[Contribution from the Chemical Laboratories of Purdue University]

Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines. III. Reduction of Aromatic Compounds Containing Functional Groups

By Robert A. Benkeser, Charles Arnold, Jr., Rogers F. Lambert and Owen H. Thomas

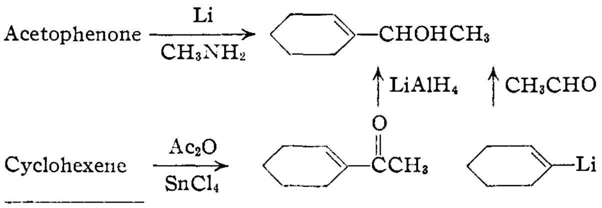
Received May 31, 1955

Representative types of substituted aromatic compounds have been subjected to reduction by lithium in methyl- and ethylamine. Reducible functional groups like olefins, ketones and nitriles are reduced in this system to saturated hydrocarbon chains, alcohols and primary amines. In most instances the attached benzene ring is concomitantly reduced to a monoölefin. Anisole and ketals structurally similar to allylic ethers undergo cleavage during reduction, but alkoxide ions and other ketals are stable under the conditions employed. Evidence is presented for the 1,4-nature of these reductions.

We have shown previously that aromatic hydrocarbons can be reduced conveniently to monoölefins by lithium dissolved in low molecular weight amines.[1] In fact so potent is this reducing medium that chemical reductions of isolated, non-terminal, olefinic centers can be effected by it.[2] We are now reporting an extension of this reaction to aromatic compounds containing reducible functional groups.

In order to test the effectiveness of this reagent on an aromatic side-chain containing an olefinic group, styrene was reduced with lithium in methylamine. A mixture, judged to contain 59% 1-ethylcyclohexene and 41% ethylcyclohexane, was obtained in one hour. Thus an aliphatic double bond conjugated with an aromatic group is rapidly reduced. In all of the amine reductions thus far studied, the position of the remaining double bond has been such as to form the most highly branched olefin. In the case of styrene this would correspond either to the double bond being *exo* to a six-membered ring (a situation demonstrated previously to be unstable[3]) or to the Δ^1-position. Presumably the final position of the double bond in these reductions, then, corresponds to the most thermodynamically stable olefin,[4] which in the case of a substituted six-membered ring is usually represented by an *endo* double bond adjacent to the substituent group.

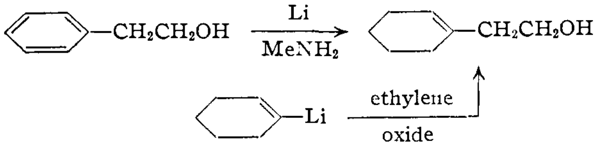
In order to test the effectiveness of this reducing medium in the reduction of carbonyl groups, acetophenone was reduced and found to produce 1-[1-cyclohexenyl-ethanol] in 65% yield. The proof of structure of the latter was accomplished by two independent syntheses. One of these involved the reaction of cyclohexenyl-lithium with acetaldehyde, and the other the reduction of acetylcyclohexene with lithium aluminum hydride. The α-naphthylurethan of the alcohol prepared by all three methods melted at 106–107°, and these samples showed no depression in melting point when mixed.



An attempt was made to reduce the ketal of acetophenone to determine whether protection of the carbonyl was afforded by the ketal linkage. However in this case 1-ethylcyclohexene (67%) was produced indicating fission had occurred. Likewise, when an attempt was made to protect the –OH group in benzyl alcohol by forming the tetrahydropyran derivative,[5] fission occurred and a mixture of 1-methylcyclohexene and methylcyclohexane was produced. Allyl ethers are known to be cleaved readily in the sodium–ammonia system,[6] and consequently the instability of the two aforementioned ketals is not surprising in view of their structure similarity to the allylic ethers.

It is interesting that no cleavage occurred in the reduction of acetophenone to 1-[1-cyclohexenyl-ethanol] since benzyl alcohols of this type do suffer loss of the –OH group in reductions with sodium or potassium in ammonia in the presence of an alcohol like ethanol or *t*-butyl alcohol.[7] The reason for the stability in this instance presumably lies in the highly basic nature of the amine system and the *absence* of a strong acid like ethanol. Both of these factors ensure that the alcohol produced is in the form of its alkoxide. Salt formation of this type is known to afford stability toward reductive fission.[6]

That ordinary alcohols can be reduced by this system was indicated by the successful reduction of 2-phenylethanol to 2-[1-cyclohexenyl]-ethanol in 67% yield by lithium in methylamine. Identification of the product was established by comparing it with an authentic sample made from cyclohexenyllithium and ethylene oxide.



In order to determine whether ketal linkages afford protection if removed sufficiently far from an aromatic ring, the reduction of benzylacetone diethyl ketal was undertaken. In this case a 77%

---

(1) (a) R. A. Benkeser, R. E. Robinson and H. Landesman, This Journal, **74**, 5669 (1952); (b) R. A. Benkeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, *ibid.*, **76**, 631 (1954); (c) **77**, 3230 (1955).

(2) (a) R. A. Benkeser, G. Schroll and D. M. Sauve, Abstracts of Papers Presented to the Division of Organic Chemistry of the American Chemical Society, Cincinnati, Ohio, March, 1955, p. 21N; (b) see also R. A. Benkeser, *et al.*, This Journal, **77**, 3378 (1955).

(3) H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

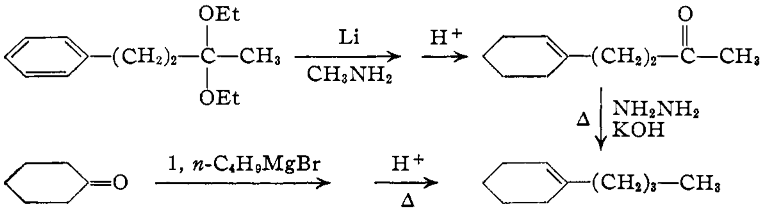
(4) For a similar conclusion in the ammonia system see D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954).

(5) W. E. Parham and E. L. Anderson, This Journal, **70**, 4187 (1948).

(6) A. J. Birch, *Quart. Revs.*, **4**, 69 (1950).

(7) A. J. Birch, *J. Proc. Roy. Soc. N. S. W.*, **83**, 245 (1950). See also A. R. Pinder and H. Smith, *J. Chem. Soc.*, 113 (1954).

yield of β-(1-cyclohexenyl)-ethyl methyl ketone was obtained after acid hydrolysis. Proof of structure was established by submitting the product to a modified Wolff–Kishner reduction. A nitrosyl chloride of this product showed it to be identical with an authentic sample of 1-butylcyclohexene.

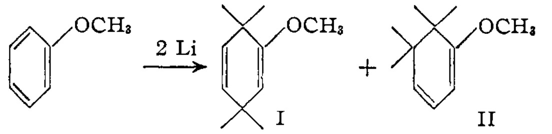


In order to substantiate the results of this experiment, the stability of the diethyl ketal of acetone was tested under the conditions of the reduction. It was observed that this ketal could be recovered virtually intact after five hours of reaction. It must be concluded, therefore, that ketal linkages, if sufficiently far removed from the aromatic ring, offer adequate carbonyl protection in this system.

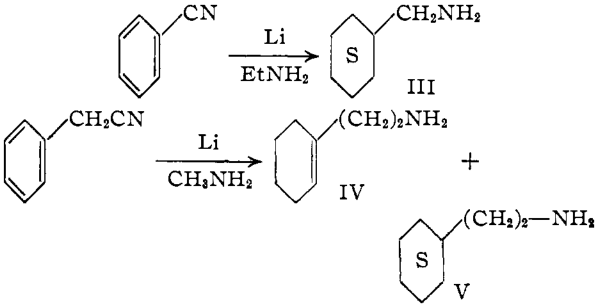
When phenol was reduced in methyl- or ethylamine a 96% conversion to cyclohexanone was realized if hydrolysis of the reaction mixture was carried out rapidly with only a trace of excess lithium remaining. Apparently, again, the reagent leaves one unreduced double bond, forming, in this case, a vinyl alcohol which immediately tautomerizes to cyclohexanone. When slow hydrolysis of the reaction mixture was carried out in the presence of a large excess of lithium (a modification of the usual reduction procedure) a considerable amount of cyclohexanol was isolated in addition to cyclohexanone. The former was derivatized as the α-naphthylurethan and the 3,5-dinitrobenzoate; the latter as the 2,4-dinitrophenylhydrazone. These derivatives gave undepressed mixed melting points with authentic samples.

Anisole in ethylamine, on the other hand, suffered fission and a mixture of phenol (48%) and cyclohexanone (40%) was produced. This is in agreement with results obtained in the sodium–ammonia system[8] wherein a 27% yield of phenol from anisole was realized.

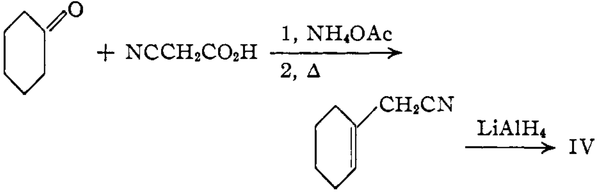
In order to gain an insight into the mechanism of these reductions, anisole was treated with only two equivalents of lithium in another experiment and the reaction was worked up quickly. In this case the product consisted of both 2,5-dihydroanisole (I) and the 2,3-dihydro isomer (II), in 53 and 47%, respectively, estimated from the ultraviolet absorption spectrum. Thus, even under the very favorable isomerizing conditions which prevailed in this experiment, a preponderance of the 1,4-reduction product was observed. There would seem to be little doubt that the *actual* amount of 1,4-addition was much greater than the 53% observed, since an unconjugated isomer like 2,5-dihydroanisole would certainly isomerize quickly to a conjugated system in the strongly basic medium which prevailed. It must be concluded that the initial attack in such a reduction is by a 1,4-mechanism. Since nucleophilic reagents like n-butyllithium routinely attack anisole at a position *ortho* to the ether link[9] it is not unreasonable that electrons should do likewise, the orientation in both of these instances being governed by the inductive effect (-I) of the methoxy group.



To extend this reduction to nitriles, benzonitrile and benzylnitrile were reduced with lithium in methyl- and ethylamine. Benzonitrile was found to yield in addition to tars, cyclohexanemethylamine (III) in 47% yield. From the reduction of benzylnitrile on the other hand, a mixture of β-(1-cyclohexenyl)-ethylamine (IV) (51%) and β-cyclohexylethylamine (V) was isolated.



Identification of these products was accomplished by independent syntheses. Thus III was produced by the lithium aluminum hydride reduction of cyclohexanecarboxamide. Compound V resulted from the catalytic reduction of β-phenylethylamine. β-(1-Cyclohexenyl)-ethylamine (IV) was prepared in a two-step operation as shown



Derivatives of the authentic samples prepared in this fashion did not depress the melting point of the compounds obtained from the reduction.

It should be pointed out that the reduction of benzonitrile represents the only instance in our experience thus far in which monoölefin was not the predominant product of the reaction. Two possible explanations occur to us at this time. It is possible that the electron-attracting properties of the nitrile group so depletes the electronic density of the ring that complete reduction is favored. Or more likely, perhaps, monoölefin was produced, but was lost in the polymeric tars which inevitably accompanied the reaction.

Experimental

General Reduction Procedure.—The experimental procedure used in most of the amine reductions was similar to

---

[8] A. J. Birch, *J. Chem. Soc.*, 102 (1947).

[9] H. Gilman and R. L. Bebb, This Journal, **61**, 109 (1939).

TABLE I

	Compound, mole	Li, g. atom	Solvent	Reacn. time, hr.	Products, % yield
1	Styrene, 0.15	1.2	CH_3NH_2	1	1-Ethylcyclohexene, 25, ethylcyclohexane, 18
2	Acetophenone, 0.15	0.9	CH_3NH_2	1	1-[1-Cyclohexenylethanol], 65
3	Acetophenone diethyl ketal, 0.11	.88	CH_3NH_2	1	1-Ethylcyclohexene, 67
4	Acetone diethyl ketal, 0.054	.14	CH_3NH_2	5	Starting material, 83
5	Benzylacetone diethyl ketal, 0.2	.82	CH_3NH_2	3	β-(1-Cyclohexenyl)-ethyl methyl ketone, 77
6	2-Benzoxytetrahydropyran, 0.14	.84	$EtNH_2$	1	1-Methylcyclohexene, methylcyclohexane, 68
7	2-Phenylethanol, 0.4	2	CH_3NH_2	1	2-[1-Cyclohexenyl]-ethanol, 67
8	Phenol, 0.2	1.6	$EtNH_2$	6	Cyclohexanone, 96, cyclohexanol
9	Anisole, 0.2	1.6	$EtNH_2$	6	Phenol, 48, cyclohexanone, 40
10	Benzyl cyanide, 0.1	0.82	$EtNH_2$	4.5	β-[1-Cyclohexenyl]-ethylamine, 50, β-cyclohexylethylamine
11	Benzonitrile, 0.1	1.2	$EtNH_2$	9	Cyclohexanemethylamine, 47

that employed previously unless otherwise indicated. (For a detailed account of this procedure the reader is referred to earlier papers in this series.[1c,2b]) Table I lists pertinent data regarding the reduction runs.

Styrene.—Distillation of the reduction product gave 7 g. (42%) of a colorless liquid boiling at 133–136°, n^{20}_{D} 1.4474. This refractive index corresponded to a mixture containing 59% of 1-ethylcyclohexene and 41% ethylcyclohexane. (It was shown previously that refractive indices of this mixture followed a linear relationship.[1c] A nitrosyl chloride of this liquid melted at 100–101° and was undepressed by an authentic specimen[10] prepared from 1-ethylcyclohexene.

Authentic 1-[1-Cyclohexenyl]-ethanol.—(A) Cyclohexenyllithium was prepared by the method of Braude and Coles[11] from 40 g. (0.34 mole) of 1-chlorocyclohexene and 4.78 g. (0.685 mole) of lithium. Twenty-two grams (0.50 mole) of acetaldehyde was added dropwise over a one-hour period to an ethereal solution of the lithium reagent. After it warmed to room temperature the mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride. After working up in the usual way, the product was distilled, giving 14 g. (41%) of an alcohol boiling at 86–87° (15 mm.), n^{20}_{D} 1.4842. *Anal.* Calcd. for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.15; H, 11.30. The α-naphthylurethan melted at 106–107° and did not depress the melting point of a corresponding derivative prepared from the lithium–amine reduction of acetophenone. *Anal.* Calcd. for $C_{19}H_{21}NO_2$: C, 77.28; H, 7.11; N, 4.74. Found: C, 77.12; H, 6.93; N, 5.09. (B) 1-Acetylcyclohexene[12] was reduced in 90% yield to 1-[1-cyclohexenyl]-ethanol by a standard lithium aluminum hydride reduction procedure.[13]

Acetophenone Diethyl Ketal[14] with Lithium in Methylamine.—The reduction product was distilled to give 8 g. (67%) of a liquid (1-ethylcyclohexene) boiling at 134–135°, n^{20}_{D} 1.4560. A nitrosyl chloride derivative melted at 101–102° alone, or when mixed with an authentic sample.[10]

Benzylacetone Diethyl Ketal[15] with Lithium in Methylamine.—The ether extracts from the reaction product were refluxed several hours with aqueous hydrochloric acid. The ether layer was separated, dried and the product distilled to give 23 g. (77%) of a ketone β-[1-cyclohexenyl]-ethyl methyl ketone boiling at 90–91° (7 mm.), n^{20}_{D} 1.4733, d^{20}_{4} 0.934; *MR* calcd. 45.72, *MR* found 45.76. The 2,4-dinitrophenylhydrazone melted at 90–91°. *Anal.* Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.02; N, 16.86. Found: C, 57.84; H, 6.04; N, 16.72.

Wolff–Kishner Reduction.—Twenty grams of the ketone obtained from the reduction of benzylacetone diethyl ketal was subjected to a modified Wolff–Kishner reduction.[16] There was obtained 13.8 g. (72%) of a liquid boiling at 178–179°, n^{20}_{D} 1.4568. A nitrosyl chloride of this liquid melted at 94–95° and was undepressed in a mixed melting point with an authentic specimen[17] of 1-butylcyclohexene.

2-Phenylethanol with Lithium in Methylamine.—Distillation of the product gave 35 g. (67%) of 2-[1-cyclohexenyl]-ethanol boiling at 74–75° (2 mm.), n^{20}_{D} 1.4878. The 3,5-dinitrobenzoate melted at 78–80° and did not depress the melting point of a sample prepared by the action of cyclohexenyllithium[11] on ethylene oxide. The compound was prepared also by the method of Cook and Dansi.[18] The melting point of the 3,5-dinitrobenzoate prepared by the latter method agreed with the other two samples.

2-Benzoxytetrahydropyran[19] with Lithium in Ethylamine.—The reduction product, after acid hydrolysis, boiled at 103–107°, n^{20}_{D} 1.4432. The material dissolved almost completely in concentrated sulfuric acid and absorbed bromine readily. A nitrosyl chloride of this material melted at 93–94° and a 2,4-dinitrobenzenesulfenyl chloride at 138–139°. Both of these melting points agree with those reported for 1-methylcyclohexene.[20] The incomplete solubility in sulfuric acid, and the lowered refractive index (authentic 1-methylcyclohexene, n^{20}_{D} 1.4500) indicated the product was contaminated with methylcyclohexane (n^{20}_{D} 1.4230).

Phenol with Lithium in Ethylamine (Modified Procedure).—After 6 hours at the reflux temperature of ethylamine, the unreacted lithium was not removed but, instead, 20 g. of absolute ethanol was added slowly over a two-hour period. The product, after isolation in the normal manner, boiled at 160–164°, 14 g., n^{20}_{D} 1.4618. Based on 2,4-dinitrophenylhydrazone this was adjudged to contain 18% of mixed ketones. The remaining 82% was cyclohexanol. Unreacted phenol (16%) was also recovered as the 2,4,6-tribromo derivative. The cyclohexanol was identified as the α-naphthylurethan (126–127°) and the 3,5-dinitrobenzoate (112°). These also were undepressed by authentic samples.

Anisole with Lithium in Ethylamine.—After carrying out the reduction and hydrolysis in the usual manner, the aqueous layer was acidified with hydrochloric acid, and then bromine was added slowly until the solution retained a yellow color. Thirty-one grams of 2,4,6-tribromophenol was isolated (m.p. 94°), indicating that 48% of the anisole was converted to phenol. There was isolated by distillation of the ether layer, 7.3 g. of product, b.p. 156–158°, n^{20}_{D} 1.4516. A 2,4-dinitrophenylhydrazine derivative of this material melted at 161–162° and was not depressed by authentic 2,4-dinitrophenylhydrazone of cyclohexanone. The latter product was thus formed in 40% yield.

Rapid Reduction of Anisole Using Two Equivalents of Lithium.—Finely cut lithium (2.8 g., 0.4 g. atom) was added over a 15-minute period to an ethylamine solution containing 12.6 g. (0.2 mole) of anisole. The amine was evaporated off as soon as all the lithium had disappeared. Hydrolysis and isolation of products were accomplished in

---

(10) B. A. Kazanskii and N. F. Glushnev, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 642 (1938); *C. A.*, **33**, 1280 (1939).

(11) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950).

(12) E. E. Royals and C. M. Hendry, *J. Org. Chem.*, **15**, 1147 (1950).

(13) W. G. Brown, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1951, VI, p. 469.

(14) Prepared by the method of G. J. Pfeiffer and H. Adkins, THIS JOURNAL, **53**, 1048 (1931).

(15) This material again was prepared by the method of ref. 14. Our starting ketal had the following physical constants: b.p. 119–120°, n^{20}_{D} 1.4782; *MR*D calcd. 66.41, *MR*D found 66.83.

(16) See Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(17) F. K. Signaigo and P. L. Cramer, *ibid.*, **55**, 3326 (1933); W. M. Dehn and K. E. Jackson, *ibid.*, **55**, 4284 (1933); S. I. Khromov and Z. A. Rumyantseva, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 363 (1945).

(18) J. W. Cook and A. Dansi, *J. Chem. Soc.*, 500 (1935).

(19) Prepared according to the procedure given in reference 5. Our material boiled at 174–177° and had an index of refraction of 1.5220 (n^{20}_{D}).

(20) E. Evans, *Ann.*, **360**, 50 (1907); N. Kharasch and J. Buess, THIS JOURNAL, **71**, 2724 (1948).

the usual manner. The product was distilled through a modified Widmer column and a 3-g. cut boiling in the range 148–149° was collected (n^{20}D 1.4805). This material corresponded in physical constants to 2,5-dihydroanisole (b.p. 148–149°, n^{25}D 1.4782) reported by Wilds.[21] A 2,4-dinitrophenylhydrazone of this cut using the Wilds procedure[21] at 0° melted at 132–133° and gave no melting point depression with authentic 3-cyclohexanone 2,4-dinitrophenylhydrazone. An estimated minimum purity of 90% was obtained by determining the yield of this derivative. Since both 2,3- and 2,5-dihydroanisole will give this hydrazone, ultraviolet absorption was used to estimate the percentage of these two isomers. The results (Cary recording spectrophotometer) showed $\lambda_{\max}^{\text{abs EtOH}}$ 268 mμ (2000) for the 2,3-dihydroanisole, indicating 47% to be this product and 53% therefore the 2,5-isomer.[22]

Benzyl Cyanide[23] with Lithium in Ethylamine.—Distillation of this reduction product gave 7 g. (55%) of liquid boiling 49–52° (2 mm.), n^{20}D 1.4851 to 1.4868. Using authentic samples of β-(1-cyclohexenyl)-ethylamine and β-cyclohexylethylamine it was observed that the percentage composition *vs.* refractive index relationship was practically linear. Employing this relationship it was adjudged that the above mixture comprised about 90% β-(1-cyclohexenyl)-ethylamine and 10% β-cyclohexylethylamine.

Authentic β-(1-Cyclohexenyl)-ethylamine.—The procedure of Schneider and Hellerbach[24] was followed. The final product boiled at 50–51° (1 mm.), n^{18}D 1.4882. The hydrochloride melted at 162–165° (reported 160–163°).[24] Various derivatives of this authentic sample were prepared, such as the picrate (174–175°), *p*-nitrobenzamide (124–125°), and phenylthiourea (121–122°). The identical derivatives were obtained from the reduction product and these did not depress the melting points of the authentic specimens. *Anal.* Calcd. for $C_{14}H_{18}N_4O_7$ (picrate): C, 47.45; H, 5.08. Found: C, 47.65; H, 5.03. Calcd. for $C_{15}H_{18}N_2O_3$ (*p*-nitrobenzamide): C, 65.69; H, 6.57. Found: C, 65.70; H, 6.48. Calcd. for $C_{15}H_{20}N_2S$ (thiourea): C, 69.23; H, 7.61; N, 10.76. Found: C, 69.33; H, 7.59; N, 10.99.

Authentic β-Cyclohexylethylamine.—Prepared by the catalytic reduction of β-phenylethylamine.[25] The product was obtained in 66% yield boiling at 180–183°, n^{20}D 1.4649. The presence of this material in the reduction product was established by infrared spectra.

Benzonitrile with Lithium in Ethylamine.—Fractionation of the reduction product gave 5.4 g. (47%) of a liquid boiling at 162–164°, n^{20}D 1.4632. The melting points of the benzamide (105–106°) and picrate (184–185°) agreed well with the literature values[26] for cyclohexanemethylamine.

Authentic Cyclohexanemethylamine.—This product was prepared by the sequence: cyclohexanecarboxylic acid → cyclohexanecarbonyl chloride → cyclohexanecarboxamide → cyclohexanemethylamine. Each step was accomplished employing classical procedures. The final step was carried out with lithium aluminum hydride. The authentic material boiled at 161–162° (747 mm.), n^{20}D 1.4630. The phenylthiourea melting at 128–129° and the picrate at 185–186° were not depressed when admixed with the lithium–amine reduction product.

Acknowledgment.—The authors are grateful to the Eli Lilly Co. and the Ethyl Corporation whose financial assistance in the form of free-grant fellowships made this research possible.

---

[21] A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5360 (1953).

[22] A. J. Birch [*J. Chem. Soc.*, 1551 (1950)] has reported $\lambda_{\max}^{\text{abs EtOH}}$ 268 mμ (4270) for 2,3-dihydroanisole.

[23] R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 107.

[24] O. Schneider and J. Hellerbach, *Helv. Chim. Acta*, **33**, 1437 (1950).

[25] B. L. Zenitz, E. B. Macks and M. L. Moore, THIS JOURNAL, **69**, 1117 (1947).

[26] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 178; I. M. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, England, 1943, p. 167.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Partial Hydrolysis of Methyltri-*n*-propoxysilane, Methyltriisopropoxysilane and Methyltri-*n*-butoxysilane

BY M. M. SPRUNG AND F. O. GUENTHER

RECEIVED MAY 13, 1955

The hydrolysis of methyltri-*n*-propoxysilane, methyltriisopropoxysilane or methyltri-*n*-butoxysilane in benzene solution with an acid catalyst proceeds with difficulty and leads mainly to resinous products. In isobutyl methyl ketone, low yields of distillable products were obtained. Octamethyloctasilsesquioxane $(CH_3SiO_{1.5})_8$, was obtained in about 10% yield during the hydrolysis of methyltri-*n*-butoxysilane. The molecular weight was established from the vapor density above the sublimation temperature. A crystalline polycyclosiloxane containing a single functional group (butoxy) was also isolated from the hydrolysis products of methyltri-*n*-butoxysilane.

Introduction

The sensitivity to hydrolysis of $MeSi(OMe)_3$, $MeSi(OEt)_3$ and $EtSi(OEt)_3$ decreases markedly in that order.[1] Methyltripropoxy-, isopropoxy- and butoxysilanes are difficult to hydrolyze. However, when some of the heavy alkoxy groups are removed, the intermediate hydrolysis products are very susceptible to further attack and rapidly condense to resinous products. Yields of lower molecular weight hydrolysis products are accordingly very poor.

Methyltri-*n*-propoxysilane was recovered unchanged after heating for several hours in benzene solution with three molar equivalents of water, 0.09 *N* in hydrochloric acid. With the addition, at the start, of some *n*-propyl alcohol to provide a more favorable reaction medium a low yield of distillable partial hydrolysis products was obtained. The chief components were cyclic tetra- and pentasiloxanes having three to four residual propoxy groups per molecule. A redistilled mid-cut had the composition of a tripropoxybicyclopentasiloxane.[2] The major product was, however, a gelled resin that retained, on the average, one propoxy group for each three siloxane units. The only product obtained from methyltriisopropoxysilane (in benzene with 3 moles of water, 0.09 *N* in HCl) was a gelled

---

[1] (a) M. M. Sprung and F. O. Guenther, THIS JOURNAL, **77**, 3990 (1955); (b) **77**, 3996 (1955); (c) **77**, 4173 (1955). The reader is referred particularly to the first of these papers for a survey of earlier literature.

[2] The major component would be 3,9-epoxy-1,3,5,7,9-pentamethyl-1,5,7-tri-*n*-propoxy*cyclo*pentasiloxane. No simple isomeric modification of this structure would seem possible.