triphenylsilylmetallic solutions give a positive Color Test I,[4] and can be titrated for the content of the organometallic reagent by the double titration method,[5] although these results do not appear to be entirely reliable. The reagents have been derivatized with trimethylchlorosilane to give yields of the known 1,1,1-triphenyl-2,2,2-trimethyldisilane (I) in excess of 70%.

Unfortunately the solutions of triphenylsilylmetallic reagent are not stable with time in ethylene glycol dimethyl ether. If the solution is stirred in contact with excess metal, the metal is slowly consumed, and the concentration of the triphenylsilylmetallic reagent decreases, as indicated by the yield of the derivative obtained. That this further reaction is probably due to reaction of the triphenylsilylmetallic reagent with the solvent is indicated by studies of Dr. K. M. Tai of this Laboratory who has found that solutions of the reagent, in absence of excess metal, likewise decrease in concentration, particularly if refluxed Such behavior is best explained on the basis of a reaction of the reagent with the solvent, probably resulting in the cleavage of the ether. These cleavage fragments must be such that they are capable of reacting with excess metal, if present, since several equivalents of the metal are consumed over a period of days if the reaction is permitted to proceed. It therefore appears highly advisable to use the triphenylsilylmetallic reagent as soon as prepared, in order to minimize further reaction.

Experimental[6]

Cleavage of Hexaphenyldisilane with Sodium-Potassium Alloy.—To a suspension of 5.0 g. (0.00965 mole) of hexaphenyldisilane in 10 ml. of sodium-dried, redistilled ethylene glycol dimethyl ether was added 2 ml. of 1:5 sodium-potassium alloy. A green color formed at the surface of the alloy and as the mixture was stirred, the color changed through yellow to brown; the material appeared to dissolve. After 15 minutes an additional 25 ml. of the ether was added. At the end of 2 hours all the material was in the dark brown solution with the excess alloy floating on top. A 5-ml. aliquot was removed and run into a solution of 0.5 ml. (0.0046 mole) of trimethylchlorosilane in 5 ml. of the ether. The color immediately was discharged, and a small amount of white precipitate was formed. After 5 minutes the reaction mixture was drowned in about 100 ml. of water, which was thrice extracted with ether. The extracts were dried over sodium sulfate. The ether was removed under reduced pressure and the resulting white solid was recrystallized from 95% ethanol to yield a total of 0.7 g. (77%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, m.p. 103–104°, identified by mixed melting point.

The main bulk of the solution gave a strong positive Color Test I and a 2-ml. aliquot, 1 hour after the reaction was apparently complete, indicated by the double titration method, that the concentration of the reagent was 59% of the theoretical. The main bulk of the solution was stirred at room temperature an additional 30 hours, by which time all the sodium-potassium alloy (originally present in excess) was consumed. A 5-ml. aliquot, derivatized as before with trimethylchlorosilane, gave only 0.35 g. (38%) of triphenyltrimethyldisilane.

Cleavage of Hexaphenyldisilane with Sodium.—To 5.0 g. (0.00965 mole) of hexaphenyldisilane in 5 ml. of ethylene glycol dimethyl ether was added 1.0 g. (0.043 g. atom) of sodium. After stirring for about 15 minutes the reaction started, as evidenced by the formation of a green color on the surface of the sodium. After 1 hour an additional 30 ml. of the ether was added. The time required for completion of the reaction, as evidenced by complete solution of the white solid, was considerably greater than when sodium-potassium alloy was employed, because the sodium agglomerated together into a large lump; almost 36 hours of stirring was required before all the hexaphenyldisilane had reacted. Titration of an aliquot indicated a 71% yield of reagent. A 10-ml. aliquot was added to 2.0 ml. of trimethylchlorosilane in 5 ml. of ethylene glycol dimethyl ether, and after 5 minutes this was drowned in water and worked up as before to give 1.25 g. (68%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, m.p. 101–103°. The main bulk of the solution gave a positive Color Test I.

Cleavage of Hexaphenyldisilane with Lithium.—To 5.0 g. (0.00965 mole) of hexaphenyldisilane in 5 ml. of ethylene glycol dimethyl ether was added 1.0 g. (0.144 g. atom) of lithium wire, cut into 2–3 mm. lengths. At the end of 30 minutes, the reaction definitely had started, for the suspension was dark brown, and the lithium was shiny. An additional 35 ml. of the ether was added. The supernatant liquid gave a strong positive Color Test I. After 4 hours of stirring, the dark brown reaction mixture was homogeneous, except for the excess unreacted lithium. A 20-ml. aliquot was added to 1.5 ml. of trimethylchlorosilane in 5 ml. of the ether. The color of the reagent disappeared immediately and the reaction mixture became warm. A white solid was precipitated. After 5 minutes, the reaction mixture was drowned in 200 ml. of water, which was thrice extracted with ether. The ether extracts were dried over sodium sulfate, the ether was removed under reduced pressure, and the residual solid was recrystallized from 95% ethanol to yield a total of 2.8 g. (72%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, m.p. 102–104°, identified by mixed melting point with an authentic sample.[3]

Attempted Cleavage of Hexaphenyldisilane with Magnesium.—To 5.0 g. (0.00965 mole) of hexaphenyldisilane in 10 ml. of ethylene glycol dimethyl ether was added 1.0 g (0.042 g. atom) of powdered magnesium. The grey suspension was stirred at room temperature for 3 days, during which time no change occurred, even when a trace (0.5 ml.) of methyl iodide was added, or when additional magnesium powder, decanted from a Grignard preparation of phenylmagnesium bromide, was introduced. The reaction mixture at the end of the 3 days was derivatized with trimethylchlorosilane, and then acidified. A white insoluble residue weighing 4.65 g. (93%) was filtered off, and identified as hexaphenyldisilane by its melting point of 360–362°, which was not depressed when the material was admixed with an authentic sample. No other product was isolated.

A repetition of this reaction was carried out with 1.0 g. (0.041 g. atom) of magnesium turnings, and 1.0 g. (0.00193 mole) of hexaphenyldisilane in 2 ml. of ethylene glycol dimethyl ether. The reaction was catalyzed with a trace of triphenylsilylpotassium, so that a positive Color Test I was obtained shortly after stirring was started, but the magnesium did not appear to be consumed after 1 day of stirring. An additional 10 ml. of solvent was added. The reaction mixture was refluxed for 24 hours, and then stirred at room temperature an additional 48 hours. It was then derivatized with trimethylchlorosilane and worked up as before. Only hexaphenyldisilane, m.p. 361–363°, was recovered in 97% yield.

A third attempt, identical to the above, except that the reaction mixture was treated several times over the first 24 hours with small amounts of triphenylsilylsodium in ethylene glycol dimethyl ether, and was then stirred at room temperature for an additional 48 hours, gave similar results to those above.

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Reaction of Cycloheptene Oxide with Formic Acid

BY ARTHUR C. COPE AND WARREN N. BAXTER

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Since the solvolysis of cyclooctene oxide with formic acid followed by saponification has been observed to form 1,4-cyclooctanediol by a "trans-

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(4) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(5) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

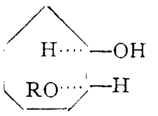
(6) Melting points are uncorrected. Organometallic reactions were carried out in a dry, oxygen-free nitrogen atmosphere.

annular reaction" in addition to the expected *trans*-1,2-cyclooctanediol,[1] it was of interest to determine what products were formed on solvolysis of cycloheptene oxide. Transannular oxidations of cyclodecene to 1,6-cyclodecanediol[2] and cyclononene to 1,5-cyclononanediol[3] have also been observed; Prelog, Schenker and Küng[3] state that only *trans*-1,2-cycloheptanediol is formed from cycloheptene and performic acid.

Addition of formic acid to cycloheptene oxide formed a mixture from which 42% of *trans*-1,2-cycloheptanediol monoformate (I) and 28.5% of 2,2′-dihydroxydicycloheptyl ether diformate (III) were isolated. Formation of the ether III was favored by a high concentration of cycloheptene oxide compared to formic acid, for reversal of the order of addition changed the yields to 60% of I and 19% of III. The structure of the monoformate I was established by saponification to the known *trans*-1,2-cycloheptanediol (II),[4] m.p. 62.1–63° (85%), and by preparation of an identical sample from II and formic acid in 88% yield. Presumably esterification of II proceeds only as far as formation of the monoformate I under the conditions employed because of hydrogen bonding between the hydroxyl and carbonyl groups of I.

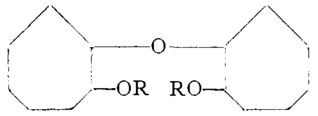
The structure of the ether III was established by saponification to 2,2′-dihydroxydicycloheptyl ether (IV) (73%), which was re-esterified with formic acid to III in 82% yield. An identical authentic sample of III was prepared in 59% yield from cycloheptene oxide and *trans*-1,2-cycloheptanediol in the presence of boron trifluoride.

No evidence was obtained for the presence of any product from the reaction of cycloheptene oxide and formic acid derived from a cycloheptanediol other than 1,2-cycloheptanediol. Accordingly, no chemical "transannular effect" appears to influence this reaction of cycloheptene oxide.



I, R = $-\overset{\displaystyle O}{\underset{}{\|}}\!\!$ → I, R = $-\mathrm{CH}(=\mathrm{O})$

II, R = H



III, R = $-\mathrm{CH}(=\mathrm{O})$

IV, R = H

Experimental[5]

Solvolysis of Cycloheptene Oxide with Formic Acid.—Cycloheptene oxide was prepared from 75 g. of cycloheptene and 220 ml. of commercial 40% peracetic acid to which 36 g. of sodium acetate trihydrate had been added (to neutralize the sulfuric acid present), by a procedure similar to the one used for preparation of cyclooctene oxide from cyclooctene (ref. 1, p. 5887); the yield was 69.5 g. (80%), b.p. 83–85° (50 mm.), n^{25}_{D} 1.4615–1.4620. A 40-g. sample of the cycloheptene oxide was heated at 100°, and 150 ml. of 87% formic acid was added dropwise with stirring during a period of 30 minutes, after which the solution was heated under reflux for 30 minutes. Excess formic acid was removed under reduced pressure and the residue was distilled through a semimicro column, yielding 23.5 g. (42%) of *trans*-1,2-cycloheptanediol monoformate (I), b.p. 81–83° (0.5 mm.), n^{25}_{D} 1.4632–1.4644. A redistilled analytical sample had b.p. 82° (0.5 mm.), n^{25}_{D} 1.4641, d^{25}_{4} 1.1202.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.96; H, 8.97.

2,2′-Dihydroxydicycloheptyl ether diformate (III) was isolated in a yield of 15.2 g. (28.5%) by fractionation of the residue from the distillation of I; b.p. 155–160° (0.3 mm.), n^{25}_{D} 1.4848–1.4861. A redistilled analytical sample had b.p. 155° (0.25 mm.), n^{25}_{D} 1.4861, d^{25}_{4} 1.0734.

Anal. Calcd. for $C_{16}H_{26}O_5$: C, 64.40; H, 8.78. Found: C, 64.34; H, 9.05.

In a reaction in which the order of addition was reversed, 20 g. of cycloheptene oxide was added during a period of 20 minutes to 50 ml. of 87% formic acid with cooling in an ice-bath, after which the mixture was heated on a steam-bath for 30 minutes; the yield of I was 17 g. (60%), while the yield of III was 5 g. (19%).

***trans*-1,2-Cycloheptanediol Monoformate (I).**—A 5-g. sample of I prepared by the method described above was saponified by stirring and heating on a steam-bath for 15 minutes with 100 ml. of 10% aqueous sodium hydroxide. The cooled solution was extracted with two 100-ml. portions of methylene chloride, which were dried over magnesium sulfate and concentrated, yielding 3.7 g. (91%) of II, m.p. 61.1–62.3°. Two recrystallizations from toluene yielded 3.5 g. (85%) of pure I, m.p. 62.1–63°, identical with a sample prepared in 87% yield by the procedure of ref. 4 (hydrolysis of 4.0 g. of cycloheptene oxide with 100 ml. of 0.1 *N* hydrochloric acid by heating under reflux for several hours).

A 3.5-g. sample of the glycol II was heated under reflux with 20 ml. of 87% formic acid for 1 hour, after which distillation yielded 3.75 g. (88%) of the monoformate I, identical in physical properties and infrared spectrum with the sample prepared from cycloheptene oxide and formic acid.

2,2′-Dihydroxydicycloheptyl Ether Diformate (III).—A 4.5-g. sample of III was heated under reflux on a steam-bath for 20 hours with 100 ml. of a 20% solution of potassium hydroxide in aqueous ethanol. The ethanol was removed at 35 mm., and the aqueous residue was extracted with two 100-ml. portions of methylene chloride. The extracts were dried over magnesium sulfate, concentrated, and the residue was crystallized from 30–60° petroleum ether. After two recrystallizations from this solvent, the yield of 2,2′-dihydroxydicycloheptyl ether (IV) was 2.67 g. (73%), m.p. 85.7–86.2°.

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 69.37; H, 10.81. Found: C, 69.24; H, 10.82.

A 2.0-g. sample of IV was heated under reflux with 15 ml. of 87% formic acid for 1 hour, after which distillation under reduced pressure yielded 2.0 g. (82%) of the diformate III with physical properties and an infrared spectrum identical with III obtained from cycloheptene oxide and formic acid.

2,2′-Dihydroxydicycloheptyl Ether (IV).—An authentic sample of IV was prepared by adding several drops of boron trifluoride etherate to a solution of 1.0 g. of the glycol II and 0.87 g. of cycloheptene oxide in 10 ml. of dry ether, and heating the solution under reflux for 3 days.[6] The solution was washed with dilute sodium hydroxide, dried over magnesium sulfate, concentrated, and the residue was crystallized from 30–60° petroleum ether. After recrystallization to a constant melting point of 85.5–86.1° the yield of IV was 1.1 g. (59%); this sample and IV obtained by saponification of III were identical (mixed m.p.).

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[1] A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

[2] V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

[3] V. Prelog, K. Schenker and W. Küng, *ibid.*, **36**, 471 (1953).

[4] J. Böeseken and H. Derx, *Rec. trav. chim.*, **40**, 529 (1921).

[5] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[6] Conditions similar to those used by A. A. Petrov, *J. Gen. Chem. U.S.S.R.*, **10**, 981 (1940); *C. A.*, **35**, 3603 (1941), for the reaction of cyclohexene oxide with alcohols.

Polarographic Reduction of Furfural

BY R. A. DAY, JR.

RECEIVED JULY 1, 1953

Data in the literature on the polarographic reduction of furfural are in disagreement. Korshunov