loaned to us for this study by the Johnson-Matthey Co.

Registry No. I, 86365-69-7; II, 86365-70-0; III, 86365-71-1; IV, 23611-14-5; V, 2819-48-9; VI, 86365-72-2; VII, 86365-73-3; VIII, 86365-74-4; IX, 86365-75-5; X, 86365-76-6; $Pd(OAc)_2$, 3375-31-3; $P(o\text{-tol})_3$, 6163-58-2; (*Z*)-1-bromo-1,5-hexadiene, 86365-77-7; 2-bromo-1,6-heptadiene, 86365-78-8; 2-bromo-1,7-octadiene, 86365-79-9; (*E*)-2-bromo-1,6-octadiene, 86365-80-2; 2-bromo-1,7-nonadiene, 86365-81-3; (*Z*)-6-bromo-1,5-heptadiene, 86365-82-4; 5-hexen-1-ol, 821-41-0; 3-butyn-1-ol, 927-74-2; (*Z*)-2,4-dibromo-2-butene, 86365-83-5; (*E*)-2,4-dibromo-2-butene, 86365-84-6; (*E*)-6-bromo-1,5-heptadiene, 86365-85-7; 5-bromo-1-hexene, 4558-27-4; piperidine, 110-89-4; allylmagnesium bromide, 1730-25-2.

Supplementary Material Available: Table II containing the boiling points, NMR spectra, and molecular weights determined for the bromo dienes prepared and Table III with the same data for the cyclized products obtained (3 pages). Ordering information is given on any current masthead page.

A New Reducing System: Calcium Metal in Amines. Reduction of Aromatic Hydrocarbons

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A new reducing system consisting of calcium dissolved in a mixture of amines (methylamine–ethylenediamine) is described. Representative aromatic hydrocarbons have been reduced by this new reagent largely to monoalkenes. Hydrocarbons like tetralin, *m*- and *p*-xylene, and indan are reduced in excellent yields by the calcium system to a crude product containing 88% or better of a single alkene. A new technique involving oxymercuration–demercuration is used to purify two of the monoalkene isomer mixtures obtained in these reductions. Unexpectedly, durene is reduced by the calcium reagent to 1,2,4,5-tetramethyl-1,4-cyclohexadiene in excellent yield. Likewise anthracene is reduced in one step to 1,2,3,4,5,6,7,8,9,10-decahydroanthracene. Experiments designed to elucidate why the calcium system does not reduce durene or anthracene to monoalkenes are described. Similarities and differences between the calcium–amine and the lithium–amine reducing systems are discussed.

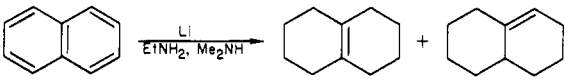
Introduction

Several years ago we disclosed[1] that calcium metal dissolved in a mixture of methylamine and ethylenediamine was capable of reducing simple aromatic hydrocarbons to cyclic alkenes. In this regard, it resembled the lithium–amine reducing system[2] first reported in 1955. As early as 1916, Russian workers[3] reported that calcium dissolved in liquid ammonia or calcium hexaammine $[Ca(NH_3)_6]$ suspended in anhydrous diethyl ether would reduce simple aromatics to monoolefins. The Russian procedures were cumbersome, and, despite claims to the contrary,[4] usually gave products that were highly impure.[5] As a result, calcium reductions never gained wide acceptance[6] and were used only sporadically through the years.

In this paper, we report the reduction of representative aromatic hydrocarbons employing a new calcium–mixed amine reducing system. In several of the examples given, excellent yields of a crude product can be obtained which contain 88% or better of a single cyclic alkene. In these cases, reduction by calcium may develop into the method of choice for obtaining the corresponding cyclic mono- or diene.

Results

Naphthalene–Tetralin. In earlier work,[7] naphthalene was reduced to an 80/20 mixture of Δ^9- and $\Delta^{1(9)}$-octalin by lithium dissolved in a mixture of ethylamine–dimethylamine. Δ^9-Octalin of greater than 99% purity could



80 20

be obtained from this mixture by selective hydroboration of the less sterically hindered $\Delta^{1(9)}$ isomer with disiamylborane.[8] The calcium–amine reduction of both naphthalene and tetralin (Table I, entries 1 and 2) also results in an approximate 80/20 mixture of Δ^9 and $\Delta^{1(9)}$ isomers. A more convenient purification method (see Experimental Section) has been developed involving oxymercuration–demercuration,[9] which permits isolation of the Δ^9 isomer with a minimum purity of 98%.

Durene–Anthracene. Both of these compounds are reduced by the calcium system to unconjugated dienes rather than to the usual monoalkenes. One[10] of the published procedures for preparing 1,2,4,5-tetramethyl-1,4-cyclohexadiene by a Birch reduction of durene reports only an 8% yield of product. This low yield is the result of using a toluene–liquid ammonia mixture to increase[11] the

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(3) Dumanskii, A. V.; Zvyereva, A. V. *J. Russ. Phys. Chem. Soc.* **1916**, *48*, 994.
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(5) Unpublished studies from this Laboratory.
(6) Kaiser, E. M. *Synthesis* **1972**, 391.
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(8) Brown, H. C. "Hydroboration"; W. A. Benjamin: New York, 1962; p 191.
(9) Brown, H. C.; Geoghegan, P. Jr. *J. Am. Chem. Soc.* **1967**, *89*, 1522; See also: Chatt, J. *Chem. Rev.* **1951**, *48*, 7 for other pertinent references.
(10) Hückel, W.; Cramer, R. *Liebigs Ann. Chem.* **1960**, *630*, 89.
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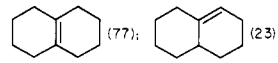
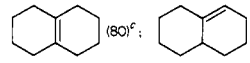
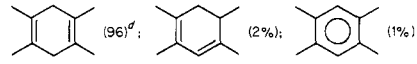
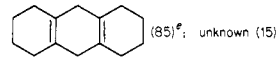
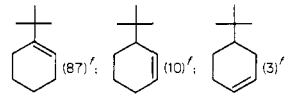
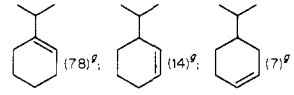
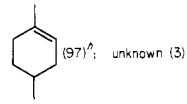
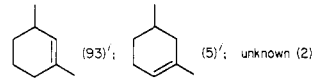
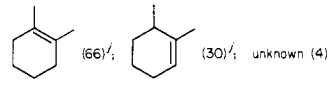
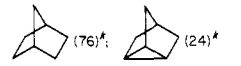
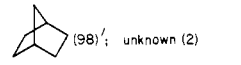
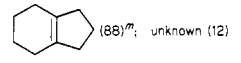
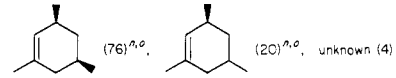
0022-3263/83/1948-2796$01.50/0

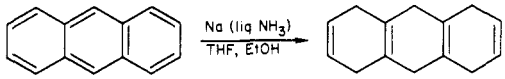
Table I. Reduction of Hydrocarbons with Calcium in Methylamine-Ethylenediamine

entry	hydrocarbon (mmol)[a]	mol of Ca	reaction time, h	product (composition, %)	yield, %
1	naphthalene (100)	1.0	23	 (77); (23)	92
2	tetralin (100)[b]	0.50	26	 (80)[c]; (19)	92
3	durene (100)[b]	0.60	25	 (96)[d]; (2%); (1%)	90
4	anthracene (50)[b]	0.70	52	 (85)[e]; unknown (15)	100
5	*tert*-butylbenzene (100)	0.60	22	 (87)[f]; (10)[f]; (3)[f]	87
6	cumene (100)	0.60	22	 (78)[g]; (14)[g]; (7)[g]	82
7	*p*-xylene (100)[b]	0.60	22	 (97)[h]; unknown (3)	84
8	*m*-xylene (100)[b]	0.60	24	 (93)[i]; (5)[i]; unknown (2)	86
9	*o*-xylene (100)	0.60	22	 (66)[j]; (30)[j]; unknown (4)	89
10	norbornadiene (15)	0.12	47	 (76)[k]; (24)[k]	74
11	norbornene (100)	0.30	23	 (98)[l]; unknown (2)	71
12	indan (100)[b]	0.60	24	 (88)[m]; unknown (12)	83
13	mesitylene (100)	0.60	24	 (76)[n,o]; (20)[n,o]; unknown (4)	71

[a] In every case except anthracene (entry 4) and norbornadiene (entry 10) the solvent was a mixture of 150 mL of methylamine and 150 mL of ethylenediamine. In the case of anthracene, 50 mL of THF was added to 150 mL of methylamine and 150 mL of ethylenediamine. In the case of norbornadiene, 75 mL of methylamine and 75 mL of ethylenediamine were used. [b] See Experimental Section for a more detailed description of this reduction. [c] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.50-1.72 (m, 8 H), 1.72-2.00 (m, 8 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.22, 30.50, 127.99. [d] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.59 (s, 12 H), 2.51 (s, 4 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.98, 40.06, 123.46. [e] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.45-1.75 (m, 8 H), 1.75-2.10 (m, 8 H), 2.38 (s, 4 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.25, 29.53, 37.59, 125.87. [f] GLPC analysis was performed on a Carbowax 20 M capillary column (15 m × 0.25 mm) at 60 °C. An authentic mixture of the three *tert*-butylcyclohexenes and *tert*-butylcyclohexane was prepared for comparison by the lithium-methylamine reduction of *tert*-butylbenzene (see ref 22). [g] GLPC analysis was performed on a Carbowax 20 M capillary column (15 m × 0.25 mm) at 70 °C. An authentic mixture of the three isopropylcyclohexenes and isopropylcyclohexane was prepared, for comparison, by the lithium-methylamine reduction of cumene (see ref 22). [h] GLPC analysis was performed on a Carbowax 20 M capillary column (15 m × 0.25 mm) at 31 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (d, 3 H, J = 6.5 Hz), 1.00-2.30 (7 H), 1.61 (s, 3 H), 5.33 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.82, 23.58, 28.39, 30.23, 31.37, 34.02, 120.77, 133.68. [i] The ^{13}C NMR and ^{1}H NMR were of the isomeric mixture. 1,3-Dimethylcyclohexene: ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.94, 22.04, 23.84, 30.07, 30.39, 31.25, 127.84, 133.34. For 2,4-dimethylcyclohexene: ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.99, 23.75, 25.42, 28.98, 30.72, 38.83, 120.71, 133.61; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83-1.02 (3 H, d, 7 Hz, methyls), 1.62 (3 H, s, allylic methyls), 1.02-2.50 (7 H, ring hydrogens), 5.17-5.40 (1 H, m, vinyl hydrogens). [j] GLPC analysis was performed on a Carbowax 20 M capillary column (15 m × 0.25 mm) at 55 °C. The two isomers were separated by preparative GLPC on a 10% FFAP on 80-100 mesh Chromosorb G column (12 ft × 0.25 in.) at 87 °C. For 1,2-dimethylcyclohexene: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.40-1.69 (m, 4 H), 1.58 (s, 6 H), 1.72-2.03 (m, 4 H). This was consistent with the ^{1}H NMR found in Sadtler. For 2,3-dimethylcyclohexene: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.00 (d, 3 H, J = 7 Hz), 1.64 (s, 3 H), 1.14-2.10 (7 H), 5.36 (m, 1 H). [k] GLPC analysis was performed on a 10% Carbowax 20 M on a Chromosorb A column (12 ft × $^1/_8$ in.) at 80 °C. The same column was used for a preparative separation. Identification was by ^{1}H NMR. [l] GLPC analysis was performed on a Carbowax 20 M capillary column (15 m × 0.25 mm) at 40 °C. Identification was by ^{1}H NMR. [m] GLPC analysis was carried out on a SE-30 capillary column (15 m × 0.25 mm) at 60 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.50-1.72 (m), 1.72-2.05 (m), 2.05-2.40 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.74, 23.26, 25.86, 36.14, 134.23. [n] GLPC analysis was carried out on a Carbowax 20 M capillary column (15 m × 0.25 mm) at 53 °C. ^{1}H NMR and ^{13}C NMR analysis were performed on the mixture of cis and trans isomers. Isomer (76%): ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.20, 22.35, 23.51, 29.56, 31.65, 39.04, 40.85, 127.67, 133.17. Isomer (20%): ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.37, 21.74, 23.82, 24.79, 28.62, 37.70, 38.51, 126.74, 132.42. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.76-1.05 (3 H, methyls), 1.05-2.40 (6 H, ring hydrogens), 1.60 (3 H, allylic methyls), 5.10-5.32 (1 H, vinyl hydrogens). [o] Stereochemistry uncertain.

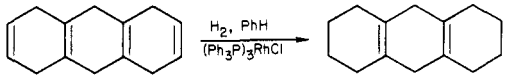
solubility of the durene. If THF (tetrahydrofuran) is substituted for the toluene and lithium for sodium, an excellent yield of 1,2,4,5-tetramethyl-1,4-cyclohexadiene can be obtained.[5,12] Nevertheless, the calcium–amine reduction of durene to 1,2,4,5-tetramethyl-1,4-cyclohexadiene is quite competitive in both yield and product purity with the modified Birch reduction (Table I, entry 3).

Currently, one of the best methods for preparing 1,2,3,4,5,6,7,8,9,10-decahydroanthracene involves a two-step procedure (eq 1 and 2). The first step is a Birch reduction



(1)

44%



(2)

88%

of anthracene to form 1,4,5,8,9,10-hexahydroanthracene[13] followed by a catalytic reduction of the latter by hydrogen in the presence of tris(triphenylphosphine)chlororhodium[14,15] (eq 2). Calcium reduction of anthracene gives decahydroanthracene directly in a crude yield of 85%. Although several crystallizations from acetone are necessary to obtain pure product, the overall simplicity of the calcium method makes it quite attractive.[16]

***m*-Xylene and *p*-Xylene.** The reduction of *p*-xylene (Table I, entry 7) with calcium gave an 83% yield of crude product containing 97% of 1,4-dimethylcyclohexene. While the literature contains several methods for preparing this alkene, one of the most attractive procedures involves reducing *p*-xylene with lithium in methylamine.[17,30] An isolated yield of 60% was reported. The calcium reduction would seem to be an improvement on this procedure.

The reduction of *m*-xylene by calcium gave an 86% of crude product (Table I, entry 8), which contained 93% 1,3-dimethylcyclohexene and 5% 2,4-dimethylcyclohexene along with 2% unknown. Again, there are numerous literature procedures for preparing 1,3-dimethylcyclohexene, but virtually all of them lead to isomer mixtures.[18] The 93/7 ratio of isomers obtained by the calcium reduction is clearly superior to the 60/38 ratio obtained by the acid-catalyzed[19] dehydration of 1,3-dimethylcyclohexanol.

Indan. Two of the most attractive methods[20,21] for preparing 4,5,6,7-tetrahydroindan involve the reduction of indan by lithium in a solvent mixture of ethylamine–dimethylamine. In one case[20] a crude yield of 75% was realized and in the other case[21] 77% yield of crude product was obtained containing 85% 4,5,6,7-tetrahydroindan. Purification[21] by the addition of disiamylborane permitted the isolation of pure 4,5,6,7-tetrahydroindan in a 48% yield. Our calcium procedure yields 83% crude product of which 88% is the desired 4,5,6,7-tetrahydroindan (Table I, entry 12). Our new oxymercuration–demercuration purification procedure yields 81% (based on the amount of 4,5,6,7-tetrahydroindan in the crude product) material that is 98% pure.

Monosubstituted Aromatics. The reduction of cumene (Table I, entry 6) by the calcium–mixed amine system leads to mixtures of 1-, 3-, and 4-isopropylcyclohexenes as with lithium in methylamine.[22,23] Clearly, the calcium reagent is more selective than the lithium–methylamine system in that the amount of 1-isopropylcyclohexene relative to the 3- and 4-isomers is greater with calcium. Only when diluents like morpholine are added to the lithium–methylamine system does the relative amount of 1-isopropylcyclohexene approximate that which is obtained with calcium. Early reduction potential data[24] for lithium and calcium in liquid ammonia at −50 °C indicate lithium to be a stronger reducing agent (−2.99 V) than calcium (−2.39 V). Our present work would indicate the same trend is likely true in amine solvents.

Discussion

An examination of Table I reveals that the calcium–amine reducing system differs from the lithium system in several important ways. First of all, formation of Birch-type diene products as from durene and anthracene (Table I, entries 3 and 4) in the absence of an alcohol generally does not occur in lithium–amine systems (see ref 16, however). It may be simply coincidence that the central ring of anthracene bears four substituents in the same structural relationship to the four methyl groups in durene, and this arrangement somehow causes both compounds to reduce to dienes. It was this structural similarity (possibly totally irrelevant) that prompted us to attempt the reduction of anthracene after durene gave such unexpected results. By contrast, when durene is reduced by lithium in methylamine (unpublished work), 87% of the product consists of monoalkenes.

Most of the reactions in Table I were carried out several times to approximate optimal conditions. It became apparent that an excess of calcium was desirable to eliminate what probably were diene impurities in the product. In most cases a rather large excess of calcium was used as well as long reaction times. A study is presently under way to optimize the experimental conditions for some of these reactions.

Another difference between the calcium- and lithium–amine systems is their relative ability to reduce internal double bonds. Lithium–amine systems are capable of such reductions.[25] By contrast, calcium–amine combinations show little or no propensity for reducing internal double bonds despite a large excess of calcium which may be employed. From a synthetic viewpoint this often proves advantageous, since in calcium reductions saturated compounds are never a significant contaminant in the final product. In a graphic demonstration of this point, 1 equiv of cyclohexene was stirred with 2.5 equiv of calcium for 23 h in a typical solvent mixture of methylamine and

(12) See Paquette et al. (Paquette, L. A.; Kakihana, T.; Hansen, J. F.; Philips, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 152) where this same compound is reported. We are indebted to Dr. Hansen for calling our attention to this reference.
(13) Birch, A. J.; Fitton, P.; Smith, D. C. C.; Steere, D. E.; Stelfox, A. R. *J. Chem. Soc.* **1963**, 2209.
(14) Birch, A. J.; Walker, K. A. M. *Aust. J. Chem.* **1971**, *24*, 513.
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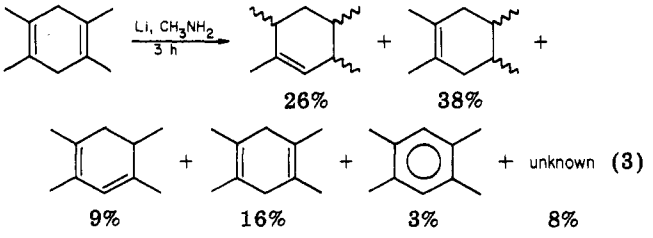
(20) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1968**, *33*, 47.
(21) Becker, K. B.; Boschung, A. F.; Grob, C. A. *Helv. Chim. Acta* **1973**, *56*, 2733. Krapcho, A. P.; Donn, R. *J. Org. Chem.* **1965**, *30*, 641.
(22) Benkeser, R. A.; Agnihotri, R. K.; Burrous, M. L.; Kaiser, E. M.; Mallan, J. M.; Ryan, P. W. *J. Org. Chem.* **1964**, *29*, 1313.
(23) Filler, R.; Camara, B. R.; Naqvi, S. M. *J. Am. Chem. Soc.* **1959**, *81*, 658. It is unclear why these workers report incomplete reduction of both cumene and *tert*-butylbenzene by lithium in ethylamine. We surmise they used insufficient lithium since we have never encountered these difficulties.
(24) Pleskov, V. A. *Zh. Fiz. Khim.* **1937**, *9*, 12.
(25) Benkeser, R. A.; Schroll, G.; Sauve, D. M. *J. Am. Chem. Soc.* **1955**, *77*, 3378. Benkeser, R. A.; Hazdra, J. J.; Lambert, R. F.; Ryan, P. W. *J. Org. Chem.* **1959**, *24*, 854.

ethylenediamine. All the metal was consumed and a grayish white solid formed, but a maximum yield of only 2% cyclohexane was realized. It will be noted in Table I (entries 10 and 11) that considerable amounts of norbornane are obtained when either norbornadiene or norbornene is reduced by calcium. Both of these alkenes represent highly strained systems so that their facile reduction is not unexpected.[26a]

In virtually all of the calcium reductions where a solvent mixture of methylamine and ethylenediamine was used, the metal was almost entirely consumed even when present in large excess. A grayish white precipitate forms during the course of such reductions and remains until hydrolysis. Seemingly, this grayish white solid is a calcium alkyl amide. Since the solvent consists of an amine mixture, one can envisage several formulations for calcium alkyl amides formed under such conditions. To establish that this material did not contain appreciable amounts of finely divided calcium, the gray solid which formed during the attempted reduction of cyclohexene was stirred for 41 h in the presence of *p*-xylene. No reduction of the *p*-xylene occurred despite the fact that the calcium–amine system reduces this compound readily (Table I, entry 7). Obviously, the excess calcium in these reductions is being consumed by direct reaction with the solvent forming calcium alkylamides. When calcium alone was stirred for 24 h in a solvent mixture of methylamine–ethylenediamine, no reaction occurred and the calcium could be recovered. This would indicate that the calcium–solvent reaction requires a catalyst. In the attempted reduction of cyclohexene, the calcium was used up rather rapidly despite the small amount of cyclohexane formed. While the cyclohexene was carefully distilled prior to use, the possibility always exists that traces of an unsuspected impurity is the actual catalyst rather than cyclohexene itself. This point is being investigated further.

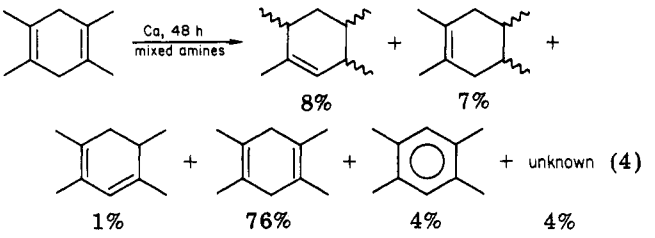
Another difference between the lithium- and calcium–amine systems is that the latter seems to require a solvent mixture of methylamine–ethylenediamine to obtain products in good yield and high purity. Using methylamine alone routinely resulted in low yields of impure products. With ethylenediamine alone, only tetralin and *p*-xylene gave results comparable to the solvent mixture (see Experimental Section). Additional work designed to clarify the need for the dual solvent system is presently under way.[26b]

Several experiments were carried out in an attempt to elucidate why diene products formed from durene in the calcium system rather than the usual monoalkenes formed in the lithium–amine system (unpublished studies). In one instance 1,2,4,5-tetramethyl-1,4-cyclohexadiene was treated with lithium in methylamine. The products and their percent distribution are shown in eq 3. Clearly extensive



(3)

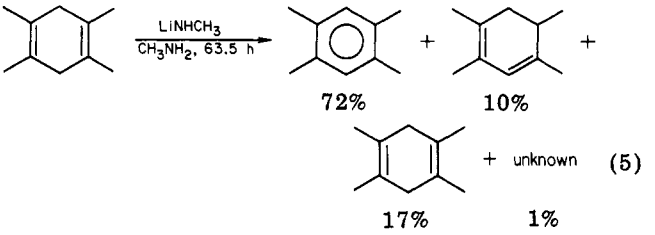
reduction occurred since 64% of the product consisted of monoalkenes. In another experiment 1,2,4,5-tetramethyl-1,4-cyclohexadiene was treated with calcium in a typical methylamine–ethylenediamine solvent mixture. This reaction was allowed to proceed for 48 h with the results shown in eq 4. The product from the calcium–



(4)

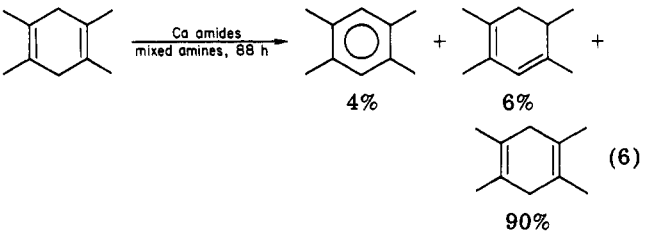
amine system consisted of only 15% monoalkenes and 76% starting material.

In still another experiment lithium methylamide (formed by first reducing benzene with lithium in methylamine) was allowed to react with 1,2,4,5-tetramethyl-1,4-cyclohexadiene in methylamine for 63.5 h in accord with eq 5. Finally, 1,2,4,5-tetramethyl-1,4-cyclo-



(5)

hexadiene was allowed to react for 88 h with calcium amides preformed in methylamine–ethylenediamine by first reducing benzene with calcium in the aforementioned amine mixture. These results are shown in eq 6. It is clear



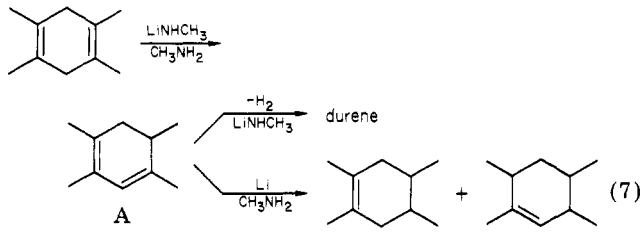
(6)

that lithium methylamide (eq 5) was more effective than the calcium system (eq 6) in conjugating the double bonds to form 1,2,4,5-tetramethyl-1,3-cyclohexadiene and especially in effecting aromatization. Significantly, no monoalkenes were formed in either case, thus eliminating the possibility of disproportionation.[27] The picture which emerges from eq 5 and 6 is tantalizingly similar to that presented by Reggel[28] and co-workers regarding the capacity of the lithium salt of ethylenediamine to conjugate and aromatize diene systems. One might hypothesize that lithium methylamide isomerizes 1,2,4,5-tetramethyl-1,4-cyclohexadiene to 1,2,4,5-tetramethyl-1,3-cyclohexadiene (compound A, eq 7), which by loss of hydrogen aromatizes to durene or in the presence of lithium metal as in eq 3 can be reduced to monoalkenes as depicted in eq 7. It is obvious from eq 6 that the calcium amides are much slower to bring about any transformations of 1,2,4,5-tetramethyl-1,4-cyclohexadiene since 90% of the product consisted of this unchanged diene even after 88 h.

(26) (a) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1958**, *80*, 1700. Turner, R. B.; Meador, W. R.; Winkler, R. E. *Ibid.* **1957**, *79*, 4116. Traynham, J. G. *J. Org. Chem.* **1960**, *25*, 833. Krapcho, A. P.; Nadel, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 1096. (b) **Note Added in Proof:** Recently we have found conditions such that both cumene and *tert*-butylbenzene can be reduced quite successfully in ethylenediamine alone. This may indicate that experimental procedures can be developed in which methylamine can be omitted from most of these calcium reductions. We are currently attempting to achieve this goal.

(27) Birch, A. J. *J. Chem. Soc.* **1947**, 1642. Zelinsky, N. D. *Chem. Ber.* **1924**, *57*, 2058. Linstead, R. P.; Michaelis, K. O. A.; Thomas, S. L. S. *J. Chem. Soc.* **1940**, 1139.

(28) Reggel, L.; Friedman, S.; Wender, I. *J. Org. Chem.* **1958**, *23*, 1136.



(7)

The results depicted in eq 3–6 provide a rationale as to why the calcium–mixed amine system reduces durene to 1,2,4,5-tetramethyl-1,4-cyclohexadiene while the lithium–amine system reduces it to monoalkenes. It must be emphasized that eq 7 is purely speculative and that additional work is necessary to test its validity. We have not determined whether hydrogen is evolved as eq 7 would demand. Likewise, while we have detected the presence of 1,2,4,5-tetramethyl-1,3-cyclohexadiene (compound A) in reactions 3–6, this does not mean that the durene and monoalkenes in eq 7 *must* have formed from *this* conjugated diene. The fact that the other possible conjugated diene, 2,3,5,6-tetramethyl-1,3-cyclohexadiene, was not detected could mean that *this* is the pivotal diene from which the durene and monoalkenes form.

Experimental Section

All melting points were recorded on a Mel-Temp apparatus and are uncorrected. All gas chromatography analyses in which a capillary instrument was used were carried out on either a Varian Model 3700 instrument or a Perkin-Elmer 226. When samples were collected for spectroscopic studies, either a Varian Associates 1400 instrument or an Aerograph 200 instrument was used. The ^{1}H NMR spectra were recorded on either a Perkin-Elmer R-32 spectrometer operating at 90 MHz or a Varian XL-200 spectrometer operating at 200 MHz in 5-mm tubes. The ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer operating at 50.3 mHz in 10-mm tubes. All chemical shifts are reported in ppm relative to Me_4Si. All ^{1}H NMR spectra are 90 MHz unless otherwise stated. The ^{13}C NMR spectra (50.3 mHz) were recorded with spectral widths of 10 000 Hz and 16 000 data points zero filled to 32 K. The ^{1}H NMR spectra (200 MHz) were recorded with spectral widths of 2000 Hz and 8000 data points. The GC–MS (70 eV) data were obtained on a Finnigan 4000 mass spectrometer (utilizing a Nova 4 data system) interfaced with a Finnigan 9610 gas chromatograph. The latter was equipped with a 10% Carbowax 20-M (on chromosorb Q; 80–100 mesh) glass column (6 ft × 2 mm). The column temperature was 100–120 °C; injector temperature was 200 °C; flow rate was 30 mL/min.

The calcium used in all of this work was purchased from Alfa Products. Both calcium turnings (99% pure) and calcium shot (99.5% pure) were used. No difference in results between the two forms could be detected.

General Procedure for Reduction with Calcium–Methylamine–Ethylenediamine. Methylamine (Matheson) was distilled through a potassium hydroxide drying tube into a three-neck, round-bottom flask (capacity of approximately three times that of the solvent mixture) equipped with a mechanical stirrer, gas inlet tube, and a reflux condenser through which ethylene glycol was circulated (−25 °C).[29] All exits were protected with mercury–mineral oil bubblers. The compound to be reduced, calcium (turnings or shot), and ethylenediamine (Aldrich) freshly distilled from sodium were placed in the reaction flask. The mixture was then stirred for the indicated amount of time. If the reaction became too vigorous, it was controlled with a dry ice–acetone bath or by surrounding the flask with a small amount of dry ice. Prolonged cooling caused the reaction to stop (it resumed when allowed to warm up) and the ethylenediamine to solidify. A deep blue color often developed, but other colors were also observed, and considerable amounts of a gray solid formed. The latter when dry often sparked upon exposure to the atmosphere and reacted vigorously with water. The methylamine was allowed to evaporate slowly by disconnecting the cooling liquid from the condenser. The flask was cooled to 0 °C and either diethyl ether or *n*-pentane was added. The mixture was hydrolyzed by the cautions, dropwise addition of 2 M aqueous NH_4Cl. A vigorous reaction accompanied this addition. When necessary, 2–3 M hydrochloric acid was added to dissolve the calcium salts completely. The layers were separated and the aqueous layer extracted with either two portions of diethyl ether or *n*-pentane. The organic extracts were combined with the organic phase from the reaction mixture, then washed with two portions of water, two portions of 5% HCl, one portion of 5% $NaHCO_3$, and one portion of brine, and then dried over anhydrous Na_2SO_4. The solvent was removed either by rotary evaporation or fractional distillation depending on the volatility of the product. In some cases reduced pressure was necessary to remove the last traces of solvent.

Tetralin. As described above 150 mL of methylamine and 150 mL of ethylenediamine were placed in a 1000-mL three-neck round-bottom flask. Calcium (20.04 g; 0.5 mol) and 13.22 g (100 mmol) of tetralin (Aldrich) were then added and the mixture was stirred for 26 h. After workup (see General Procedure), the solvent was removed by rotary evaporation under a vacuum. There remained 12.52 g (92%) of a light yellow oil. Analysis of this oil by GLPC (OV-101 capillary column; 25 m × 0.25 mm; 85 °C) indicated it to be Δ^9-octalin (80%), $\Delta^{1(9)}$-octalin (19%), and 1% of an unknown material. See Table I, entry 2.

The above procedure was repeated with 13.22 g (100 mmole of tetralin and 20.04 g (0.50 mol) of calcium in 150 mL of only ethylenediamine. The mixture was stirred for 24.5 h. At the end of this time, an appreciable amount of calcium remained and the usual gray solid was present. After the customary workup, 13.19 g (97%) of a light yellow oil was obtained which contained 80% Δ^9-octalin and 19% $\Delta^{1(9)}$-octalin along with 1% of an unknown.

Purification of Δ^9-Octalin by Oxymercuration–Demercuration. Mercuric acetate (8.81 g; 27.7 mmol) was dissolved in 30 mL of deionized water. To this clear solution was added 30 mL of THF and 12.52 g (92.1 mmole of the octalin mixture obtained above. A bright yellow color developed immediately and after 20 min became milky white. After 1 h of stirring, 30 mL of 3 M NaOH was added followed by 30 mL of a solution which was 3 M in NaOH and 0.5 M in $NaBH_4$. A black precipitate formed immediately. The mixture was stirred for about 30 min, whereupon the aqueous layer was saturated with NaCl. The mixture was extracted with 3 × 100 mL portions of *n*-pentane. The combined pentane extracts were washed with 2 × 50 mL portions of brine and then dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum by rotary evaporation afforded a clear oil. Chromatography of this oil on a 11 in. × 1.25 in. alumina (Fisher, 80–200 mesh) column (*n*-pentane eluent; 450 mL) afforded 8.7 g (63.6 mmol, 64% overall yield based on tetralin, 97% purity) of Δ^9-octalin.

Indan. The general procedure (vide supra) was used: 11.82 g (100 mmol) of indan (Aldrich) and 24.05 g (0.60 mol) of calcium were placed in 150 mL of methylamine and 150 mL of ethylenediamine. The mixture was stirred for 23.5 h during which time a large amount of gray solid had formed. After the usual workup, 10.17 g (83.2 mmol, 83% yield) of a light yellow oil was obtained. The oil was shown by ^{1}H NMR, ^{13}C NMR, and GLPC to consist of 88% 4,5,6,7-tetrahydroindan and 12% unknown material. See Table I, entry 12.

Purification of 4,5,6,7-Tetrahydroindan by Oxymercuration–Demercuration. Mercuric acetate (1.87 g; 5.87 mmol) was dissolved in 40 mL of deionized water. To this solution was added 3.59 g (29.4 mmol) of the crude 4,5,6,7-tetrahydroindan (see above) and 40 mL of THF. This material was purified in essential accordance with the procedure described above for the purification of Δ^9-octalin by oxymercuration–demercuration except that the reaction time was 2 h. The clear oil obtained after solvent removal by rotary evaporation was chromatographed on a 7.5 in. × 1.25 in. alumina (Fisher, 80–200 mesh) column (*n*-pentane eluent, 500 mL) to afford 2.55 g (81% based on the amount in the crude mixture) of 4,5,6,7-tetrahydroindan as a clear oil with 98% purity.

Durene. As described under General Procedure (vide supra) 13.42 g (100 mmol) of durene (Eastman), 24.05 g of calcium (0.60 mole in 150 mL of ethylenediamine, and 150 mL of methylamine

(29) A dry ice condenser works equally well.

were stirred for 25 h. By this time, all the calcium was consumed and the flask contained a large amount of gray solid. The usual workup was used: 12.28 g (90.1 mmol; 90% yield) of a white solid was obtained. This was shown by GLPC (Carbowax 20 M capillary column; 15 m × 0.25 mm; 60 °C) to be composed of 96% 1,2,4,5-tetramethyl-1,4-cyclohexadiene, 2% 1,2,4,5-tetramethyl-1,3-cyclohexadiene, and 1% durene. One crystallization of this solid from acetone gave 9.85 g (72%) of long white needles melting at 61.5–63 °C (lit. mp 61.9–62.2 °C)[10,12] (99% purity). Additional product could be obtained from the mother liquor which raised the total yield to 79%.

Anthracene. The general procedure was followed (vide supra): 8.96 g (50 mmol) of anthracene (Aldrich), 28.06 g (0.70 mol) of calcium, 50 mL of THF (freshly distilled from $LiAlH_4$) along with 150 mL of methylamine, and 150 mL of ethylenediamine were stirred together for 52 h. After 25 h, most of the calcium remained and only a small amount of gray solid had formed. After 52 h, most of the calcium had reacted and the flask now contained a large amount of gray solid. After the usual workup, 9.75 g (51.8 mmol) of a yellow–white solid was obtained which contained traces of residual solvent. After one crystallization from acetone an 87% yield of material was obtained which by GLPC (OV-101 capillary column, 25 m × 0.25 mm at 155 °C), ^1H NMR, and ^{13}C NMR analysis was shown to be a mixture of 1,2,3,4,5,6,7,8,9,10-decahydroanthracene (85%) and 15% impurities. Three more crystallizations from acetone gave a 25% yield of the decahydroanthracene of 98% purity melting at 66–68 °C (lit. mp 66–67 °C).[14]

***m*-Xylene.** The general procedure (vide supra) was followed: 10.62 g (100 mmol) of *m*-xylene (Aldrich) and 24.05 g (0.60 mol) of calcium in a mixture of 150 mL of ethylenediamine and 150 mL of methylamine were stirred for 24 h. Workup afforded 9.50 g (86%) of a yellow oil. Analysis by GLPC (Carbowax 20 M capillary column, 15 m × 0.25 mm) at 57 °C showed the oil contained a 98% mixture of two monoalkenes and 2% unknown. The ratio of the two isomers was determined by quantitative ^{13}C NMR as being 93% 1,3-dimethylcyclohexene and 5% 2,4-dimethylcyclohexene.

For a comparison of spectroscopic and chromatographic data an authentic sample of a mixture of 1,3-dimethylcyclohexene and 2,4-dimethylcyclohexene was prepared.[19,30] A pure sample of 1,3-dimethylcyclohexene purchased from Chemical Samples was also available for comparison purposes.

***p*-Xylene.** To *p*-xylene (Baker) (10.62 g; 100 mmol) was added 20.04 g (0.60 mol) of calcium in a mixture of 150 mL of ethylenediamine and 150 mL of methylamine. After stirring for 22 h, the mixture was worked up in the usual way and afforded 9.25 g (84%) of a light yellow oil. This was shown by GLPC (without further purification) to be composed of 1,4-dimethylcyclohexene (97%) and 3% impurities. See Table I, entry 7.

The above procedure was repeated using 5.31 g (50 mmol) of *p*-xylene and 10 g (0.25 mol) of calcium in 150 mL of ethylenediamine alone. The mixture was stirred for 24 h. At the end of the reaction, an appreciable amount of calcium remained and a gray solid was present. After the usual workup, 5.17 g (94%) of a light yellow oil was obtained, which by GLPC (see Table I, entry 7) was shown to contain 1,4-dimethylcyclohexene (95%) and 5% unknown material.

Cyclohexene. *n*-Nonane (2.57 g, 20 mmol, internal standard) and 8.22 g (100 mmol) of cyclohexene (freshly distilled) were weighed into a 25 mL glass-stoppered volumetric flask. The solution was mixed thoroughly and analyzed by GLPC (three chromatograms were obtained). From the three chromatograms the average ratio of cyclohexene to *n*-nonane was determined. This mixture was added to a reaction flask along with 10.02 g (0.25 mol) of calcium and 150 mL each of methylamine and ethylenediamine. The mixture was stirred for 23 h. At the end of this time a large amount of gray solid had formed, and only a small amount of finely divided calcium was visible. The mixture was worked up as described under General Procedure. It was then analyzed by GLPC (Carbowax 20 M capillary column, 15 m × 0.25 mm, at 55 °C) to determine the ratio of cyclohexene to *n*-nonane. A standard solution of cyclohexane and *n*-nonane was also prepared to determine the relative response factor. Analyses of the reaction product indicated a minimum recovery of 93% cyclohexene and less than 2% cyclohexane.

Attempted Reduction of *p*-Xylene with Gray Solid. Cyclohexene, 4.11 g (50 mmol), was treated with 5.01 g (0.125 mol) of calcium in 75 mL of methylamine and 75 mL of ethylenediamine for 25 h. At the end of this time all the calcium appeared to be gone, and a large amount of gray solid had formed. *p*-Xylene (5.31 g; 50 mmol) was added and the mixture was stirred for 41 h. There was little evidence of any reaction. After the usual workup, a clear oil was obtained which contained only *p*-xylene and cyclohexene.

Reduction of 1,2,4,5-Tetramethyl-1,4-cyclohexadiene by Lithium in Methylamine. The same setup described under General Procedure was employed. Into a 200-mL flask was placed 50 mL of methylamine, 1.01 g (7.43 mmol) of 1,2,4,5-tetramethyl-1,4-cyclohexadiene, and 0.25 g (0.036 mol) of lithium wire (Alfa) prewashed with anhydrous ether and cut into 0.25–0.50-in. lengths. The mixture was stirred for 3 h after which it was worked up in the usual fashion. There was obtained 0.91 g (89%) of a clear oil, which by GLPC (Carbowax 20 M capillary column; 15 m × 0.25 mm; 60 °C) was shown to consist of an isomeric mixture of 1,3,4,6-tetramethylcyclohexene (26%), 1,2,4,5-tetramethylcyclohexane (38%) along with 1,2,4,5-tetramethyl-1,3-cyclohexadiene[31] (9%), durene (3%), starting diene (16%), and 8% of unknown material.

Three or more of the possible isomers of 1,3,4,6-tetramethylcyclohexene were separated as a single mixture from the crude product by preparative GLPC on a 10% Carbowax 20 M on chromosorb A column (12 ft × $^1/_8$ in.) at 65 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.1 (CH_3's, 9 H), 1.63 (allylic CH_3's, 3 H, s), 1.1–2.2 (ring H's, 5 H), 5.12 (vinyl H's, 1 H).

One or both isomers of 1,2,4,5-tetramethylcyclohexene were separated from the crude product by preparative GLPC on a 10% Carbowax 20 M on Chromosorb A column (12 ft × $^1/_8$ in.) at 65 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (CH_3's, 6 H, 5 Hz, d), 1.66 (allylic CH_3's, 6 H), 1.00–2.10 (ring H's, 6 H).

The 1,2,4,5-tetramethyl-1,3-cyclohexadiene[31] structure was established by a combination of mass spectroscopy (*m/e* 136; calcd 136) and NMR. A slightly impure sample of the compound was collected by preparative GLPC (10% Carbowax 1500 on chromosorb W (60–80 mesh) column, 12 ft × $^1/_8$ in., at 120 °C). The ^1H NMR (200 mHz) showed several characteristic resonances for the suspected conjugated diene: a doublet at 0.93 ppm (non-allylic methyl, J = 8 Hz), singlets at 1.67, 1.71, and 1.76 (allylic methyls), and a singlet at 5.46 (vinyl H).

Reduction of 1,2,4,5-Tetramethyl-1,4-cyclohexadiene by Calcium–Methylamine–Ethylenediamine. The same setup described under General Procedure was employed. Into the 200-mL reaction flask was placed 50 mL of methylamine, 0.62 g (15.5 mmol) of calcium, 1.05 g (7.72 mmol) of 1,2,4,5-tetramethyl-1,4-cyclohexadiene, and 50 mL of ethylenediamine. The mixture was stirred for 48 h at which time all the calcium appeared to be consumed. The usual workup afforded 1.07 g (100%) of a white sticky solid which by GLPC (Carbowax 20 M capillary column, 15 m × 0.25 mm at 60 °C) was shown to consist of an isomeric mixture[32] of 1,3,4,6-tetramethylcyclohexene (8%) and 1,2,4,5-tetramethylcyclohexene (7%) along with 1,2,4,5-tetramethyl-1,3-cyclohexadiene[31] (1%), 1,2,4,5-tetramethyl-1,4-cyclohexadiene (76%), durene (4%), and 4% unknown material.

Isomerization of 1,2,4,5-Tetramethyl-1,4-cyclohexadiene by Preformed Lithium Methylamide. The same setup described under General Procedure was employed. Into the 200-mL reaction flask was placed 50 mL of methylamine, 2.30 g (29.5 mmol) of benzene (Baker Reagent 99.9%), and 0.41 g (59.1 mmol) of lithium wire (Alfa) prewashed with anhydrous ether and cut into 0.25–0.5-in. lengths. The mixture was stirred for 2 h and then 2.00 g (14.7 mmol) of 1,2,4,5-tetramethyl-1,4-cyclohexadiene was

(30) The reduction of *p*-xylene by lithium in methylamine is reported to give 1,4-dimethyl-1-cyclohexene in 65% yield. Likewise reduction of *m*-xylene by the same reagent yields a mixture of 1,3-dimethylcyclohexene (61%) and 2,4-dimethylcyclohexene (37%). Agnihotri, R. K. Ph.D. Thesis, Purdue University, 1963.

(31) Downes, A. M.; Gill, N. S.f Lions, F. *J. Am. Chem. Soc.* **1950**, *72*, 3464.

(32) Spectroscopic data will be found in Experimental Section under the heading: "Reduction of 1,2,4,5-Tetramethyl-1,4-cyclohexadiene by Lithium in Methylamine".

added. It was then stirred for an additional 63.5 h. The usual workup afforded 2.05 g (100%) of a light yellow sticky solid, which by GLPC (Carbowax 20 M capillary column, 15 m × 0.25 mm, at 60 °C) was shown to consist of durene (72%), 1,2,4,5-tetramethyl-1,4-cyclohexadiene (17%), and 1,2,4,5-tetramethyl-1,3-cyclohexadiene[31,32] (10%).

Isomerization of 1,2,4,5-Tetramethyl-1,4-cyclohexadiene by Preformed Amides Derived from Calcium–Methylamine–Ethylenediamine. The same setup described under General Procedure was employed. Into the 200-mL reaction flask was placed 50 mL of methylamine, 50 mL of ethylenediamine, 1.82 g (23.3 mmol) of benzene, and 0.93 g (0.023 mol) of calcium. The mixture was stirred for 28.6 h, during which time a gray solid formed and all the calcium appeared to be consumed. At this point 1,2,4,5-tetramethyl-1,4-cyclohexadiene (1.58 g; 11.6 mmol) was added and the mixture was stirred for an additional 88 h. The usual workup afforded 1.47 g (93%) of a white sticky solid, which by GLPC (Carbowax 20 M capillary column, 15 m × 0.25 mm, at 60 °C) was shown to consist of durene (4%), 1,2,4,5-tetramethyl-1,4-cyclohexadiene (90%), and 1,2,4,5-tetramethyl-1,3-cyclohexadiene[31,32] (6%).

Acknowledgment. This work was supported by the Department of Energy Office of Basic Energy Sciences under Contract DE-AC02-81ER10989. The Varian XL-200 spectrometer used in this work was purchased with funds from NSF Grant CHE-8004246. This support is gratefully acknowledged.

Registry No. Naphthalene, 91-20-3; tetralin, 119-64-2; durene, 95-93-2; anthracene, 120-12-7; *tert*-butylbenzene, 98-06-6; cumene, 98-82-8; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *o*-xylene, 95-47-6; norbornadiene, 121-46-0; norbornene, 498-66-8; indan, 496-11-7; mesitylene, 108-67-8; calcium, 7440-70-2; methylanine, 74-89-5; ethylenediamine, 107-15-3; Δ^9-octalin, 493-03-8; $\Delta^{1(9)}$-octalin, 1194-95-2; 1,2,4,5-tetramethyl-1,4-cyclohexadiene, 26976-92-1; 1,2,3,4,5,6,7,8,9,10-decahydroanthracene, 3485-60-7; 1-*tert*-butylcyclohexene, 3419-66-7; 1-isopropylcyclohexene, 4292-04-0; 3-isopropylcyclohexene, 3983-08-2; 1,4-dimethylcyclohexene, 2808-79-9; 1,3-dimethylcyclohexene, 2808-76-6; 1,2-dimethylcyclohexene, 1674-10-8; norbornane, 279-23-2; nortricyclene, 279-19-6; 4,5,6,7-tetrahydroindane, 695-90-9; *cis*-1,3,5-trimethylcyclohexene, 24583-97-9; *trans*-1,3,5-trimethylcyclohexene, 86436-70-6; 1,3,4,6-tetramethylcyclohexene, 86436-71-7; 1,2,4,5-tetramethylcyclohexene, 86436-72-8.

Diels–Alder Reactions of Cycloalkenones. 3. Effects of Specific Reaction Parameters[1]

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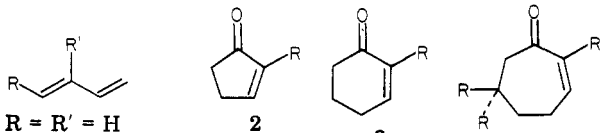
The effects of the Lewis acid–ketone complexation time and temperature, the nature and amount of catalyst, and the concentrations of ketone and diene on the Diels–Alder reactions of 2-cyclopentenones, 2-cyclohexenones, and 2-cycloheptenones with 1,3-butadiene, isoprene, and (*E*)-piperylene are described.

The recent past has witnessed the widespread use of acid catalysis in Diels–Alder reactions, especially of 2-cycloalkenones with butadienes. Since a survey of the literature reveals the use of a broad range of reaction conditions and the consequent acquisition of a variety of product yields, it became necessary to investigate the reaction parameters responsible for the previous observations and to standardize the reaction conditions at an optimum yield level, thus enhancing the great potential of the cycloaddition process in organic synthesis. The study was initiated with the reactions between the dienes 1,3-butadiene (**1a**), isoprene (**1b**), and (*E*)-piperylene (**1c**) and the cycloalkenones 2-cyclopentenone (**2a**), 2-methyl-2-cyclopentenone (**2b**), 2-cyclohexenone (**3a**), 2-methyl-2-cyclohexenone (**3b**), 2-cycloheptenone (**4a**), and 2,6,6-trimethylcycloheptenone (**4b**) and indicated at an early stage



1a, R = R′ = H
b, R = H; R′ = Me
c, R = Me; R′ = H

2

3

4

a, R = H
b, R = Me

Table I. Products of the Aluminum Chloride Catalyzed Reactions of Dienes 1 and Cycloalkenones 2–4 in Toluene Solution

starting materials	products	product ratio	total yield, %
1a-2a	5a (n = 2), 6a (n = 2)	1.2:1	95
1a-3a	5a (n = 3), 6a (n = 3)	9:1	84
1a-2b	6d (n = 2)		92
1a-3b	6d (n = 3)		93
1b-2a	5b (n = 2), 6b (n = 2)	1:1.7	80
1b-3a	5b (n = 3), 6b (n = 3)	18:1	70
1b-4a	5b (n = 4), 6b (n = 4)	1:45	73
1b-2b	6e (n = 2), 9 (n = 2)	6.3:1	73
1b-3b	6e (n = 3), 9 (n = 3)	32:1	79
1b-4b	8b		90
1c-2a	5c (n = 2), 6c (n = 2)	200:1	77
1c-3a	5c (n = 3), 6c (n = 3)	1:1.8	81
1c-4a	5c (n = 4), 6c (n = 4)	1:>200	80
1c-3b	6f (n = 3), 7	2.2:1	92
1c-4b	8c		85

that products 5–9 can be obtained in high total yield (Table I) in toluene solution with aluminum chloride catalysis. Whereas an earlier report described the experimental details of these reactions and the structure analysis of the products,[1b] the present communication illustrates the effect of specific reaction parameters on the product yield.

The Complexation Process. The complexation of the cycloalkenones with the Lewis acids represents a key operation in the catalyzed Diels–Alder reaction and influences the final product yield by its dependence on the

(1) For previous papers see: (a) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *Synth. Commun.* **1979**, *9*, 391. (b) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056. (c) Fringuelli, F.; Minuti, L.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *Ibid.* **1983**, *48*, 1810.

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