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 Hydride[1]

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 nitropropanols[4] 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[e]
4-Methyl-4-nitropentanoate[a]	4-Methyl-4-nitropentanol[d]	76[e]
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.

Experimental[6]

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

4-Nitropentanol.—Methyl 4-nitropentanoate[7] (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 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., $n^{20}\text{D}$ 1.4479; lit. value[3] b.p. 91–92.5° at 1 mm., $n^{20}\text{D}$ 1.4475. The alcohol was converted in a Nef[8] reaction to 5-hydroxy-2-pentanone and the ketone was characterized by its 2,4-dinitrophenylhydrazone, m.p. 146–147°; lit. value[3] 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 $C_7H_{14}N_2O_6$: 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 $C_{21}H_{24}N_4O_8$: 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.

---

(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).

(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 reported[1] previously that triphenylsilylpotassium reacts with formaldehyde in diethyl ether to form, along with other unidentified material, triphenylhydroxymethylsilane (I). The same authors report[2] that triphenylsilylpotassium

$$(C_6H_5)_3SiK + HCHO \xrightarrow{H_2O} \underset{\text{I}}{(C_6H_5)_3SiCH_2OH}$$

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

$$(C_6H_5)_3SiK + (C_6H_5)_2CO \xrightarrow{H_2O} \underset{\text{II}}{(C_6H_5)_3SiOCH(C_6H_5)_2}$$

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.

$$(C_6H_5)_3GeLi + HCHO \xrightarrow{H_2O} \underset{\text{III}}{(C_6H_5)_3GeCH_2OH}$$

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.*, **75**, 2935 (1953).

glycol dimethyl ether to give triphenylgermyldiphenylcarbinol and not benzohydryloxytriphenylgermane.

$$(C_6H_5)_3GeLi + (C_6H_5)_2CO \xrightarrow{H_2O} \underset{\text{IV}}{(C_6H_5)_3GeC(OH)(C_6H_5)_2}$$

In both cases the addition to the carbonyl group gives a product (III, IV) containing the germanium atom bonded to the carbon atom of the carbonyl group.

Triphenylhydroxymethylgermane (III) was prepared authentically by the reduction of methyl triphenylgermanecarboxylate with lithium aluminum hydride.

$$(C_6H_5)_3GeCOOCH_3 + LiAlH_4 \xrightarrow{H_2O} (C_6H_5)_3GeCH_2OH$$

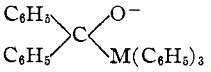
Authentic specimens of triphenylgermyldiphenylcarbinol (IV) were prepared by the reactions of both phenyllithium and phenylmagnesium bromide with methyl triphenylgermanecarboxylate.

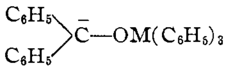
$$C_6H_5M + (C_6H_5)_3GeCOOCH_3 \xrightarrow{H_2O} (C_6H_5)_3GeC(OH)(C_6H_5)_2$$

M = Li and MgBr

Triphenylgermyldiphenylcarbinol appears to be unstable, for when a sample is left in contact with the air the melting point decreases. For this reason purification is difficult and yields of the authentic specimens were low due to the necessity of repeatedly recrystallizing the product.

The reaction of triphenylsilylpotassium with benzophenone[2] has been interpreted as possibly occurring by initial "normal" adddition of the triphenylsilyl group to the carbon atom of the carbonyl group to give structure V followed by rearrangement to the more stable structure VI.

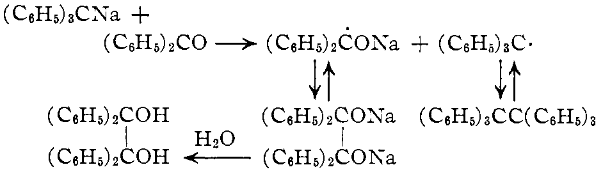

V


VI

An alternate mechanism stated that structure VI apparently was a better model of the transition state of the reaction due to the stabilizing of this structure by means of resonance with the phenyl groups.

It is difficult to see why triphenylgermyllithium should react differently with benzophenone considering the similarities in physical properties between silicon and germanium. One might perhaps have expected the above mechanisms to apply equally well to triphenylgermyllithium.

It is interesting to note that both triphenylmethylsodium[3] in diethyl ether and triphenylmethylmagnesium bromide[4] in an ether–benzene mixture react with benzophenone to give ketyls which are converted to benzopinacols upon hydrolysis.



$$\begin{tikzcd}
(C_6H_5)_3CNa + (C_6H_5)_2CO \arrow[r] & (C_6H_5)_2\dot{C}ONa \arrow[d, shift left] & + (C_6H_5)_3C\cdot \arrow[d, shift left] \\
(C_6H_5)_2COH \arrow[d, dash] & (C_6H_5)_2CONa \arrow[u, shift left] \arrow[d, dash] & (C_6H_5)_3CC(C_6H_5)_3 \arrow[u, shift left] \\
(C_6H_5)_2COH & (C_6H_5)_2CONa \arrow[l, "H_2O"'] &
\end{tikzcd}$$

Experimental[5]

Reaction of Triphenylgermyllithium with Formaldehyde.—Triphenylgermyllithium was prepared by the cleavage of 6.0 g. (0.01 mole) of hexaphenyldigermane with 1.0 g. (0.144 g. atom) of lithium in 5 ml. of sodium-dried, redistilled ethylene glycol dimethyl ether using exactly the same procedure as previously described[6] for the preparation of triphenylgermyllithium from tetraphenylgermane and lithium. The time required for the cleavage to begin was 15 minutes. After 3.5 hours an additional 10 ml. of solvent was added and the mixture stirred for a total of 6 hours. The dark solution was pipetted into another nitrogen-flushed flask and formaldehyde gas, generated by heating paraformaldehyde,[7] was introduced over the surface of the stirred triphenylgermyllithium by a stream of dry nitrogen. After 3 hours the dark solution had turned white. Water was added to hydrolyze the mixture and it was filtered to give 5.2 g. of paraformaldehyde. The aqueous solution was extracted three times with ether, the ether was dried over anhydrous sodium sulfate and the solvent was distilled to leave a liquid which was heated in a vacuum to remove all solvents. On cooling the residue it solidified. Washing with petroleum ether (b.p. 60–70°) gave a solid weighing 4.5 g. and melting over the range 96–100°. This material was fractionally crystallized from petroleum ether (b.p. 60–70°) to give 2.1 g. (31.4%) of triphenylhydroxymethylgermane melting at 115–116° and 0.3 g. (4.8%) of hexaphenyldigermoxane (mixed melting point) melting at 185–187°. The identity of other possible products from this reaction mixture has not been established.

Anal.[8] Calcd. for $C_{19}H_{18}OGe$: Ge, 21.68. Found: Ge, 21.84, 21.95.

Preparation of Triphenylhydroxymethylgermane from the Reduction of Methyl Triphenylgermanecarboxylate.—To 0.18 g. (0.0048 mole) of lithium aluminum hydride dissolved in 25 ml. of ether was added 1.7 g. (0.0047 mole) of methyl triphenylgermanecarboxylate[9] dissolved in 30 ml. of ether over a period of 10 minutes. After stirring for 4 hours, 20 ml. of ethyl acetate was added, followed by water to destroy the excess lithium aluminum hydride. The ether layer was separated and the aqueous layer extracted twice with ether. The combined ether portions were dried over anhydrous sodium sulfate and the solvent distilled to leave a residue which was crystallized from petroleum ether (b.p. 60–70°) to give 1.25 g. of impure product melting over the range 100–110°. Recrystallization from the same solvent gave 0.55 g. (35%) of triphenylhydroxymethylgermane melting at 114–115°. A mixed melting point with the product from the reaction of triphenylgermyllithium with formaldehyde showed no depression and their infrared spectra were identical.

Reaction of Triphenylgermyllithium with Benzophenone.—To a stirring ethylene glycol dimethyl ether solution of triphenylgermyllithium prepared from the cleavage of 6.0 g. (0.01 mole) of hexaphenyldigermane with 1.0 g. (0.14 g. atom) of lithium, was added 3.6 g. (0.02 mole) of solid benzophenone. Heat was evolved and the mixture turned a deep green. After stirring for 24 hours the reaction mixture was hydrolyzed by the addition of water. The mixture was then extracted three times with ether, the ether dried over anhydrous sodium sulfate and the solvent distilled to leave a yellow oil. This oil was refluxed with absolute ethanol and filtered hot to give 3.5 g. of solid melting over the range

---

(3) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916).

(4) W. E. Bachmann, This Journal, **53**, 2758 (1931).

(5) All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

(6) H. Gilman and C. W. Gerow, This Journal, **77**, 4675 (1955).

(7) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 188.

(8) Germanium analyses were carried out by placing about 0.2 g. of the sample for analysis in a Vycor glass crucible followed by 1 ml. of concentrated sulfuric acid and a few drops of fuming nitric acid. The crucible was then cautiously heated by means of a Rogers ring burner in the manner used for silicon analyses by H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, This Journal, **72**, 5767 (1950). When all acid was gone the oxide was ignited to constant weight by means of a bunsen burner. When a Meeker burner was used for the final ignition the results were low, presumably due to the sublimation of the oxide, for some of the oxide was deposited in the crucible lid.

(9) Prepared according to the directions of A. G. Brook and H. Gilman, *ibid.*, **76**, 77 (1954).

148–155°. Further cooling and volume reduction gave 2.4 g. of material melting over the range 145–155°. Fractional crystallization of the above materials from petroleum ether (b.p. 77–115°) gave 3.6 g. (37%) of triphenylgermyldiphenylcarbinol melting at 153–155° and 1.0 g. (16%) of hexaphenyldigermoxane (mixed melting point) melting at 184–186°.

A repetition of the above reaction gave 1.1 g. (16.3%) of hexaphenyldigermoxane[10] melting at 185–187° and 1.0 g. (10.3%) of triphenylgermyldiphenylcarbinol melting at 153–155°.

Anal. Calcd. for $C_{31}H_{26}OGe$: Ge, 14.91. Found: Ge, 14.93, 15.21.

Preparation of Triphenylgermyldiphenylcarbinol.—To 22 ml. of an ether solution of phenylmagnesium bromide prepared from 0.34 g. (0.014 g. atom) of magnesium and 2.17 g. (0.014 mole) of bromobenzene was added dropwise 2.0 g. (0.0055 mole) of methyl triphenylgermanecarboxylate dissolved in 50 ml. of ether. After refluxing for 4 hours the mixture was hydrolyzed by pouring it into a mixture of ammonium chloride and cracked ice. The ether layer was separated and the aqueous portion washed three times with ether. The combined ether portions were dried over anhydrous sodium sulfate and the solvent was distilled to leave a residue which was crystallized from petroleum ether (b.p. 60–70°) to give 1.54 g. (64%) of impure triphenylgermyldiphenylcarbinol melting over the range 143–153°. Purification was extremely difficult due to the instability of the material. After numerous crystallizations from ethanol and petroleum ether (b.p. 60–70°) the melting point was raised to 153–155°. A mixed melting point with the product from the addition of triphenylgermyllithium to benzophenone showed no depression and the infrared spectra were identical, showing a typical hydroxyl absorption. On standing in air the melting point of this compound was lowered, indicating that some change was taking place.

A repetition of the above experiment using phenyllithium in place of the phenylmagnesium bromide gave 1.7 g. (71%) of impure triphenylgermyldiphenylcarbinol melting over the range 142–147°. Repeated recrystallization from petroleum ether (b.p. 60–70°) gave 0.6 g. (25%) of product melting at 154–155°. Again a mixed melting point with the product from the reaction of triphenylgermyllithium with benzophenone showed no depression and the infrared spectra were identical.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance. They also are grateful to the Institute for Atomic Research, Iowa State College, and Dr. V. A. Fassel, and Messrs. R. Hedges, R. Kross and R. McCord for assistance in the infrared determinations.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

[10] If any benzohydryloxytriphenylgermane were formed in this reaction, it is probable on the basis of some other unpublished studies that it would be hydrolyzed under these experimental conditions of working up the mixture to give hexaphenyldigermoxane.

Benzhydrylmagnesium Bromide from Potassium Diphenylmethide and Magnesium Bromide

BY CHARLES R. HAUSER AND DAVID S. HOFFENBERG[1]

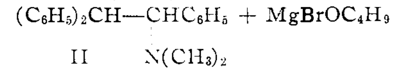
RECEIVED JUNE 23, 1955

Because of its tendency to couple to form tetraphenylethane, benzhydryl bromide or chloride has been difficult to convert satisfactorily to the Grignard reagent.[2] Even when the reagent was prepared from the bromide in a high dilution cyclic reactor and then carbonated, only a 25% yield of diphenylacetic acid was obtained.[3]

We have prepared benzhydrylmagnesium bromide by a new method in which the coupling reaction was avoided. This consisted in metalating diphenylmethane with potassium amide in liquid ammonia, replacing the ammonia with ether and treating the resulting red suspension of potassium diphenylmethide with magnesium bromide in the latter solvent (equation 1). In the last step the red color characteristic of the diphenylmethide ion disappeared rapidly indicating the formation of the more covalent carbon–magnesium bond.

$$(C_6H_5)_2CH_2 \xrightarrow[\text{2, ether}]{\text{1, KNH}_2\text{ (liq. NH}_3\text{)}} (C_6H_5)_2CHK \xrightarrow[\text{ether}]{MgBr_2} (C_6H_5)_2CHMgBr \quad (1)$$

The reagent prepared in this manner was shown to undergo a reaction characteristic of the Grignard reagent but not of potassium diphenylmethide. Thus, it reacted with α-amino ether I to form tertiary amine II in 82% yield, whereas the potassium reagent failed to react under similar conditions. This yield was based on amino ether I since, as usual, an excess of the reagent was employed. Recently[4] a somewhat lower yield (50%) of II was obtained with benzhydrylmagnesium chloride prepared from a large excess of benzhydryl chloride and powdered magnesium.



$$(C_6H_5)_2CHMgBr + \underset{\text{I}}{C_4H_9O\text{—}\underset{\displaystyle N(CH_3)_2}{\underset{|}{C}}HC_6H_5} \longrightarrow \underset{\text{II}}{(C_6H_5)_2CH\text{—}\underset{\displaystyle N(CH_3)_2}{\underset{|}{C}}HC_6H_5} + MgBrOC_4H_9$$

It should be pointed out that for many reactions there is no advantage in converting the potassium diphenylmethide to the Grignard reagent since equally good yields may be obtained with the potassium reagent. For example, potassium diphenylmethide has been carbonated to form diphenylacetic acid in 90% yield.[5]

Experimental

An ether suspension of potassium diphenylmethide was prepared from 0.11 mole of potassium amide and 0.10 mole of diphenylmethane essentially as described previously.[5] The potassium amide was obtained from 4.4 g. (0.11 g. atom) of potassium, a crystal of ferric nitrate and 300 ml. of liquid ammonia. After adding the diphenylmethane, the ammonia was replaced by an equal volume of ether, and the resulting suspension refluxed until practically all of the ammonia had been removed (1 hour).

To the stirred red suspension was added during 15–20 minutes a magnesium bromide–ether mixture which was added through a stopcock attached to the bottom of the flask in which it was prepared, the potassium diphenylmethide reagent being decolorized rapidly. The magnesium bromide–ether mixture was prepared essentially as described by Swain and Boyles[6] by adding dropwise with stirring 17.0 g. (0.105 mole) of bromine to 3.0 g. (0.12 g. atom) of magnesium turnings and 300 ml. of ether, the stirring being continued until the bromine color disappeared (about 15 minutes).

To the resulting gray benzhydrylmagnesium bromide re-

---

[1] Allied Chemical and Dye Corp. Fellow, 1954–1955.

[2] See H. Gilman and J. E. Kirby, THIS JOURNAL, **48**, 1773 (1926).

[3] D. C. Rowlands, K. W. Greenlee and C. E. Boord, Abstracts of Papers, 117th Natl. Meeting, Am. Chem. Soc., Philadelphia, Pa., April 9–13, 1950, p. 8-L.

[4] A. T. Stewart and C. R. Hauser, THIS JOURNAL, **77**, 1098 (1955).

[5] R. S. Yost and C. R. Hauser, *ibid.*, **69**, 2325 (1947).

[6] C. G. Swain and H. B. Boyles, *ibid.*, **73**, 870 (1951).