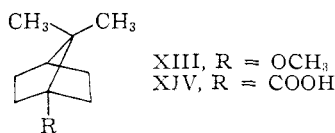


The possibility that relatively unstable carbonium ions can be generated from carboxylic acids at high voltages is indicated by the formation of apocamphyl methyl ether (XIII) from the acid (XIV) (methanol, 150 volts).^{12,13}



(12) Data of H. J. Dauben and M. A. Muhs quoted by D. E. Applequist and J. D. Roberts in *Chem. Rev.*, **54**, 1079 (1954).

(13) Joint contribution from Harvard University (a) and the University of Illinois (b). We are indebted to Drs. T. Traylor, J. Berson and H. Schmid for samples and to the National Science Foundation and U. S. Public Health Service for support.

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RECEIVED APRIL 4, 1960

REACTION OF METHYLETHYLPHENYLBENZYLIDENEPHOSPHORANE WITH BENZONITRILE

Sir:

The typical orange color of a solution of racemic methylethylphenylbenzylidenephosphorane (I) in ether is not discharged when 1.45 equivalents of benzonitrile is added and the mixture stirred at 25° for 12 hours. However, removal of the ether and treatment of the residue with a solution of potassium hydroxide in aqueous methanol under reflux gives desoxybenzoin (II) in 78% yield and racemic methylethylphenylphosphine oxide (III) in 71% yield. This appears to be the first recorded example of the reaction of a methylenephosphorane with a nitrile.

When optically active I, prepared by the action of phenyllithium on levorotatory methylethylphenylbenzylphosphonium iodide,^{1,2} is treated in the same manner as cited above for racemic I, the phosphine oxide, III, obtained is optically active, $[\alpha]^{25}_D + 8.3^\circ$ (*c*, 3.856 in water). Inasmuch as optically pure dextrorotatory III has a specific rotation of 22.8°,^{3,4} and since it has been demonstrated² that levorotatory methylethylphenylbenzylphosphonium iodide belongs to the same configurational family as levorotatory III, it follows that the reaction of I with benzonitrile and the subsequent treatment with alkali gave III with 68% inversion.

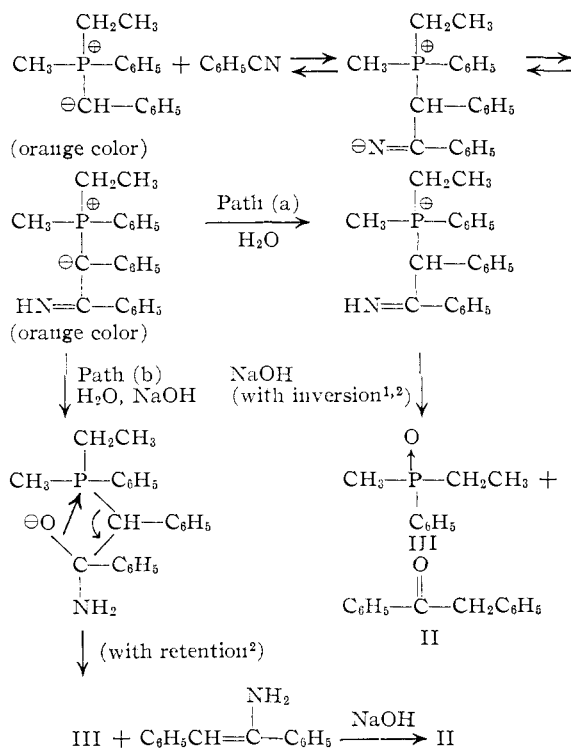
These observations suggest that two competing reactions are taking place, the major path (a) giving III with inversion of configuration of the phosphorus atom, and the minor path (b) giving III with retention.

(1) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *THIS JOURNAL*, **81**, 248 (1959).

(2) A. Bladé-Font, C. A. VanderWerf and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

(3) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *ibid.*, **81**, 3805 (1955).

(4) (a) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911); (b) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 213 (1926).



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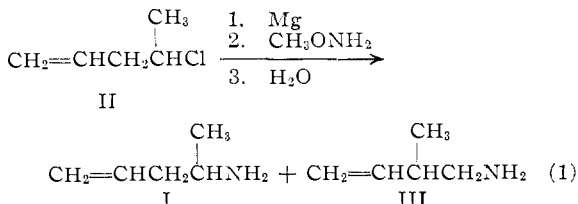
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RECEIVED APRIL 8, 1960

SMALL-RING COMPOUNDS. XXVIII. ISOTOPE-POSITION REARRANGEMENTS OF ALLYL-CARBINYLL GRIGNARD REAGENTS¹

Sir:

We have observed a remarkable rearrangement while attempting to prepare 4-penten-2-ylamine (I) through the reaction of the Grignard reagent derived from 4-penten-2-yl chloride (II) with methoxylamine,² in that part of the amine formed appeared to be 2-methyl-3-butenylamine (III).



(1) (a) Supported in part by the Office of Naval Research and the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund. (b) Presented in part at the Sixteenth National Organic Symposium, Seattle, Washington, June 15, 1959.

(2) R. Brown and W. E. Jones, *J. Chem. Soc.*, 781 (1946).