chromatography on a 1 × 24 cm. neutral alumina (Fisher Scientific Co. no. A540) column and provided a 22% yield (based on the starting hydrazone) of benzophenone phenylhydrazone, m.p. 134–137° (lit.[22] m.p. 137°).

B. Reverse Addition, Approximate 1:1 Ratio of Reactants.—A solution of 8.39 g. (0.018 mole) of lead tetraacetate in 60 ml. of methylene chloride was added to a cooled, stirred solution of 5.72 g. (0.02 mole) of benzophenone N-methyl-N-phenylhydrazone[23] in 50 ml. of methylene chloride over a period of 1.5 hr. keeping the temperature between 0 and 5°. Turbidity developed almost immediately, followed by the formation of a white precipitate. The reaction mixture was stirred at room temperature for 1 hr. The solvent and all volatile products were then evaporated under reduced pressure and condensed in a trap cooled by a Dry Ice–trichloroethylene mixture. The condensate gave a positive Tollens test. Extraction with water and treatment of the extract with 2,4-dinitrophenylhydrazine reagent[22] gave formaldehyde 2,4-dinitrophenylhydrazone, m.p. 163–164°.

The residue left after removal of the volatile material was washed with benzene to separate the organic fraction from the lead diacetate. In order to remove acetic acid, the benzene solution was chromatographed on a 1 × 24 cm. neutral alumina (Fisher Scientific Co. no. A540) column and developed with benzene. The yellow eluate was collected and concentrated by vacuum evaporation. The residue weighed 5.90 g. and crystallized on standing. The ultraviolet spectrum of this material showed absorption maxima at 240, 300, and 340 mμ, characteristic of benzophenone phenylhydrazone. This residue was washed with three 15-ml. portions of cold pentane to leave 3.25 g. (71%, based on lead tetraacetate) of benzophenone phenylhydrazone, m.p. 132–135° (lit.[24] m.p. 137°).

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[23] This procedure was not extended to other hydrazones.

[24] Reference 14, p. 318.

Reduction of Ketones with Triisobutylaluminum. The Stereochemistry of Reduction of 3,3,5-Trimethylcyclohexanone

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The reduction of 3,3,5-trimethylcyclohexanone (dihydroisophorone) with triisobutylaluminum yields *trans*-3,3,5-trimethylcyclohexanol as the predominant epimer in an initially kinetically controlled process. The initial reduction step is followed, in the presence of excess ketone, by epimerization to the more stable *cis*-3,3,5-trimethylcyclohexanol (equatorial epimer). When cyclohexanone is added to the reduction mixture the 3,3,5-trimethylcyclohexanol (aluminum salt) is oxidized back to dihydroisophorone. The mechanism and stoichiometry of the reduction is discussed in relation to the above observations.

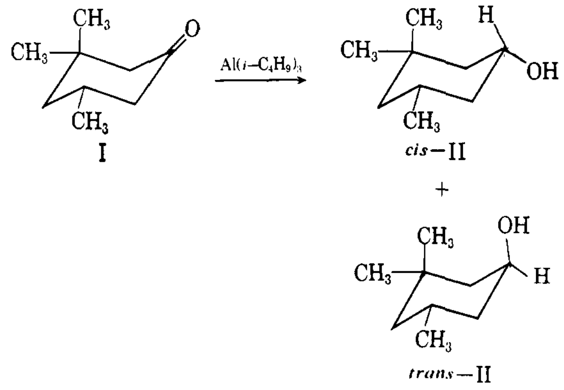
The reactivity and scope of reductions of organic compounds with aluminum alkyls[1] and dialkylaluminum hydrides[1,2] is reminiscent of reductions with lithium aluminum hydride. There are, however, several interesting aspects of the reduction of ketones with triisobutylaluminum in particular. Although this reagent is highly reactive toward the carbonyl group, there exists no aluminum–hydrogen bond analogous to that present in lithium aluminum hydride. Furthermore, in the reduction of ketones with triisobutylaluminum (and also with diisobutylaluminum hydride), only one of the possible three reducing equivalents is utilized[1] (equation 1). After the reaction of equimolar amounts of the reagent with ketone, the product, presumably diisobutylaluminum alkoxide, can apparently no longer function as a reducing agent.

$$R_2C{=}O + Al(i\text{-}C_4H_9)_3 \longrightarrow R_2CHO\text{-}Al(i\text{-}C_4H_9)_2 + (CH_3)_2C{=}CH_2 \quad (1)$$

This report describes the results of experiments which were carried out to elucidate the stereospecificity of reduction of ketones with triisobutylaluminum. The system chosen for initial study was 3,3,5-trimethylcyclohexanone (dihydroisophorone) (I), the reduction of which may lead to two epimeric alcohols, *cis*-3,3,5-trimethylcyclohexanol (*cis*-II) and *trans*-3,3,5-trimethylcyclohexanol (*trans*-II), the equatorial and axial epimers, respectively (Chart I).

CHART I

Reduction of dihydroisophorone to epimeric alcohols



The reduction of I with triisobutylaluminum in benzene at 42° was found to be highly stereospecific. However, either *cis*-II or *trans*-II could be formed as the predominant product depending on the reaction conditions. When a solution of I in benzene was added to triisobutylaluminum and an aliquot was removed while the aluminum alkyl was in excess, the product was found to consist of 96% *trans*-II and 4% *cis*-II by gas chromatographic analysis, with no detectable amount of ketone. If, on the other hand, excess ketone was present, the composition of the reaction mixture changed from predominant *trans*-II to exclusively *cis*-II.

Eliel and Rerick had previously shown that the reduction of 4-*t*-butylcyclohexanone with a reagent consisting of ethereal aluminum chloride–lithium aluminum hydride in the ratio of 3:1, or preferably 4:1, led to equilibration of the *cis* and *trans* aluminum alcoholates in the presence of excess ketone.[3] The equilibrium lay overwhelmingly in favor of the *trans* (equatorial) iso-

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[1] (a) K. Ziegler, British Patent 803,178 (1958); (b) K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed. Reinhold Publishing Corp., New York, N. Y., 1960, pp. 236–238; (c) K. Ziegler, K. Schneider, and J. Schneider, *Ann.*, **623**, 9 (1959).

[2] A. E. G. Miller, J. W. Biss, and L. H. Schwartzman, *J. Org. Chem.*, **24**, 627 (1959).

[3] (a) E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960); (b) E. L. Eliel, *Record Chem. Prog.*, **22**, 129 (1961).

mer. The effective reducing agent in the 3:1 or 4:1 aluminum chloride–lithium aluminum hydride reagent is believed to be dichloroaluminum hydride[3,4] (equation 2). It was subsequently shown that I can be reduced

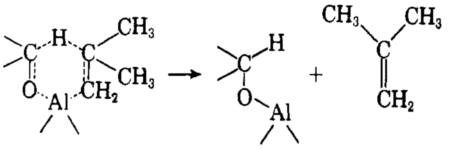
$$LiAlH_4 + 3AlCl_3 \longrightarrow LiCl + 4AlHCl_2 \qquad (2)$$

with this "mixed hydride" reagent under kinetically controlled conditions to give 85% *trans*-II, or under thermodynamically controlled conditions to give essentially 100% *cis*-II.[5] These equilibrations with dichloroaluminum hydride involve the aluminum salts of the alcohols rather than the free alcohols.[3] It is reasonable to suppose that the diisobutylaluminum alcoholates of *cis*- and *trans*-II undergo equilibration in a manner analogous to that found for the 3:1 aluminum chloride–lithium aluminum hydride reagent. The resultant equilibrium composition, as expected,[3,5] lies entirely on the side of the more stable equatorial epimer.

A plausible mechanism for the triisobutylaluminum reduction of ketones involves an initial coordination of the trivalent electrophilic reagent with the carbonyl group followed by an intramolecular hydride transfer (Chart II). This mechanism involving a cyclic intramolecular hydride transfer from the β-carbon of the isobutyl group is seen to be analogous to that involved in the Meerwein–Ponndorf–Verley reduction[6] and in reductions involving Grignard reagents[6e,f] and dialkylmagnesium compounds.[6e] The reduction of carbonyl compounds with triethylaluminum reported by Meerwein and co-workers[7] has been viewed as a particular case of the Meerwein–Ponndorf–Verley reduction.[2,8] In the triisobutylaluminum reduction of ketones, the ease of hydride transfer from the β-carbon of the reagent to the carbonyl carbon may be attributed to enhanced electron deficiency of the carbonyl carbon due to coordination of the oxygen by the aluminum species,[6a,9] partial synchronous formation of the isobutylene double bond, and to the fact that the migration origin is a tertiary carbon.

Chart II

Cyclic mechanism for reduction of ketones with triisobutylaluminum



There is another mechanism that may be considered for the reduction with triisobutylaluminum. This involves the possibility of the actual reducing agent being diisobutylaluminum hydride, formed in small amounts from triisobutylaluminum (equation 3).

$$Al(i\text{-}C_4H_9)_3 \rightleftharpoons Al(i\text{-}C_4H_9)_2H + i\text{-}C_4H_8 \qquad (3)$$

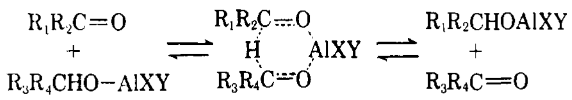
At present this possibility cannot be ruled out. However, experiments are now being carried out which involve a comparison of the stereochemical result of the kinetically controlled reduction of several ketones with both triisobutylaluminum and diisobutylaluminum hydride. These experiments may help determine whether the actual reducing species in the first reduction stage is triisobutylaluminum or diisobutylaluminum hydride.

It is interesting to note the very high proportion of *trans*-II formed in the kinetically controlled phase of the reduction of I with triisobutylaluminum. The hydride transfer occurs from the less hindered equatorial side of the molecule. This may be due to steric interference of the 3-axial methyl group with the isobutyl methyl groups in the alternative transition state leading to *cis*-alcoholate.

The observed equilibration of the aluminum alcoholates of *cis*- and *trans*-II undoubtedly represents another modification of the Oppenauer and Meerwein–Ponndorf–Verley oxidation–reduction[10] scheme (Chart III). In the conventional Meerwein–Ponndorf–Verley reduction,[11] X = Y = alkoxide.[12]

Chart III

Oxidation–reduction scheme for ketones–aluminum alcoholate reagents



X = Y = isobutyl

The equilibrations observed with the 3:1 aluminum chloride–lithium aluminum hydride reagent[3] may involve a similar pathway where X = Y = Cl.

It has been established[1] that only one isobutyl group of the aluminum alkyl is utilized in the reduction of ketones.[13] The diisobutylaluminum alkoxide continues to function as a reducing agent with hydride transfer now originating from the alkoxide group. This leads to the usual oxidation–reduction scheme already described, and therefore to equilibration of the epimeric 3,3,5-trimethylcyclohexanol alcoholates. The inability of the isobutyl group to compete with the alkoxide group in the hydride transfer may be due to the replacement of a methylene grouping with an oxygen which can better stabilize the developing positive charge on the adjacent carbon atom (Chart IV).[14]

As a consequence of the oxidation–reduction mechanism, one should observe upon the introduction of a different ketone into the mixture of triisobutylaluminum

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[4] E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 460 (1951).

[5] H. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

[6] (a) R. B. Woodward, N. L. Wendler, and F. J. Brutschy, *ibid.*, **67**, 1425 (1945); (b) L. M. Jackman and J. A. Mills, *Nature*, **164**, 789 (1949); (c) R. E. Lutz and J. S. Gillespie, Jr., *J. Am. Chem. Soc.*, **72**, 344 (1950); (d) W. von E. Doering and R. W. Young, *ibid.*, **72**, 631 (1950); (e) E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., Inc., New York, N. Y., 1959, pp. 544–546; (f) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 72–73.

[7] H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. Chem.*, **147**, 226 (1937).

[8] It has been shown (ref. 1) that the successful use of triethylaluminum as a reducing agent is much more restricted in scope than that of triisobutylaluminum.

[9] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 352; see also ref. 6e, pp. 548–549.

[10] C. Djerassi, *Org. Reactions*, **6**, 207 (1951).

[11] A. L. Wilds, *ibid.*, **2**, 178 (1944).

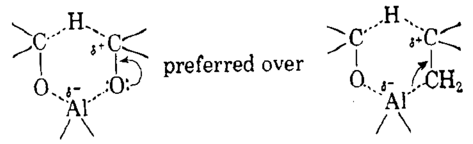
[12] For a reduction where X = isopropoxide, Y = Cl see G. Gal, G. Tokar, and I. Simonyi, *Acta Chim. Acad. Sci. Hung.*, **7**, 421 (1955), and G. Gal and E. Krasznai, *ibid.*, **15**, 211 (1958); **16**, 369 (1958).

[13] Ziegler has reported (ref. 1a) that 1 mole of triisobutylaluminum can reduce 3 moles of an aldehyde of the benzaldehyde or cinnamaldehyde type.

[14] It is conceivable, as mentioned earlier, that the first reduction stage may not involve an isobutyl group, but rather an Al–H bond. If this is so, then the diisobutylaluminum alkoxide formed in the first reduction stage cannot provide an Al–H bond. In any case, it is clear that after the initial kinetically controlled reduction step, each subsequent reduction is accompanied by an oxidation of the alcoholate, thereby leading to equilibration of the epimeric alcoholates.

CHART IV

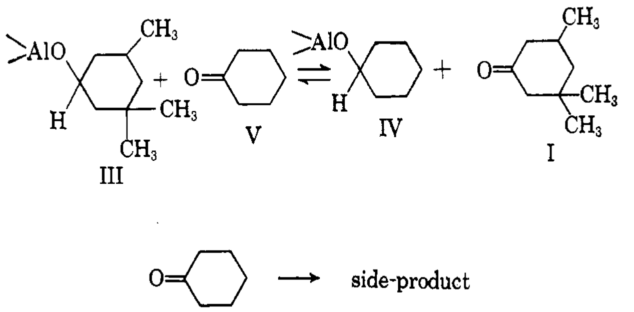
Transition states for hydride transfer



and dihydroisophorone, a reduction of the added ketone and a corresponding oxidation of the initial alcoholate to dihydroisophorone.[15,16] Dihydroisophorone was reduced with an equimolar amount of triisobutylaluminum in benzene. Sampling of the reduction mixture showed that the composition was 3% unreduced ketone I and 97% 3,3,5-trimethylcyclohexyl alcoholate. An equimolar amount of cyclohexanone was then added, and aliquots were removed at various intervals, quenched in dilute acid, and the composition of the mixtures determined by gas chromatography. The amount of cyclohexanone was found to diminish continually with time, and cyclohexanol was formed. The proportion of dihydroisophorone (I) (relative to the corresponding alcoholate) increased from 3 to 85% but then decreased. During the run the ratio of 3,3,5-trimethylcyclohexyl species (ketone + alcohol) to cyclohexyl species (ketone + alcohol) increased from 1.3 to 3.9 as judged from the relative areas of the gas chromatographic peaks. This indicated a preferential loss of cyclohexyl species, probably cyclohexanone.[17] The equilibrium involved is shown in Chart V.

CHART V

Equilibrium involving ketones and aluminum alcoholates



Initially, the effect of added cyclohexanone is to increase the amount of I (relative to its corresponding alcoholate). However, loss of cyclohexanone due to the formation of side product causes the extent of I formation to reach a maximum and then to reverse. During the reaction, the *cis–trans*-II mixture was isomerized to *cis*-II as expected. The extent to which I was formed (from the initial value of 3% to a maximum value of 85%) is indicative of the much greater preference for the formation of species similar to IV rather than III.

Experimental

Dihydroisophorone (I).—Dihydroisophorone was prepared by the oxidation of commercial 3,3,5-trimethylcyclohexanol as previously described[18] and had b.p. 62–64° (8 mm.); n^{20}_{D} 1.4462 (lit.[18] b.p. 73–74° (14 mm.); n^{20}_{D} 1.4461). A gas chromatogram on a Carbowax 20M column indicated only a trace of *cis*-alcohol.

Triisobutylaluminum.—Commercial triisobutylaluminum was distilled at 0.5 mm. and the solutions were prepared in dry benzene and stored in a drybox.

Reduction of I with Triisobutylaluminum.—A micro resin flask was equipped with a reflux condenser, stirrer, thermometer, and an equilibrated addition funnel. The apparatus was thermostated at 41° and was kept under dry nitrogen during the reaction. The reaction flask was charged by syringe with 40 ml. of 0.786 *M* triisobutylaluminum (0.03 mole) in benzene. To the stirred solution was added 26 ml. of a benzene solution of I (5.608 g., 0.04 mole) for 33 min. At appropriate times 5-ml. aliquots were removed by syringe and quenched in 10 ml. of cold 5% hydrochloric acid. The first aliquot was removed before addition of the ketone was completed. The benzene layer of each aliquot was separated by syringe and analyzed directly by gas chromatography on a Carbowax 20M column at 153°. The pure *cis*- and *trans*-epimeric alcohols (*cis*- and *trans*-II) were kindly provided by Dr. Ernest L. Eliel of the University of Notre Dame. The data obtained are shown in Table I. During this run the reactants were concentrated to some extent by partial evaporation of solvent.

TABLE I

REDUCTION OF DIHYDROISOPHORONE WITH TRIISOBUTYLALUMINUM

Aliquot no.	Time, hr.	% *trans*-II	% *cis*-II	% unreduced I[a]
1	0.13	96.2	3.8	0.0
2	2.0	82.7	17.3	32.5
3	4.0	78.6	21.4	32.3
4	8.0	70.5	29.5	32.3
5	11.7	63.3	36.7	32.0
6	23.0	27.7	72.3	31.3
7	31.0	0.3	99.7	30.7

[a] Percentage of total alcohol + ketone.

In another reduction 16.8 g. (0.12 mole) of I in 27 ml. of benzene solution was added at room temperature to 40 ml. of 1 *M* triisobutylaluminum (0.04 mole) in benzene. The temperature (*ca.* 25°) rose to 55° during the addition and gas evolution occurred. After stirring at room temperature for 48 hr., the reaction mixture was decomposed with water followed by 10% sulfuric acid. After extraction with ether, the product solution was washed with salt solution and dried over anhydrous magnesium sulfate. Solvent was removed by distillation through a small Vigreux column, and the residue was distilled to give 14.8 g. of material, b.p. 58–69^c at 4 mm. A residue of 0.7 g. remained. The distillate represents a material recovery of 88%. Gas chromatographic analysis of the distillate showed 29.6% alcohol and 70.4% ketone. On the basis of one reducing equivalent per mole of triisobutylaluminum this represents 90% of the theoretical amount of reduction. The composition of the alcohols was 56.8% *trans*-II and 43.2% *cis*-II.

Reduction of I with Addition of Cyclohexanone.—A benzene solution of I (5.615 g., 0.04 mole, in 25 ml. of solution) was added to 40 ml. of 1 *M* triisobutylaluminum (0.04 mole) in benzene. The apparatus was thermostated at 30.5°. The reaction was conducted under an atmosphere of nitrogen. The first 5-ml. aliquot was quenched after the addition of I was complete. A solution of cyclohexanone (3.927 g., 0.04 mole) in 15 ml. of benzene solution was then added. The second aliquot was removed immediately after addition of the cyclohexanone. Aliquots were then removed and quenched and analyzed as described previously. The results are shown in Tables II and III.

A duplicate experiment gave completely analogous results.

Cyclohexanone was reduced with triisobutylaluminum in a separate experiment. Distillation of the product yielded a high boiling fraction (b.p. 51–55° at <1 mm.). The material was identified as 2-cyclohexylidene cyclohexanone. The semicarbazone was prepared, m.p. 172–174° (lit.[19] m.p. 175–177°).

Anal.[20] Calcd. for $C_{13}H_{21}N_3O$: C, 66.34; H, 8.99; N, 17.85. Found: C, 66.23; H, 8.88; N, 18.00.

During the reduction of cyclohexanone a strong yellow coloration developed. A similar color change did not occur in the

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[15] Unless the added ketone is particularly unreactive, for example, being highly hindered.

[16] Eliel and Rerick (ref. 3a) had observed that the addition of acetone following the reduction of 4-*t*-butylcyclohexanone with dichloroaluminum hydride regenerated 4-*t*-butylcyclohexanone.

[17] 2-Cyclohexylidenecyclohexanone was isolated from the reduction of cyclohexanone with triisobutylaluminum in a separate experiment.

[18] E. L. Eliel and H. Haubenstock, *J. Org. Chem.*, **26**, 3504 (1961).

[19] C. Mannich, *Ber.*, **40**, 157 (1907).

[20] Microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Table II

Effect of Added Cyclohexanone

Aliquot	Time, hr.	% I	% II[a]	% V[b]	% IV[c]
1	...	3.0	97.0	...	..
2	0.0[d]	7.0	93.0	*ca.* 100	Trace
3	2.8	49.4	50.6	62.3	37.7
4	16.8	84.5	15.5[e]	26.7	73.3
5	24.9	79.9	20.1	15.7	84.3
6	48.0	68.9	31.1	17.1	82.9
7	165.0	40.7	59.3	11.3	88.7

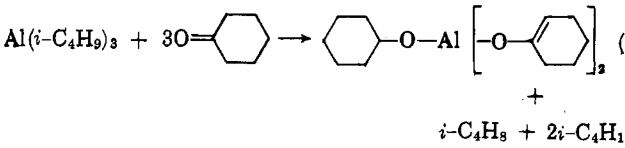
[a] *cis*- + *trans*-II. I and II are normalized to 100%. [b] V = cyclohexanone. [c] IV = cyclohexanol. V + IV are normalized to 100%. [d] Zero time taken as end of cyclohexanone addition. [e] The fourth and subsequent aliquots showed no detectable amount of *trans*-II.

Table III

Variation of C_9/C_6 Ratio

Aliquot	2	3	4	5	6	7
C_9/C_6 ratio[a]	1.3	1.5	1.5	1.9	2.0	3.9

[a] $C_9 = I + II$; C_6 = cyclohexanone + cyclohexanol. C_9/C_6 was determined by ratio of peak areas.


(4)

reduction of I under similar conditions, nor was any condensation (aldol) product isolated.

Ziegler, *et al.*,[1c] has reported that cyclohexanone forms an enolate with triisobutylaluminum after the initial reduction step, according to equation 4.

During analyses of the compositions of various reduction products, controls and synthetic mixtures were used to test the reliability of the analytical method. The data obtained on analysis of a five-component synthetic mixture are given in Table IV. All analyses were done by gas chromatography using a Carbowax 20M column. Measurement of peak areas was done by the peak-height half-width method.

Table IV

Analysis of a Synthetic Mixture

	% *cis*-II	% *trans*-II[a]	% I	% II[b]	% V[c]	% IV[d]
Theory	63.8	36.2	61.1	38.9	33.2	66.8
Found	64.7	35.3	62.0	38.0	33.0	67.0

[a] *cis*- and *trans*-II are normalized to 100%. [b] *cis*- + *trans*-II. I and II are normalized to 100%. [c] V = cyclohexanone. [d] IV = cyclohexanol. IV + V are normalized to 100%.

Acknowledgment.—The authors would like to express their appreciation to Dr. Ernest L. Eliel for providing samples of *cis*- and *trans*-II and for helpful advice. Also the authors would like to thank the Chemicals Research Division of the Esso Research and Engineering Company for providing the facilities necessary to carry out this work.

The Preparation of Lithium Acetylide·Ethylenediamine

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Received April 4, 1963

A procedure has been developed for the preparation and isolation of N-lithioethylenediamine. A thermally stable form of monolithium acetylide has been produced by allowing N-lithioethylenediamine to react with acetylene in a variety of organic solvents. Some physical properties of the resulting lithium acetylide·ethylenediamine complex are given.

In 1898 Moissan[1] prepared monolithium acetylide by adding acetylene to a solution of lithium in liquid ammonia. Although this process has undergone some refinements during the intervening years,[2] it is still the only method used today for preparing monolithium acetylide. A British patent[3] was granted on the preparation of monolithium acetylide by allowing acetylene to react with lithium dispersion in tetrahydrofuran. We were unable to duplicate this work. Attempts to isolate the monolithium acetylide from liquid ammonia have failed because the monolithium acetylide disproportionated to dilithium acetylide and acetylene.[4] The presence of ammonia probably imparted some stability through complex formation. Detection of such a complex has been reported.[4] Removal of this complexing agent led to decomposition.

$$2LiC\equiv CH \longrightarrow LiC\equiv CLi + HC\equiv CH$$

The object of this work was to find a complexing agent which would impart sufficient stability to permit isolation and eliminate the need for liquid ammonia. Ethylenediamine was found to give such a complex. This complex, monolithium acetylide·ethylenediamine can be prepared by the reaction of lithium metal dispersion with ethylenediamine to form N-lithioethylenediamine, followed by the reaction of the N-lithioethylenediamine with acetylene.

$$Li + H_2NCH_2CH_2NH_2 \longrightarrow LiHNCH_2CH_2NH_2 + 0.5H_2$$

$$LiHNCH_2CH_2NH_2 + HC\equiv CH \longrightarrow LiC\equiv CH\cdot H_2NCH_2CH_2NH_2$$

Several references are available in the literature for the preparation of N-lithioethylenediamine by adding lithium metal to refluxing ethylenediamine.[5] No reference is made to its isolation. Isolation is complicated by the high solubility of the lithium salt in ethylenediamine.

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[1] H. Moissan, *Compt. rend.*, **127**, 911 (1898).

[2] K. N. Campbell and B. K. Campbell, *Proc. Indiana Acad. Sci.*, **50**, 123 (1940).

[3] Badische Anilin- and Soda-Fabrik Akt.-Ges., British Patent 771,708 (April 3, 1957).

[4] M. Corbellini and L. Turner, *Chim. Ind.* (Milan), **42**, 251 (1950); *Chem. Abstr.*, **54**, 19250 (1960).

[5] (a) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957); (b) L. Reggel, S. Friedman, and I. Wender, *ibid.*, **23**, 1136 (1958); (c) L. Reggel, J. P. Henry, and I. Wender, *ibid.*, **26**, 1837 (1961); B. S. Tyagi, B. B. Ghatge, and S. C. Bhattacharyya, *ibid.*, **27**, 1430 (1962).