

nitrophenyl)-methane and 0.43 g. (0.0011 mole) of tri-(*p*-nitrophenyl)-carbinol were separated from the reaction products.

ROHM AND HAAS COMPANY
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

Selective Reduction of Aliphatic Nitroesters with Lithium Aluminum Hydride¹

BY HENRY FEUER AND THOMAS J. KUCERA

RECEIVED JUNE 29, 1955

The selective reduction of ethyl *p*-nitrobenzoate and ethyl *p*-nitrophenylacetate to the corresponding nitroalcohols with lithium aluminum hydride at 25° has been reported by Felkin.² We wish to report the successful reduction of aliphatic nitroesters, containing a secondary, tertiary or *gem*-dinitro group, to the corresponding nitrocarbinols in yields which compare favorably with those obtained by the reduction of aliphatic nitroaldehydes with sodium borohydride.³ The reductions were carried out smoothly at -30 to -60° by employing a slight excess of the hydride and ether as the solvent, except in the case of dimethyl 4,4-dinitropimelate where tetrahydrofuran had to be used because of the limited solubility of this ester in ether at low temperatures.

Since methyl 4-nitropentanoate did not evolve hydrogen when treated with the hydride at low temperatures, several nitroesters with more highly active hydrogens were tested. It was found that ethyl 2-nitropropanoate, ethyl 2-nitrocaproate and ethyl 3-nitropropanoate reacted with lithium aluminum hydride at -30 to -60° without the evolution of hydrogen. However, great difficulty was encountered in the isolation of the alcohols because of the high water solubility of the nitropropanols⁴ and known tendency of the 2-nitro-1-hexanol to dehydrate to the olefin upon distillation.⁵

TABLE I

Methyl ester	Product	Yield, %
4-Nitropentanoate	4-Nitropentanol	61 ^a
4-Methyl-4-nitropentanoate ^c	4-Methyl-4-nitropentanol ^d	76 ^c
4,4-Dinitropentanoate ^b	4,4-Dinitropentanol ^d	53
4,4-Dinitropimelate ^c	4,4-Dinitro-1,7-heptanediol	56

^a H. A. Bruson, U. S. Patent 2,342,119 (1949). ^b H. Shechter and L. Zeldin, *THIS JOURNAL*, **73**, 1276 (1951). ^c L. Herzog, *et al.*, *ibid.*, **73**, 749 (1951). ^d Identified by physical properties and derivatives according to H. Shechter, *et al.* (ref. 3). ^e Some of the starting ester was recovered.

Experimental⁶

The following procedure is representative of the preparation of the various nitroalcohols.

4-Nitropentanol.—Methyl 4-nitropentanoate⁷ (13.87 g., 86 mmoles) was dissolved in 60 ml. of anhydrous ether and the solution cooled to -35°. Lithium aluminum hydride solution in ether (53.7 ml. of 0.81 *M*, 43 mmole) was added

(1) From the Ph.D. thesis of Thomas J. Kucera, Purdue University, 1953.

(2) H. Felkin, *Compt. rend.*, **230**, 305 (1950).

(3) H. Shechter, D. E. Ley and L. Zeldin, *THIS JOURNAL*, **74**, 3664 (1952).

(4) "Nitrohydroxy Derivatives of the Nitroparaffins," Commercial Solvents Corp., New York, N. Y.

(5) E. F. Degering and R. Hoaglin, *Proc. Indiana Acad. Sci.*, **52**, 119 (1942).

(6) All melting points are uncorrected.

(7) H. Bruson, U. S. Patent 2,390,918 (1945).

dropwise over a 15-minute period and the solution was stirred for another 20 minutes before 5 ml. of ethyl acetate was added. Hydrolysis was then carried out at 0° with 50 ml. of 20% phosphoric acid with 6 g. of urea dissolved in it. The layers were separated and the aqueous layer extracted with two 50-ml. portions of ether. The combined ether extracts were dried with anhydrous sodium sulfate and the solvent was removed by distillation. The residue was distilled to yield 0.67 g. of the starting ester, b.p. 90-94° at 2 mm. and 4-nitropentanol (6.67 g., 61% conversion), b.p. 90-92° at 1 mm., *n*_D²⁰ 1.4479; lit. value³ b.p. 91-92.5° at 1 mm., *n*_D²⁰ 1.4475. The alcohol was converted in a Nef⁸ reaction to 5-hydroxy-2-pentanone and the ketone was characterized by its 2,4-dinitrophenylhydrazide, m.p. 146-147°; lit. value³ m.p. 146-147°.

4,4-Dinitro-1,7-heptanediol.—The same experimental procedure was followed as above except that tetrahydrofuran was employed as the solvent. The diol was obtained as a white solid, m.p. 74.5-75° after recrystallization from methylene chloride.

Anal. Calcd. for C₇H₁₄N₂O₆: C, 37.84; H, 6.35; N, 12.61. Found: C, 37.92; H, 6.56; N, 12.88.

The bis-phenylurethan, m.p. 119.5-120°, was prepared and recrystallized from ethylene chloride.

Anal. Calcd. for C₂₁H₂₄N₄O₈: C, 54.78; H, 5.25; N, 12.17. Found: C, 55.50; H, 5.40; N, 12.43.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

(8) J. U. Nef, *Ann.*, **280**, 263 (1894).

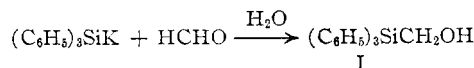
DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

The Reactions of Triphenylgermyllithium with Formaldehyde and with Benzophenone

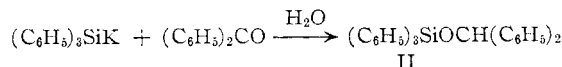
BY HENRY GILMAN AND CLARE W. GEROW

RECEIVED JUNE 4, 1955

It has been reported¹ previously that triphenylsilylpotassium reacts with formaldehyde in diethyl ether to form, along with other unidentified material, triphenylhydroxymethylsilane (I). The same authors report² that triphenylsilylpotassium

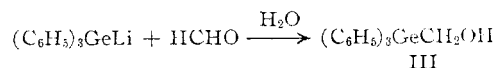


reacts with benzophenone in diethyl ether to give benzohydroxytriphenylsilane (II). In the former



reaction the triphenylsilylpotassium adds to the carbonyl group in such a manner that in the product I the silicon atom is attached to the carbon atom of the carbonyl group. In the latter reaction the product II has the silicon atom attached to the oxygen atom of the carbonyl group.

We have found that triphenylgermyllithium adds to formaldehyde in ethylene glycol dimethyl ether in the same manner as triphenylsilylpotassium to give triphenylhydroxymethylgermane.



However, we have also established that triphenylgermyllithium reacts with benzophenone in ethylene

(1) H. Gilman and T. C. Wu, *THIS JOURNAL*, **76**, 2502 (1954).

(2) H. Gilman and T. C. Wu, *ibid.*, **76**, 2935 (1953).