl ether, acetone, ethanol, chloroform and light petroleum. They were insoluble in cold sodium hydrogen carbonate solution. Tests with ferric chloride and copper acetate reagents[2] indicated the complete absence of thujaplicins. Refluxing with dilute sodium hydroxide solution followed by acidification with dilute sulfuric acid gave white crystals m. p. 88°, which is the same as that reported for dehydroperillic

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[1] Anderson and Sherrard, THIS JOURNAL, **55**, 3813 (1933).

[2] Erdtman and Gripenberg, *Nature*, **161**, 719 (1948); *Acta Chem. Scand.*, **2**, 625 (1948).

acid. Methoxyl group: calcd. for $C_{10}H_{11}O{\cdot}OCH_3$, 17.4%; found 17.4%. Mixed melting point determination with dehydroperillic acid supplied by Dr. A. B. Anderson, m. p. 88°.

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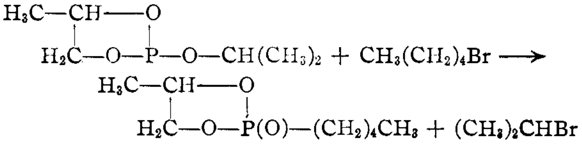
Phosphonation with a Phosphite Ester of Propanediol

By F. W. Mitchell, Jr.,[1] and H. J. Lucas

The reaction of trialkyl phosphites with alkyl halides in the Arbuzov reaction[2] is essentially a phosphonation reaction, since one product is an ester of a phosphonic acid. The reaction has been studied fairly extensively with acyclic esters,[3] and has been extended recently to cyclic trialkyl phosphites derived from ethanediol and 3-methoxy-1,2-propanediol.[4] Whereas ethyl ethylene phosphite (2-ethoxy-1,3,2-dioxaphospholane)[5] underwent the isomerization reaction with ring opening, the presence of the methoxymethyl side chain in esters of 3-methoxy-1,2-propanediol led to ring stabilization. When the isomerization reagent was ethyl bromide the reaction product was the cyclic ester of ethanephosphonic acid.

In connection with work on cyclic trialkyl phosphites derived from glycols[5] it has been found



that 2-isopropoxy-4-methyl-1,3,2-dioxaphospholane (isopropyl propylene phosphite) when heated with 1-bromopentane undergoes the Arbuzov reaction without ring opening. The product is propylene pentane-1-phosphonate (2-oxo-2-*n*-amyl-4-methyl-1,3,2-dioxaphospholane). The recovery of isopropyl bromide in 78% yield indicates this is essentially the sole reaction. The stability of the ring system in this case is in agreement with the conclusions of the Russian workers,[4] that a side chain in the glycol residue increases the stability of the ring system.

Experimental

In a boiler attached to a distillation column held at 60°, 0.2 mole (32.8 g.) of 2-isopropoxy-1,3,2-dioxaphospholane and 0.2 mole (30.2 g.) of 1-bromopentane, b. p., 127-127.5°, were heated at refluxing temperature for a period of 9 hours, during which time isopropyl bromide slowly distilled; weight 19 g. (78% yield); b. p. 57.5-58.5° at 745 mm.; $n^{25}{}_D$ 1.4216 (literature value 1.4251). Distillation of the residue gave 28 g. (73% yield) of propylene pentane-1-phosphonate, a slightly viscous liquid, b. p. 131-132° at 1.5 mm., $n^{25}{}_D$ 1.4481, $d^{25}{}_4$ 1.1052.

Hydrolysis of 10 g. (0.052 mole) with 6 *N* HCl[6] for 30 minutes, followed by slow distillation with paraformaldehyde according to the procedure of Senkus[7] gave 3 ml. (63% yield) of formal. Excess formaldehyde was removed from the boiler liquid as methalal, b. p. 44-45°, and the water was evaporated at reduced pressure, leaving a dark brown oil which partly solidified overnight. Oil and solid were separated from each other by flotation with a carbon tetrachloride-ligroin mixture. Crystallization of the solid from hot ligroin gave 2.3 g. (25% yield) of thin colorless plates, m. p. 120-122°, believed to be pentane-1-phosphonic acid.[8]

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(1) National Aniline and Film Corporation, Easton, Pa.

(2) A. E. Arbuzov and A. A. Dunin, *J. Russ. Phys.-Chem. Soc.*, **46**, 295 (1914); A. E. Arbuzov, "On the Structure of Phosphorous Acid," N. Alexandria, 1905.

(3) G. M. Kosolapoff, This Journal, **66**, 109 (1944). A number of references to earlier work are given.

(4) A. E. Arbuzov, V. M. Zoroaster and N. T. Rizpolozhenskiĭ, *Bull. acad. sci. U. R. S. S. Classe sci. chim.*, 208, 1948; *cf. C. A.*, **42**, 4932 (1948).

(5) H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, This Journal, **72**, 5491 (1950).

(6) Similar to the procedure of G. M. Kosolapoff, *ibid.*, **67**, 1180 (1945), who used concentrated acid, however.

(7) M. Senkus, *Ind. Eng. Chem.*, **38**, 913 (1946), recovered 2,3-butanediol from dilute aqueous solutions by conversion to the formal.

(8) Of the fourteen normal alkanephosphonic acids listed by Kosolapoff[6] none of the others melted higher than 106°.

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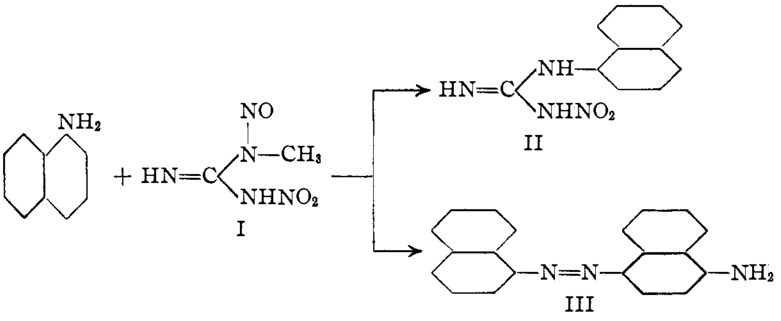
A New Method for the Preparation of Azo Dyes[1]

By Eugene Lieber and Konrad Parker[2]



While investigating the formation of N-Ar-N′-nitroguanidines, where Ar is a polycyclic aromatic hydrocarbon radical, by the method of McKay and Wright[3] using N-methyl-N-nitroso-N′-nitroguanidine (I), it was observed that α-naphthylamine gave rise to two products; N-(α-naphthyl)-N′-nitroguanidine (II), the expected product, in 25% yield (based on the nitroso compound used), and a large amount of dark brownish-green needles having dye properties. This was subsequently identified as 4-amino-α,α-azo-naphthalene[4] and amounted to 50% of the theoretical yield

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(1) Studies in the Guanidine Series. VIII.

(2) Abstracted from a portion of the thesis submitted by Konrad Parker to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree, Master of Science.

(3) A. F. McKay and G. F Wright, This Journal, **69**, 3028 (1947).

(4) Michaelis and Erdmann, *Ber.*, **28**, 2198 (1895).