ple with m.p. 142° which was characterized by comparing its infrared spectrum (in Chloroform solution) with the published[14] spectrum of d,l-estrone methyl ether and also with that of an authentic specimen of natural estrone methyl ether. All the spectra were found to be identical.

d,l-8-Isoestrone Methyl Ether (VII).—Reduction[11] of IV in benzene solution with a palladium-on-charcoal catalyst afforded

(14) W. S. Johnson, I. A. David, H. C. Dehm, R. J. Highet, E. W. Warnhoff, W. D. Wood, and E. T. Jones, J. Am. Chem. Soc. 80, 661 (1958).

a 60% yield of d,l-8-isoestrone methyl ether, m.p. 151–152°, after filtration and crystallization from methanol. The infrared spectrum in chloroform solution of this compound was found to be identical with the published[14] spectrum.

Acknowledgment.—The authors wish to thank Mr. A. Kowalsky for the ultraviolet spectra, Mr. R. Walker for the infrared spectra, and Mr. R. Boos and his associates for the microanalyses.

Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines. VII. The Preparation of Dihydroaromatics. A Comparison of the Lithium–Amine and Birch Reduction Systems

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Four different aromatic compounds are reduced by lithium–methylamine–alcohol combinations as well as by sodium–ammonia–alcohol (Birch reduction). In each case unconjugated dienes (dihydroaromatics) are formed in comparable yields. Unlike the Birch method, wherein an excess of metal may be employed, it is shown that an excess of metal in the amine–alcohol system results in the formation of considerable amounts of monoolefins rather than dihydro products. Apparently the alcohol cannot prevent isomerization of the unconjugated dihydro products to conjugated dienes entirely under these circumstances. It is shown that at least two equivalents of water (based on aromatic) can be tolerated in the lithium–amine reduction of cumene. The reduction of both the aromatic and its diene intermediates is so rapid in this system that these organic materials compete successfully for electrons with the hydrogen of the water molecules.
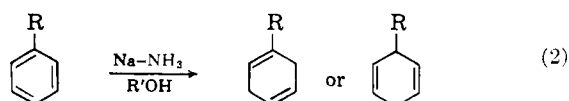
The blue solution which is formed by dissolving lithium in certain low molecular weight aliphatic amines is a potent reducing agent for aromatic ring systems.[1] The lithium–amine combination is presently the most convenient reagent for reducing an aromatic compound selectively to a monoolefin. When four equivalents of
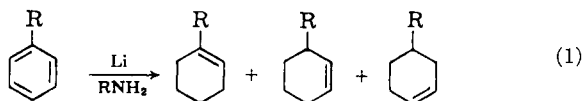
metal are used, a monosubstituted aromatic compound is reduced selectively to a mixture of the 1-, 3-, and 4-substituted olefins as shown in reaction 1. The 1-olefin usually predominates in the mixture, but the 3- and 4-isomers are formed in appreciable quantities. When a large excess of lithium is employed (*e.g.*, 6–8 equivalents based on aromatic compound) the 3- and 4-substituted olefins are reduced further in preference to the 1-isomer, and the 1-substituted olefin is obtained principally, admixed with completely saturated cyclohexanes.[1]

In order to increase the usefulness of the lithium–amine reducing agent in organic syntheses, it was deemed desirable to devise procedures whereby the selectivity of the reduction could be increased. It was found that this could be achieved quite successfully by the judicious choice of various solvent combinations for the reductions. In this paper we are reporting the effects of water and alcohols on the course of the reduction.

In an elegant series of papers by Birch[2] and his collaborators, it was shown that many aromatic ring systems could be reduced by a sodium–ammonia–alcohol com-

bination to dihydro aromatics (reaction 2). This procedure was later modified by Wilds and Nelson[3] such that lithium was used instead of sodium and the addition of alcohol to the reaction was delayed.

We have found that, in the presence of alcohol,[4] the lithium–amine combination can be used quite successfully to form dihydro aromatics. A detailed study of the reduction of four different compounds was made, in which the Birch procedure (sodium–ammonia–alcohol) was compared with the newly discovered lithium–amine–alcohol combination. As will be noted in Table I, the results obtained by the two methods are quite comparable. Actually there are advantages to both procedures. The higher boiling methylamine makes for greater ease of handling than does liquid ammonia, and is to be recommended from this standpoint. However, as Table I indicates, the Birch method gives slightly higher yields of 2,5-dihydro products in some cases. There are probably at least two reasons for this. The sodium–ammonia–alcohol system is not capable of reducing an unconjugated double bond except in certain isolated circumstances.[5] The same is not true of the lithium–amine system,[6] which is capable of 1,2-reductions of olefins. Hence, with excess metal, the 2,5-dihydro products can suffer a slow reduction of one double bond in the lithium–amine system, thereby form-

(1) R. A. Benkeser, J. J. Hazdra, R. F. Lambert, and P. W. Ryan, J. Org. Chem., 24, 854 (1959), and previous papers in this series.

(2) See A. J. Birch, Quart. Rev. (London), 4, 69 (1950); 12, 17 (1958), for pertinent references.

(3) A. L. Wilds and N. A. Nelson, J. Am. Chem. Soc., 75, 5360 (1953).

(4) We have yet to assess the importance of the kind of alcohol used in conjunction with the lithium and amine. Thus far we have employed ethanol, isopropyl alcohol and t-butyl alcohol indiscriminately. A detailed study of this point is presently underway.

(5) T. J. King, J. Chem. Soc., 898 (1951).

(6) R. A. Benkeser, G. Schroll, and D. M. Sauve, J. Am. Chem. Soc., 77, 3378 (1955).

TABLE I

COMPARISON OF BIRCH REDUCTION WITH
LITHIUM–METHYLAMINE–ALCOHOL SYSTEM

Aromatic compound	2,5-Dihydro, %[a]	1-Alkyl-cyclohexene, %	Recovered aromatic, %
Ethylbenzene[d]	89 (95)[b,g]	8 (3)	...
Isopropylbenzene[e]	88 (92)[b,h]	6 (5)	4 (0)
t-Butylbenzene[f]	79 (86)[c]	14 (8)	5 (0)
Anisole	81 (81)	17 (17)	...

[a] The value in parenthesis represents the product distribution obtained in the Birch reduction utilizing sodium in liquid ammonia with ethanol added. The first value listed in every case is the product distribution obtained by reduction in lithium–methylamine–isopropyl alcohol except for anisole in which case ethanol was used instead of isopropyl alcohol. [b] In both the Birch and lithium–amine reduction, 2–4% of an unknown product was obtained in the case of ethyl- and isopropylbenzene. Very likely this is the 1,4-dihydro product, but it has not been positively identified. [c] In the lithium–amine reduction, 2% of 1,4-dihydro-t-butylbenzene was also obtained. In the Birch method, 6% of this compound was produced. [d] In the Birch method, 0.1 mole of ethylbenzene, 0.39 g.-atom of sodium was used in 300 ml. of ammonia containing 23 g. of ethanol. [e] One-tenth mole of cumene, 0.5 g.-atom of sodium was used (Birch method) in 300 ml. of ammonia containing 23 g. of ethanol. [f] 0.15 mole of t-butylbenzene and 0.74 g.-atom of sodium (Birch method) were used in 300 ml. of ammonia containing 40 ml. of diethyl ether and 37.5 g. of ethanol. [g] The material which was analyzed boiled 133–140°. [h] The material which was analyzed boiled 149–155°.

ing a 1-substituted olefin.[7] In the Birch method excess metal (i.e., more than two equivalents based on the aromatic) can be used without fear of further reduction of the type shown in reaction 3. Likewise the lower

$$(3)$$
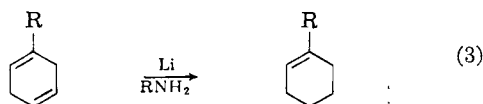
temperature achieved by liquid ammonia seems to have certain advantages. Any isomerization of the 2,5-dihydro products to conjugated olefins, will result in further reduction of the latter to monoolefins by a facile 1,4 reduction process (reaction 4). Formation of the

$$(4)$$
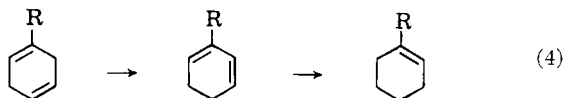
conjugated dienes seems to be favored in the higher boiling amines, and hence the selectivity of the reduction in these solvents is slightly less. However, it is obvious from Table I, that, when reaction conditions are rigorously controlled in the lithium–amine method, the two procedures are quite comparable.[8]

Birch[9] has suggested that the alcohols in such a system function as acidic protonating agents, and that the metal alkoxides thus produced are not capable, under the experimental conditions, of causing conjugation of the diene system.

(7) It was shown in previous work (ref. 1) that a double bond carrying a substituent like an alkyl group reduces more slowly than an unsubstituted olefin. Hence the preference shown in reaction 3 for one of the double bonds is justified.

(8) There has been a recent report that in some systems, the lithium-amine method may be preferable to the Birch reduction. See A. W. Burgstahler and L. R. Worden. J. Am. Chem. Soc., 83, 2587 (1961).

(9) A. J. Birch, J. Chem. Soc., 809 (1945).

We have verified this point by refluxing 2,5-dihydrocumene for four hours with sodium ethoxide in ethanol. Analysis of the product by vapor phase chromatography indicated that no conjugated dienes had formed. This
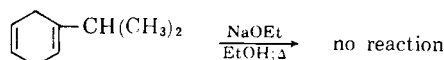
observation explains not only the small percentage of the 3- and 4-isopropylcyclohexenes formed in the presence of ethanol, but also predicts correctly that the amount of isopropylcyclohexane should be vanishingly small since this compound is known to arise principally from a reduction of the 3- and 4-isopropylcyclohexenes.

On the other hand, we also demonstrated that 2,5-dihydrocumene could be isomerized in thirty minutes by a solution of lithium–methylamide in methylamine. Vapor phase chromatography disclosed that very likely all the possible conjugated dienes were formed in this reaction. 3-Isopropylidenecyclohexene was positively identified as one of the components of the mixture since it could be isolated by fractionation. Ozonolysis of this diene produced acetone as one of the products.
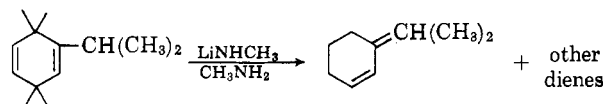
Interestingly enough, the presence of three equivalents of ethanol was not capable of stopping the lithium–amine reduction at the dihydro stage in the presence of six equivalents of metal. This can only mean that isomerization of the unconjugated 2,5-dihydrocumene was occurring despite the presence of ethanol. One must conclude that this isomerization was brought about by the presence of lithium alkylamide.[10]

Even six equivalents of ethanol did not prevent this isomerization entirely in the presence of six equivalents of lithium (see Table III), since 26% of the product in this case was 1-isopropylcyclohexene. Albeit the major product was 2,5-dihydrocumene. The reaction in this case was quite exothermic and the metal was used up entirely in about four hours. Obviously much of the metal was consumed by direct reaction with the alcohol to form hydrogen. These results clearly indicate the necessity of controlling the quantity of lithium used if one desires to prepare the unconjugated diene to the virtual exclusion of the 1-substituted olefin by the lithium–amine procedure.

It is at first sight disturbing that the presence of as much as six equivalents of ethanol is not sufficient to prevent the conjugation of the 2,5-dihydro product. A consideration of the relative acid–base strengths involved would predict the following equilibrium should lie well to the right.

$$\text{LiNHR} + \text{R'OH} \rightleftharpoons \text{LiOR'} + \text{RNH}_2$$
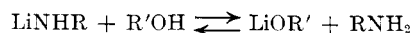
However, it must be borne in mind that the primary amine is used as the solvent in these reactions, and hence a simple mass effect would tend to shift this equilibrium to the left and thus favor formation of the alkylamide.

(10) It is possible, but seemingly unlikely, that this isomerization could be occurring by the catalytic action of the lithium metal itself.

Another factor very likely begins to assume importance when both the concentration of metal and alcohol are increased—the direct reaction of the metal with the alcohol. When the alcohol concentration was increased to six equivalents this reaction obviously became appreciable. This tends not only to increase the lithium alkoxide concentration but also to diminish the concentration of alcohol. Both effects would tend to force the above equilibrium in the direction of lithium alkylamide.

A similar observation was noted when an attempt was made to reduce cumene in methylamine with water as the proton donor rather than an alcohol. In this instance, only four equivalents of metal were used, but still monoölefins were produced as shown in Table II.

<div style="text-align:center">TABLE II</div>

REDUCTION OF ISOPROPYLBENZENE IN THE PRESENCE OF WATER WITH FOUR EQUIVALENTS OF LITHIUM IN METHYLAMINE[a]

	Trace of water	Two equivalents of water
Material balance (%)	79	60
Boiling range of product (°C.)	150–156	150–156
1-Isopropylcyclohexene (%)	50 (46)[b]	55 (46)[b]
3-Isopropylcyclohexene (%)	25 (26)	18 (26)
4-Isopropylcyclohexene (%)	25 (28)	20 (28)
Isopropylcyclohexane (%)	1 (0)	7 (0)

[a] Analyses were by v.p.c. using β,β'-oxydipropionitrile on firebrick at 20 p.s.i. The retention times of all components were compared with authentic compounds. [b] The values in parenthesis are the isomer distributions obtained in pure methylamine.

One must conclude that the water was not able to prevent diene conjugation, or else the isomerization was occurring by some other mechanism than base catalysis.

It is at first sight startling that lithium–amine reductions can be carried out successfully in the presence of water. This clearly indicates the extreme ease and rapidity with which electron transfer from the lithium to the aromatic and its diene intermediates occurs in this system. Obviously these organic species are competing successfully for electrons with the hydrogen of the water molecules. Since we[11] had shown previously that these organic species compete successfully for electrons even in the presence of such relatively strong acids like ethylamine hydrochloride, the present results are perhaps not unexpected.

In the next paper, the effect of relatively nonacidic additives, like secondary amines, on the course of the reduction will be reported.

Experimental

General Procedure for Preparation of Dihydrobenzenes by Reduction with Lithium in an Amine–Alcohol System.—These reductions were accomplished by adding lithium wire in pieces to a solution of the aromatic in an alcohol and methylamine. A three-necked flask was used, fitted with a stirrer and a Dry Ice condenser. The lithium was added in two portions, and was consumed within 30 min. At the end of this time, the Dry Ice condenser was replaced with a water condenser and the amine thereby allowed to evaporate. Hydrolysis of the residue was accomplished by adding water slowly to the cooled flask. The product was isolated by extracting with ether, drying, stripping solvent, and distilling.

(A) **Toluene.**—The reduction of 37.8 g. (0.4 mole) of toluene by 6.5 g. (0.93 g.-atom) of lithium and 60 g. (1.0 mole) of isopropyl alcohol in 400 ml. of methylamine gave 17.0 g. (45%) of crude material from which 12.8 g. (34%) was collected at 115.5–116°. This contained 95% 2,5-dihydrotoluene,[12] 3% recovered toluene, 1% 1-methylcyclohexene, and 1% of an unknown material (probably 1,4-dihydrotoluene[13]).

(B) **Ethylbenzene.**—Reduction of 21.2 g. (0.2 mole) of ethylbenzene by 3.15 g. (0.45 g.-atom) of lithium and 30.0 g. (0.5 mole) of 1-propanol in 300 ml. of methylamine, gave 16.6 g. (78%) of a crude mixture containing 89% 2,5-dihydroethylbenzene, 8% 1-ethylcyclohexene, and 3% of a mixture of 3- and 4-ethylcyclohexene. Careful fractionation on a Todd column (75:1 reflux ratio) gave 9.6 g. (46%) of pure 2,5-dihydroethylbenzene[12c] distilling at 140–142°; n^{21}D 1.4710.

(C) **Cumene.**—Reduction of 24.0 g. (0.2 mole) of cumene by 3.15 g. (0.45 g.-atom) of lithium and 30.0 g. (0.5 mole) of isopropyl alcohol in 300 ml. of methylamine gave 20.5 g. (85%) of crude product containing 88% 2,5-dihydrocumene, 4% recovered cumene, 6% 1-isopropylcyclohexene, and 2% of an unknown (probably 1,4-dihydrocumene). Fractionation at a high reflux ratio (Todd column) gave 12.8 g. (53%) of pure 2,5-dihydrocumene[12b] boiling at 157–159°; n^{24}D 1.4725.

(D) **t-Butylbenzene.**—The reduction of 26.8 g. (0.2 mole) of t-butylbenzene by 3.15 g. (0.45 g.-atom) of lithium and 30.0 g. (0.5 mole) of isopropyl alcohol in 300 ml. of methylamine gave 23.2 g. (87%) of crude material containing 79% 2,5-dihydro-t-butylbenzene, 14% 1-t-butylcyclohexene, 2% 1,4-dihydro-t-butylbenzene, and 5% recovered aromatic. Careful fractionation gave 10.8 g. (41%) of pure 2,5-dihydro-t-butylbenzene[12c] boiling at 175–176°; n^{35}D 1.4749. This sample showed only end absorption in its ultraviolet spectrum, indicating the absence of conjugated diene.

Anal. Calcd. for $C_{10}H_{18}$: C, 88.16; H, 11.84. Found: C, 88.19; H, 12.08.

(E) **Anisole.**—Reduction of 21.6 g. (0.2 mole) of anisole by 4.2 g. (0.6 g.-atom) of lithium and 27.6 g. (0.69 mole) of ethanol in 300 ml. of methylamine gave 16.1 g. (75%) of product in two fractionation cuts. The first fraction (b.p. 147–148°) contained 80% 2,5-dihydroanisole, 17% methoxycyclohexene, and 3% 2,3-dihydroanisole. The second fraction (b.p. 148–150°) contained 82% 2,5-dihydroanisole, 13% methoxycyclohexene, and 5% 2,3-dihydroanisole.

The Birch reduction of anisole utilizing sodium in liquid ammonia in the presence of ethanol gave a product which, by vapor phase chromatography, was almost identical in composition to that obtained above by the lithium–amine–alcohol method.

Birch Reductions of Alkylbenzenes.—The sodium–ammonia-alcohol reductions were all carried out utilizing classic procedures. The description which follows for the reduction of t-butylbenzene can be assumed to be typical of all. The results of these reductions are listed in Table I.

t-Butylbenzene Reduction.—Seventeen grams (0.74 g.-atom) of sodium was added over a period of 1 hr. to a solution of 20.1 g. (0.15 mole) of t-butylbenzene in 37.5 g. (0.75 mole) of ethanol, 300 ml. of ammonia, and 40 ml. of dry ether. After 1.5 hr. the metal was gone. The ammonia was allowed to evaporate before water was added. When the ether layer was distilled, 13.6 g. of liquid was obtained which boiled at 168–173°. See Table I for the analysis of this product.

Identification of Anisole Reduction Products.—The reduction of anisole by either the lithium–amine or Birch method described above gave a product showing three peaks when subjected to vapor phase chromatography.[14] The major peaks in both were identical, and could be assigned, therefore, to 2,5-dihydroanisole. When the reduction mixture was treated with dilute acid, the resulting mixture showed only two peaks by v.p.c. which were identified by their retention times as cyclohexanone and Δ^2-cyclohexenone. The percentage of cyclohexanone obtained, corresponded exactly with the percentage of the first peak in the original reduction mixture. Since cyclohexanone could arise only from a monoölefinic material, the first peak was thus labelled

(11) R. A. Benkeser, R. E. Robinson, and H. Landesman, *J. Am. Chem. Soc.*, **74**, 5699 (1952).

(12) (a) A. J. Birch, *J. Chem. Soc.*, 1642 (1947); (b) W. Hückel, *et al.*, *Ann.*, **614**, 47 (1958); (c) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

(13) The analyses of the dihydrobenzenes reported in this paper were carried out on an Aerograph vapor fractometer, Model A-110C. Either Ucon Polar packing was used, or β,β'-oxydipropionitrile on C-22 firebrick.

(14) A Perkin-Elmer vapor fractometer, Model 154C, was used for this analysis, with Column "K" packing (2-m. length).

as methoxycyclohexene (probably the 1-isomer). Since both remaining peaks in the reduction mixture gave Δ^2-cyclohexenone on acidification (one of these peaks has already been identified as 2,5-dihydroanisole), it followed that the third peak was also a methoxycyclohexadiene. From the work of Birch[15] this may well be 2,3-dihydroanisole. Evidence in favor of this assignment was obtained by refluxing 2,5-dihydroanisole for prolonged periods, during which time the ratio of 2,5-dihydroanisole/2,3-dihydroanisole decreased. This would indicate a shift in equilibrium to the more stable conjugated isomer.

When the aqueous layer from the reduction of anisole was acidified and treated with bromine, a yield of 0.2 g. of 2,4,6-tribromophenol was recovered. This indicated that less than 1% demethylation of anisole to phenol had occurred during reduction.

Reduction of Isopropylbenzene with Lithium in Methylamine in the Presence of Water.—In a 1-l., three-necked flask, fitted with a sealed stirrer and a Dry Ice condenser, was placed 0.34 mole of cumene and approximately 600 ml. of methylamine along with 3 drops of water. To this, 9.52 g. (1.36 g.-atoms) of lithium wire was added. The solution became colorless after 4 hr. After working up in the usual manner, the product was fractionated through a Todd column. A fraction boiling at 150–156° (33 g.; 79%) was collected. The olefin distribution was obtained by v.p.c. The results are shown in Table II.

The reduction of cumene was again carried out in a similar manner, with 2 equivalents of water, 4 equivalents of lithium, 0.34 mole of aromatic in 600 ml. of anhydrous methylamine. The olefin distribution was again obtained by v.p.c. and is listed in Table II.

Reduction of Isopropylbenzene by Lithium–Ethylamine in the Presence and Absence of Ethanol.—A total of 40.8 g. (0.34 mole) of cumene was dissolved in 700 ml. of anhydrous ethylamine. To this was added 15.3 g. (2.19 g. atoms) of lithium wire. After 18 hr. the mixture was worked up as described previously. Upon fractionation there was obtained 32.7 g. (81%) of product (b.p. 148–153°). Analysis of this product is shown in Table III.

TABLE III

REDUCTION OF ISOPROPYLBENZENE IN THE PRESENCE AND ABSENCE OF ETHANOL WITH SIX EQUIVALENTS OF LITHIUM IN ETHYLAMINE

	Pure ethylamine[a]	Ethylamine containing	
		3-Equiv. EtOH	6-Equiv. EtOH
Material Balance (%)	81	75	73
Boiling range of product (°C.)	148–153	148–153	148–153
1-Isopropylcyclohexene (%)	59	69	26[b]
3-Isopropylcyclohexene (%)	7	6	1
4-Isopropylcyclohexene (%)	5	2	3
Isopropylcyclohexane (%)	29	23	2

[a] All analyses were by v.p.c. A Fisher-Gulf partitioner, Model 160, was used with a 14-ft. β,β'-oxydipropionitrile on firebrick column operated at 82°, 20 p.s.i. He with a 90 ml./min. flow rate. [b] The principal product of this reaction was 2,5-dihydrocumene (64%).

The above run was repeated, using 42.0 g. (0.35 mole) of cumene, 48.5 g. (1.0 mole) ethanol, 15.9 g. (2.27 g.-atom) of lithium and 600 ml. of ethylamine. After 18 hr. of reaction, there was obtained 31.2 g. (75%) of product boiling at 149–153°. Analysis of this material is shown in Table III.

(15) A. J. Birch, J. Chem. Soc., 1551 (1950).

The above run was repeated, using 42.0 g. (0.35 mole) of cumene, 104.4 g. (2.27 moles) of absolute ethanol, 15.9 g. (2.27 g.-atoms) of lithium in 600 ml. of ethylamine. The reaction was vigorous and the metal was completely consumed at the end of 4 hr. Upon fractionation there was obtained 30.3 g. of product boiling at 149–153°. Analysis of this material is shown in Table III.

Attempted Isomerization of 2,5-Dihydrocumene by Sodium Ethoxide.—Sodium ethoxide was prepared by allowing 5.8 g. (0.25 g.-atom) of sodium to react with 160 ml. of anhydrous ethanol. To this was added 5.9 g. (0.048 mole) of 2,5-dihydrocumene. The mixture was refluxed for 4 hr. and then poured into ice–water and extracted with a small amount of ether. Distillation gave a product which, by v.p.c., showed no conjugated dienes—only 2,5-dihydrocumene.

Isomerization of 2,5-Dihydrocumene by Lithium Methylamide.—Eighteen grams (0.15 mole) of 2,5-dihydrocumene was added to a solution of 2 equivalents of lithium methylamide in methylamine. The lithium methylamide had been prepared by reducing benzene with lithium in methylamine. An orange color developed immediately following the addition of diene. After the mixture was stirred for 30 min., the color was dissipated by the addition of solid ammonium chloride. After the solvent was evaporated, water and ether were added. The product was obtained by removing the ether by distillation. Analysis of the product before distillation (Aerograph A-110C vapor phase chromatograph; 5-ft. β,β'-oxydipropionitrile on C-22 firebrick at 70–80°; 7.5–10-p.s.i. He) showed seven different fractions. Four of these were identified as 1-isopropylcyclohexene (1%), 2,5-dihydrocumene (13%), cumene (5%), and 3-isopropylidenecyclohexene (15%). Presumably the other three products were the other conjugated dienes.

Fractionation of this mixture on a Todd column gave 12.1 g. of material boiling up to 157°. The liquid distilling above this temperature was mostly 3-isopropylidenecyclohexene. The best cut (b.p. 164–165°) contained 89% of this diene. The total recovery of material was 12.8 g. (71%). The ultraviolet spectrum of 3-isopropylidenecyclohexene showed a strong broad band at 240 mμ.

Ozonolysis of 3-Isopropylidenecyclohexene.—A 0.33-g. (2.7 mmole) sample of 3-isopropylidenecyclohexene obtained by the fractionation described above was dissolved in 75 ml. of acetic anhydride. Ozone (Welsbach ozonizer) was bubbled through the solution at −78° until a light blue color developed. The mixture was then poured into 100 ml. of water containing 10 ml. of acetic acid and 8.46 g. of mossy zinc. The latter was held in a 200-ml. flask attached to a Claisen head and downward condenser. The outlet of the condenser was immersed in a solution containing 0.535 g. (2.7 mmoles) of 2,4-dinitrophenylhydrazine in 2.5 ml. of concentrated sulfuric acid, 4 ml. of water and 12.5 ml. of 95% ethanol. As the pot was warmed to 100°, a solid formed in the receiver. This solid was dissolved in chloroform and placed on a 2 ft. by 0.5 in. column packed with dry silica gel. This was eluted with a 10% ether–90% petroleum ether solution and finally with methanol. The second band was collected and the solid crystallized twice from ethanol. There was obtained 0.026 g. of a solid which melted[16] sharply at 126°. This melting point was undepressed by admixture with an authentic derivative.

(16) The literature value for the 2,4-dinitrophenylhydrazone of acetone is 126°. See R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds " J. Wiley and Sons, Inc., New York, N. Y., 1957, p. 316.