

1-diazo-3-phenoxy-2-butanone was obtained by recrystallization from benzene-petroleum ether (b.p. 30–60°; m.p. 34–35° (Kofler hot stage¹²)).

Anal. Calcd. for C₁₀H₁₀N₂O₂: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.25; H, 5.47, N, 14.26.

Wolff rearrangement was attempted with the crude solid diazoketone (total residual product from the reaction described immediately above), by the general procedure previously outlined. Gas evolution ceased after 2.5 g. of silver benzoate in 22.5 g. of triethylamine had been added. Isolation of product in the usual manner gave a residual oil, which was distilled under reduced pressure. Three fractions were collected, one of which (4.21 g.), b.p. 110–120° (0.55–0.75 mm.), solidified upon strong cooling. Recrystallization from petroleum ether (b.p. 30–60°) gave a yellow crystalline product, m.p. 34–35°, which in alcohol solution yielded a gas (presumably nitrogen) upon acidification with hydrochloric acid, and was considered to be recovered 1-diazo-3-phenoxy-2-butanone.

EVERY LABORATORY
THE UNIVERSITY OF NEBRASKA
LINCOLN, NEB.

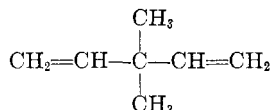
(12) L. Kofler, *Angew. Chem.*, **51**, 703 (1938).

3,3-Dimethyl-1,4-pentadiene¹

REMCO CIOLA AND ROBERT L. BURWELL, JR.

Received December 30, 1957

The previously unreported 3,3-dimethyl-1,4-pentadiene (I) is the simplest diene which cannot



conjugate by mere migration of a double bond. As such, we wished to study its catalytic hydrogenation. It is also of interest as model compound for other mechanistic studies.

The readily accessible² 1,5-dichloro-3,3-dimethylpentane (II) would seem an attractive starting material. However, attempts to dehydrochlorinate II directly with a variety of bases failed. The diiodide corresponding to II reacts very rapidly to give good yields of I when refluxed with the hindered amine, 2-methylquinoline. This appears to be an example of the general rule that, in proceeding from chlorides to bromides to iodides, ease of dehydrohalogenation increases even more rapidly than that of nucleophilic substitution.

The preparation may be simplified by refluxing a mixture of II, sodium iodide and 2-methylquinoline under conditions such that the olefin is removed as it is formed.³ This reaction is much slower than

that of the di-iodide. The rate limiting step is apparently substitution of chloride by iodide. Presumably, the sequence of intermediates is chloroiodide, chloroolefin, iodoolefin. Equally good results were obtained in converting 1-chloro-3,3-dimethylpentane to 3,3-dimethyl-1-pentene but the conversion⁴ of 1-chloro-3,3-dimethylbutane to *t*-butylethylene failed, perhaps because of lower refluxing temperatures.

Pyrolysis over calcium chloride of II at about 550° or of the corresponding dibromide at about 450° gave small yields, 5–10%, of I plus a number of difficultly removable by-products.

EXPERIMENTAL

1,5-Dichloro-3,3-dimethylpentane was prepared following Schmerling and West.² We found it important to cool the 1,3-dichloro-3-methylbutane to –40° before adding aluminum chloride and to start the ethylene flow immediately. The reaction flask can then be warmed to –25° but ethylene must be fed as fast as it is absorbed. Under these conditions, little or no hydrogen chloride appears in the small amount of exit gas and the amounts of lower and higher molecular weight materials are minimal. Yields of 70% or better result from final distillation at reduced pressure; n_D^{20} 1.4643, reported² 1.4652.

3,3-Dimethyl-1,4-pentadiene (I). A mixture of 0.5 mole of II, 2 moles of 2-methylquinoline, and 0.1 mole of sodium iodide was refluxed in a flask surmounted by a tubing 40 cm. long with a standard taper plug at the top. Just before this was a connection to a small Vigreux column at the top of which was a condenser and take-off. The reflux had to be interrupted once during a run, the plug removed, and 2-methylquinoline hydrohalide which had distilled into the tubing scraped down into the flask. The reflux rate was maintained so that the temperature at the top of the Vigreux column was between 60 and 70°. The reaction is slow; a few hours elapse before diolefin appears and the entire reaction requires about 8 hr. The product was dried with sodium sulfate and fractionated; yield, 58% at b.p. 70.2° at 750.5 mm. Further possible purification was effected by storage over sodium and azeotropic distillation with methanol, n_D^{20} 1.4067; d_4^{20} 0.7017.

Anal. Calcd. for C₇H₁₂: C, 87.4; H, 12.6. Found: C, 87.9; H, 12.5.

The diolefin absorbs 2 moles of hydrogen in the presence of platinum oxide and forms a hydrocarbon with the infrared spectrum of 3,3-dimethylpentane.

3,3-Dimethyl-1-pentene was made in 88% yield from 1-chloro-3,3-dimethylpentane⁵ by the same process, b.p. 77.2° at 755 mm.; n_D^{20} 1.3978.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

(4) W. O. Haag and H. Pines, private communication.

(5) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1152 (1945).

Lithium Cleavages of Triphenyl Derivatives of Some Group Vb Elements in Tetrahydrofuran

DIETMAR WITTENBERG AND HENRY GILMAN

Received January 2, 1958

Cleavage of various compounds with alkali metals has often proved to be a valuable tool in

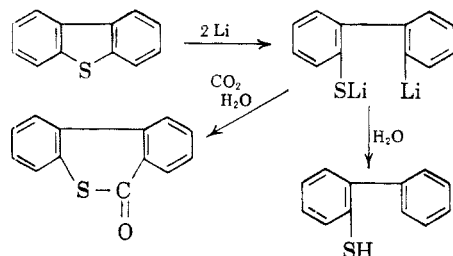
(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF18(603)-132. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **74**, 2885 (1952).

(3) We are indebted to Professor L. C. King for suggesting this one-step modification.

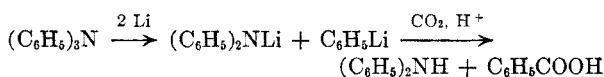
synthesis and structure proof. For the cleavage of some heterocycles, lithium in tetrahydrofuran¹ (THF) was found to be most effective.

While dibenzothiophene was not cleaved by lithium in diethyl ether even after 36 hr. at reflux, the use of refluxing dioxane² or tetrahydrofuran (THF) at room temperature¹ as solvents gave in addition to biphenyl, 2-mercaptobiphenyl or 3,4-benzothiocoumarin after hydrolysis or carbonation,



respectively. Dibenzo-*p*-dioxin, thianthrene, dibenzofuran, and diphenyl ether were also successfully cleaved by lithium in THF.¹

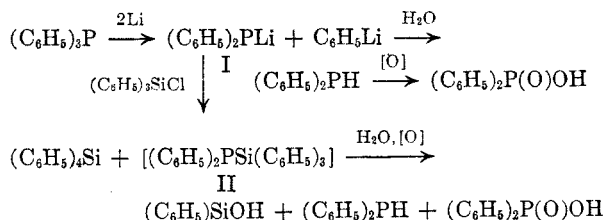
On refluxing triphenylamine with lithium in the same solvent for 3 hr.³ diphenylamine had been obtained in 9.7% yield, together with large amounts of unreacted starting material. In an extension of this work we noticed that after an induction period the cleavage of triphenylamine in this solvent proceeds smoothly even at room temperature. The reaction was started by employing first only a small amount of the solvent, the main part of which was added after Color Test I⁴ had become positive. Carbonation after 4 hr. of stirring gave diphenylamine and benzoic acid in 59% and 25% yields, respectively.



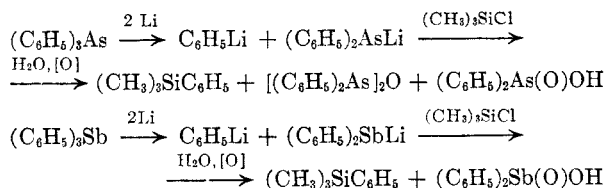
Other triphenyl derivatives of group Vb elements, such as triphenylphosphine, triphenylarsine, and triphenylstibine, were also easily cleaved by lithium in THF. In all cases the reactions were exothermic giving rise to a dark red or brown color; in the case of triphenylamine, however, the resulting solution was deep green. Color Test I⁴ usually was positive within one minute after the reaction was started.

The cleavage of triphenylphosphine to diphenylphosphinolithium⁵ (I) and phenyllithium gave, after hydrolysis, diphenylphosphine in good yields,

together with small amounts of its oxidation product, diphenylphosphinic acid. When the cleavage products were allowed to react with chlorotriphenylsilane, tetraphenylsilane was isolated in a 64% yield. The expected triphenylsilyldiphenylphosphine (II), however, has not been isolated. Only its hydrolysis and oxidation products, triphenylsilanol, diphenylphosphine, and diphenylphosphinic acid, were identified.



The lithium cleavage products of triphenylarsine were reacted with chlorotrimethylsilane to give trimethylphenylsilane (76%), bis(diphenylarsenic) oxide (54%), and diphenylarsinic acid (3%) after hydrolysis and contact with air. Triphenylstibine similarly gave trimethylphenylsilane (62.5%) and diphenylstibinic acid (69.5%).



The reaction of triphenylbismuthine and lithium in THF was not investigated, but a similar cleavage^{5a} would be expected in this case also.

EXPERIMENTAL⁵

Cleavage of triphenylamine. Ten grams (0.0408 mole) of triphenylamine was cleaved in 80 ml. of THF with 2.1 g. (0.3 g.-atom) of finely cut lithium wire. The reaction was started by adding only a small amount of the solvent. After stirring for 0.5 hr. at room temperature the solution slowly turned brown, and a few minutes later deep green. Then the rest of the solvent was added slowly and the solution stirred for 4 additional hours. The reaction mixture was filtered through glass wool and carbonated in the usual manner. The resulting products were treated with dilute acid in order to destroy any possibly formed diphenylcarbamic acid, followed by the addition of some ether and extraction with dilute sodium hydroxide. The aqueous solution was acidified and extracted with ether. The removal of the solvent left a brown oil, which was subsequently extracted with boiling petroleum ether (b.p. 60–70°), using five 25-ml. portions. Recrystal-

(1) H. Gilman and J. J. Dietrich, *J. Org. Chem.*, **22**, 851 (1957).

(2) H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.*, **75**, 2947 (1953).

(3) H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, **80**, 380 (1958).

(4) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925); G. Wittig, *Angew. Chem.*, **53**, 243 (1940).

(5) The preparation and properties of the corresponding sodium compound have recently been described by W. Kuchen and H. Buchwald, *Angew. Chem.*, **69**, 307 (1957).

(5)(a) Prof. W. Rüdorff kindly informed us recently that triphenylphosphine, -arsine, and -stibine have also been successfully cleaved by sodium in liquid ammonia. See Walter Müller, Dissertation, Tübingen (1957).

(6) All melting points and boiling points are uncorrected. The tetrahydrofuran was dried and purified by successively shaking with sodium hydroxide pellets, refluxing over sodium metal for at least 24 hr., and finally distilling immediately before use from lithium aluminum hydride. The cleavage reactions were carried out in an atmosphere of dry, oxygen-free nitrogen.

lization of the resulting product from water gave 1.2 g. (24.5%) of benzoic acid, m.p. 120–121.5°, identified by mixture melting point.

The neutral organic layer was distilled and the residue chromatographed on alumina. The product eluted with petroleum ether (b.p. 60–70°) and carbon tetrachloride was recrystallized from petroleum ether of the same boiling point to give 4.05 g. (59%) of diphenylamine, m.p. 53–54°, identified by mixture melting point and infrared spectra.

When a mixture of 12.25 g. (0.05 mole) of triphenylamine, 1 g. (0.15 g.-atom) of lithium, and 50 ml. of THF was stirred for 1.5 hr. at room temperature and refluxed for 3 additional hours,^{6a} a brown color had developed, but Color Test I⁴ was still negative. After hydrolysis, 8.3% of diphenylamine was isolated, together with 58% of triphenylamine. In another experiment,^{6a} employing the same amount of starting materials and solvent, a positive Color Test I was obtained after 3 hr. at reflux. Subsequent carbonation gave no benzoic acid, but diphenylamine in a 9.7% yield, together with unreacted triphenylamine (60%).

Cleavage of triphenylphosphine. To a stirred mixture of 10 g. (0.0382 mole) of triphenylphosphine and 1.4 g. (0.2 g.-atom) of finely cut lithium wire was added slowly 100 ml. of THF. The reaction started immediately, the solution turned dark red, heat was evolved, and Color Test I⁴ was positive. Stirring was continued for 1 hr., at which time the mixture had cooled to room temperature. The solution was filtered through glass wool, hydrolyzed, and after the addition of some ether, extracted with dilute acid and water. The dried organic layer was distilled to give 5.2 g. (68.5%) of diphenylphosphine, b.p. 150–154° (11 mm.).⁷ The infrared spectrum showed the characteristic P-H absorption band at 4.4 μ .

In a second experiment 15.0 g. (0.0572 mole) of triphenylphosphine was cleaved with 1.4 g. (0.2 g.-atom) of lithium in 100 ml. of THF at –10° to 0° (stirring for 4 hr.). The work-up in the manner described above gave 4.95 g. (47%) of diphenylphosphine, b.p. 150–154° (11 mm.). The distillation residue was recrystallized from ethanol and yielded 2.5 g. (20.2%) of diphenylphosphinic acid, m.p. 190–191.5°, which was identified by its infrared spectrum.

In a third experiment the cleavage products were allowed to react with chlorotriphenylsilane. After hydrolysis, tetraphenylsilane, m.p. 232–234°, was isolated in a 64% yield from the ether insoluble part of the reaction mixture. Chromatography of the ether soluble part gave crude triphenylsilanol, diphenylphosphinic acid, and diphenylphosphine, which were identified by their infrared spectra.

Cleavage of triphenylarsine. To a stirred mixture of 10 g. (0.034 mole) of triphenylarsine and 1.4 g. (0.2 g.-atom) of finely cut lithium wire was added slowly 100 ml. of THF. The reaction started immediately, the solution turned red and showed a positive Color Test I.⁴ After stirring for 1 hr. while cooling with ice and one additional hour at room temperature, a solution of 7.4 g. (0.068 mole) of chlorotrimethylsilane in 10 ml. of THF was added. The color of the solution faded after the addition of the second equivalent. The work-up by filtration through glass wool, addition of some ether, extraction with dilute acid, drying of the organic layer with sodium sulfate, and distillation gave 3.9 g. (76%) of trimethylphenylsilane, b.p. 166–169°, n_D^{20} 1.4870, which was identified by its infrared spectrum. The high boiling fractions, 1.5 g., b.p. 160–230° (0.1 mm.), and 5.1 g., b.p. 230–240° (0.1 mm.), both yellow oils, which slowly solidified, were treated with cold benzene. The benzene insoluble part was recrystallized from water to give 0.25 g. (3%) of di-

phenylarsinic acid, m.p. 171–172.⁸ The benzene soluble part was recrystallized from ethanol to give 4.3 g. (54%) of bis(diphenylarsenic) oxide, m.p. 92–93.5°.⁸

Cleavage of triphenylstibine. The cleavage of 10 g. (0.0283 mole) of triphenylstibine with 1.4 g. (0.2 g.-atom) of lithium in 80 ml. of THF was carried out as described in the previous experiment. The cleavage products were allowed to react with 6.5 g. (0.06 mole) of chlorotrimethylsilane. The deep red-brown color faded immediately, leaving a small amount of black precipitate (apparently metallic antimony). The reaction mixture was filtered through glass wool, hydrolyzed, and after the addition of some ether, washed with dilute acid. The dried organic layer deposited on standing a white precipitate, which was filtered off, washed with ether and water to give 5.25 g. (60%) of diphenylstibinic acid, m.p. 283–286°. Distillation of the filtrate yielded 2.65 g. (62.5%) of trimethylphenylsilane, b.p. 55–60° (10 mm.), n_D^{20} 1.4865, which was identified by its infrared spectrum. The distillation residue upon treatment with benzene left 0.85 g. (9.5%) of insoluble diphenylstibinic acid, m.p. 282–286°. Addition of petroleum ether (b.p. 60–70°) to the benzene solution gave 0.2 g. (2%) of a colorless, crystalline compound, m.p. 170–172°, which is thought to be diphenylantimony trichloride.⁹

Relevant to the studies now reported are some experiments in progress on the reaction of triphenylsilyllithium with inorganic salts as well as with aryl derivatives like those described in this paper.

Acknowledgment. This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Miss M. Powers for the spectra.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

(8) W. La Coste and A. Michaelis, *Ann.*, **201**, 229, 231 (1880), report a melting point of 174° for diphenylarsinic acid and a melting point of 91–92° for bis(diphenylarsenic) oxide.

(9) H. Schmidt, *Ann.*, **421**, 236 (1920) reports a melting point of 285° for diphenylstibinic acid and a melting point of 175° for diphenylantimony trichloride.

Reaction of Xanthates with β -Propiolactone

MARTIN W. FARRAR

Received January 10, 1958

The reaction of β -propiolactone with a variety of nucleophilic reagents has been described during the last decade. An excellent review on this subject has appeared recently.¹ As described in this article, β -propiolactone can react either at the carbonyl carbon to produce derivatives of β -hydroxypropionic acid or at the β -carbon to produce β -carboxyethyl derivatives of the nucleophile. The course of

(6) (a) Experiments of J. J. Dietrich.

(7) S. I. Vol'fkovich, V. K. Kustov, and K. F. Koroteeva, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, **1954**, 5 [*Chem. Abstr.*, **49**, 6859 (1955)] report a boiling point of 272° (760 mm.) and 170° (3 mm.) for diphenylphosphine.

(1) H. E. Zaugg, *Org. Reactions*, **VIII**, 305 (1954).