Registry No.—I, 13428-10-9; III, 13422-27-0; IV, 13422-28-1; V, 13407-19-7; VI, 13422-27-2; β-(o-hydroxyphenyl)ethyl mercaptan, 13407-20-0.

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Reduction of Aromatic Compounds with Alkali Metals in Amine Solvents and in Aprotic Liquids Containing Ammonia

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The properties of the alkali metals and mixtures thereof have been compared for the reduction of aromatic compounds in neat methylamine (and related media) at elevated temperatures, 60–190°. Like lithium, potassium and rubidium readily reduce benzene and alkyl-substituted benzenes to cyclic monolefins. While sodium is ineffective, sodium in the presence of small amounts of potassium or rubidium does reduce benzene. Potassium is considerably more selective than lithium for the synthesis of 1-alkylcyclohexenes from alkylbenzenes. The coproduct, potassium methylamide, readily isomerizes alkylcyclohexenes to an equilibrium distribution of the olefin isomers. Tetralin is reduced by potassium to a mixture containing $\geq 95\%$ $\Delta^{9,10}$-octalin. Aprotic liquids containing ammonia in quantities stoichiometric or less to the metal also are suitable media for the reduction of aromatic compounds.

Aromatic compounds in a suitable solvent are reduced readily by alkali metals,[1–4] alkaline earth metals,[3,5] and even by two rare earth elements, europium and ytterbium.[6] The course of the reaction is dependent upon the temperature, the metal, and the solvent. For example, benzene is reduced mainly to 1,4-cyclohexadiene by sodium in liquid ammonia at *ca.* −34°, provided a substance (alcohols, water, etc.) more acidic than ammonia is present.[1–4] On the other hand, added acids are not required and the product is exclusively cyclohexene when the reaction temperature is ~60–130°.[7] At the higher temperatures, the reduction can be stopped at the diene stage if lithium is used.[7] In refluxing ammonia, lithium is better than sodium for the conversion of certain aromatic compounds to dienes.[8] Benkeser and co-workers found low molecular weight monoamines, particularly methylamine and ethylamine, to be excellent media for reductions with lithium.[9–16] In neat monoamines, aromatic compounds are reduced to monoolefins[9,13,15] whereas in monoamine–alcohol solutions diolefins are obtained.[14] The isomeric distribution of monoolefins obtained from naphthalene or substituted benzenes is dependent upon the composition of mixed amine solvents.[13,15,16] Under certain conditions, lithium–monoamine reagents are strong enough to reduce isolated double bonds.[10,12] The most potent but least selective of the metal reagents thus far developed is lithium in ethylenediamine (reaction temperature, 90–100°).[17] The latter is useful for completely saturating ring systems and for the reduction of very inert materials.

In most cases, the above experiments were performed at the reflux temperature of the solvent. Since this temperature varies, it is difficult to sort out observed effects which are due to the intrinsic properties of the solvent or metal and effects which are due to temperature differences. We would like to report the results of an investigation wherein aromatic compounds were reduced by metals in neat amines or in aprotic media containing limited amounts of ammonia.[18] An autoclave system was used which made it possible to vary the conditions at will regardless of the boiling point of the solvent. The reducing capabilities of several alkali metals and alloys thereof have been compared. These comparisons are necessarily qualitative since the solubilities of the metals under the various conditions are not known.

Results and Discussion

An autoclave was charged with the aromatic hydrocarbon, alkali metal, and solvent and heated to the desired temperature (>25°). Stirring was applied with a paddle speed of 1000 rpm. The resultant organic product, excess solvent, and metal amide[19] were separated by distillation. In all cases, part of the metal reacted with the amine or ammonia solvent forming metal amides and hydrogen. This side reaction lowers the efficiency of metal utilization. In order to facilitate comparisons of the metals, the yields of products

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TABLE I

REDUCTION OF AROMATIC COMPOUNDS BY VARIOUS METALS[a]

							Reduced product	
Expt	ArH, moles	Metal, g-atom	Solvent, moles	Temp, °C	Time, hr	Convn of ArH,[h] %	Compn, %	Yield[b] based on metal, %
1	C_6H_6, 0.05	Li, 0.25	CH_3NH_2, 1.3	100	6.5	74.5	C_6H_{10},[c] 98.2 C_6H_{12},[d] 1.8	60
2	C_6H_6, 0.1	Li, 0.4	$C_2H_5NH_2$, 1.1	85	8	77.4	C_6H_{10},[c] 100	77.4
3	*t*-BuC_6H_5, 0.1	Li, 0.4	CH_3NH_2, 2.0	100	12	61.2	*t*-BuC_6H_9,[e] 100	61.2
4	*o*-Xylene, 0.1	Li, 0.4	CH_3NH_2, 1.9	100	12	52	$(CH_3)_2C_6H_8$,[f] 100	52
5	C_6H_6, 0.1	K, 0.4	CH_3NH_2, 2.0	61[g]	0.7	39.2	C_6H_{10},[c] 100	39.2
6	C_6H_6, 0.026	K, 0.038	CH_3NH_2, 1.0	28 50	1.3 0.5	5.7	C_6H_{10},[c] 100	15.2
7	C_6H_6, 0.033	Rb, 0.034	CH_3NH_2, 1.0	26 46	1.5 1.0	4.8	C_6H_{10},[c] 100	18.9
8	C_6H_6, 0.031	Cs, 0.038	CH_3NH_2, 1.0	32 53	1.8 0.8	~0		0
9	C_6H_6, 0.1	Na, 0.34 K, 0.05	CH_3NH_2, 2.0	100	5	41.1	C_6H_{10},[c] 100	>41.1
10	C_6H_6, 0.1	Na, 0.35 Rb, 0.05	CH_3NH_2, 2.0	60	4.5	23.3	C_6H_{10},[c] 100	>23.3

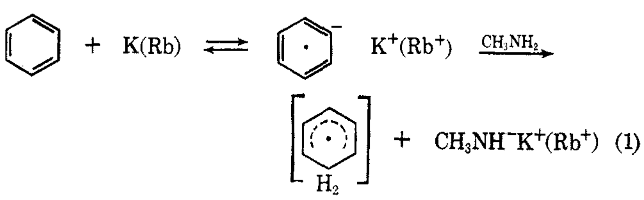
[a] Hydrocarbon material balances were ususally 90–100%. All of the metal reacted, except in expt 9 and 10. [b] Percent of the reacted metal which effected the reduction of the aromatic compound. The remainder reacted with the solvent. [c] Cyclohexene. [d] Cyclohexane. [e] *t*-Butylcyclohexenes. [f] A mixture of 1,2-, 1,6-, 3,4-, and 4,5-dimethylcyclohexenes. [g] Reduction also occurs at 18°. [h] % conversion of ArH = 100 [(initial moles of ArH − recovered moles of ArH)/initial moles of ArH].

are based on the metal which reacted (see footnote *b*, Table I).

A comparison of the data in Table I with those obtained previously[7] shows that, under similar conditions (85–100°), lithium in methylamine or ethylamine produces higher yields of cyclohexene from benzene than does sodium in neat ammonia. Apparently, lithium does not react directly with the amine solvent as readily as does sodium with ammonia. The lithium–amine reagents are considerably more potent for the reduction of alkylbenzenes than is sodium in ammonia. The yields, based on the metal, for the reduction of *t*-butylbenzene and *o*-xylene are only 1–2% for the latter reagent[7] compared to 50–60% for the former reagents (expt 3 and 4). It is interesting that little cyclohexane is obtained from benzene with the lithium–amine reagents under the present conditions since Benkeser and co-workers obtained a mixture of cyclohexene and cyclohexane at a lower reaction temperature (17°).[9,10] However, the Li/ArH molar ratio they employed was higher than that presently used, which may account for the difference in the results.

There is a marked difference between the reducing properties of lithium and sodium. For example, very little reduction of benzene occurred at temperatures of 100–190° with sodium in ethylamine, methylamine, or ethylamine containing substantial amounts of ammonia. The only significant reaction to occur was a slow one between the metal and amine to form sodium alkylamides. Potassium in methylamine behaves more like lithium than like sodium. The potassium reagent converts benzene exclusively to cyclohexene at 18–60° (Table I, expt 5). The yield of cyclohexene, based on the metal, is lower with potassium than with lithium (compare expt 1 and 2 with 5). Whereas rubidium behaves like potassium, cesium reacts more rapidly with the methylamine solvent to produce hydrogen (compare expt 6, 7, and 8). Some reduction of benzene could be obtained with cesium at higher metal concentrations.

While sodium alone in methylamine is ineffective, sodium in the presence of small amounts of potassium or rubidium does reduce benzene. For example, with metal mixtures where the Na/K and Na/Rb g-atom ratios were ~7:1, at least 34 and 11.5%, respectively, of the sodium participated in the reduction (expt 9 and 10). With cesium present, the participation by sodium was considerably less. There are several paths whereby sodium might be consumed in these reactions. Possibly, potassium or rubidium initiates the reduction (eq 1) and sodium reduces only the resultant, more reactive radical or diene intermediates. Alternatively, the reduction potential of sodium in the alloys may be sufficiently high to allow participation by sodium in eq 1. Also, sodium may participate in one or both of the exchange reactions given by eq 2 and 3.



(1)

(2)

$$CH_3NH^-K^+(Rb^+) + Na \rightleftharpoons CH_3NH^-Na^+ + K(Rb) \quad (3)$$

Several amine solvents were tested for the potassium reduction of benzene; however, methylamine proved to be best. For a given quantity of metal (0.4 g-atom), the following conversions of benzene (0.1 mole) to cyclohexene were obtained at 60° in 70–100 ml of methylamine, ethylamine, and *n*-butylamine: 39.2, 15.2, and 11.7%, respectively. Little or no reaction occurred in dimethylamine. Unlike lithium,[17] potassium in ethylenediamine gave a poor yield of reduced material. The residue remaining after removal of the liquid product by distillation was an intractable, purple slurry. Usually, white powdery metal alkylamides were obtained.

Potassium and lithium in methylamine differ in several respects for the reduction of toluene at ~60° (Table II). The former metal reacted more rapidly,

TABLE II

REDUCTION OF AROMATIC COMPOUNDS IN METHYLAMINE[a]

Expt	ArH, moles	Metal	Time, hr	Convn of ArH,[b] %	Reduced product	
					Compd	Compn, %
11	Toluene, 0.1	Li	4 (2.5)[e]	83.6	1-Methylcyclohexene	65
					3- and 4-methylcyclohexene	33
					Methylcyclohexane	2
12	Toluene, 0.1	K	7.5	44	1-Methylcyclohexene	92.7
					3- and 4-methylcyclohexene	7.3
13	Toluene, 0.1	K	0.8	48	1-Methylcyclohexene	83.7
					3- and 4-methylcyclohexene	15.1
					Methylcyclohexane	1.2
14	Cumene, 0.1	K	3	62	1-Isopropylcyclohexene[c]	83.4
					3- and 4-isopropylcyclohexene	10.3
15	*t*-Butylbenzene, 0.1	K	2	75.5	1-*t*-Butylcyclohexene	86.1
					3- and 4-*t*-butylcyclohexene	13.9
16	*t*-Butylbenzene, 0.1	Li	8	59.8[d]	1-*t*-Butylcyclohexene	69.6
					3- and 4-*t*-butylcyclohexene	30.4
17	*o*-Xylene, 0.1	K	1.3	33.6	1,2-Dimethylcyclohexene	83
					1,6-, 3,4- and 4,5-dimethylcyclohexene	17
18	Naphthalene, 0.05	K	3	100	Unidentified dimers	36.1
					Octalins	63.9[f]
19	Tetralin, 0.1	K	2.3	40.3	$\Delta^{9,10}$-Octalin	≥95
					$\Delta^{1,9}$-Octalin	≤5[g]
					No dimers	
20	1,3,5-Trimethylbenzene, 0.1	K	2	50.4	1,3,5-Trimethylcyclohexene	100[h]

[a] Methylamine, 2.0 moles; metal, 0.4 g-atom; temperature, 60–68°. The metal was completely reacted in all experiments except 16. Hydrocarbon balances were 88–100% as determined by glpc. The product compositions were normalized to 100%. [b] In these experiments where the K/ArH ratio is 4:1 and all of the metal has reacted, the yields of the cyclic monoolefins, based on the metal, are the same as the per cent conversions of the substrates. [c] Diene (6.3%), also may have been formed. [d] A lower than expected conversion resulted because part of the metal had not reacted. [e] The metal was consumed in ~2.5 hr. [f] Isomer distribution was not determined. [g] Part of the material listed as $\Delta^{1,9}$-octalin could be other double-bond isomers. [h] Identified by mass spectrometric analysis only. Some methylenedimethylcyclohexane could be present.

~0.8 hr *vs.* ~2.5 hr (expt 13 and 11, respectively),[20] but the yield of methylcyclohexenes was greater with lithium (83.6%) than with potassium (48%). Potassium is more selective, ~93% (expt 12) *vs.* ~65% (expt 11), for the synthesis of 1-methylcyclohexene. The product composition we obtained with lithium in methylamine at 60° is similar to the 59% 1-methylcyclohexene and 41% 3- and 4-methylcyclohexenes obtained with the same reagent at −7°.[21] The measured equilibrium concentrations of the olefins at 118° are 91–93% 1-methylcyclohexene and 9–7% 3- and 4-methylcyclohexenes.[15] Apparently, an equilibrium distribution of methylcyclohexenes results with potassium but not with lithium. Benkeser and co-workers found that the coproduct lithium methylamide was a poor double-bond isomerization catalyst at −7°. Independently, we demonstrated that lithium methylamide in methylamine isomerizes 4-methylcyclohexene only slowly even at 60°. Therefore, in the case of lithium, the isomer distribution of monoolefins must be predetermined, by the nature and concentrations of the precursors, which upon reduction produce the monoolefins. These precursors are very likely cyclohexadienes.[15] On the other hand, we found that potassium methylamide in methylamine rapidly isomerized 4-methylcyclohexene at 60° (see Experimental Section). It appears that double-bond isomerization is responsible for the equilibrium distribution of methylcyclohexenes obtained from the potassium reduction of toluene in methylamine. Consistent with this proposal, the relative amount of 1-methylcyclohexene increased with the reaction time (compare expt 12 and 13).

In addition to toluene, several exemplary aromatic compounds also were reduced with potassium in methylamine (Table II). In each instance, the isomer with the most substituents on the double bond was the dominant product. As was the case for the formation of 1-methylcyclohexene from toluene, potassium is more selective than lithium for the synthesis of 1-*t*-butylcyclohexene from *t*-butylbenzene (compare expts 15 and 16). The relative amount of 1-*t*-butylcyclohexene, ~86%, obtained with potassium is higher than the measured equilibrium concentration of the isomer, 76–79% at 118°.[15]

It is possible to increase the yield of $\Delta^{9,10}$-octalin, obtained from the lithium reduction of naphthalene, from 52 to 80% (20% $\Delta^{1,9}$-octalin also formed) by using a dimethylamine–ethylamine mixture rather than neat ethylamine as the solvent.[15,16] Potassium in neat methylamine produced considerable dimer besides octalins (expt 18). However, potassium in methylamine reduced tetralin to a mixture composed of ≥95% $\Delta^{9,10}$-octalin and ≤5% $\Delta^{1,9}$-octalin[22] (expt 19). This appears to be a procedure of choice for the preparation of the former compound.

When a mixture of benzene and an alkylbenzene (toluene, *t*-butylbenzene, etc.) was reduced by potassium in methylamine, benzene was more extensively converted than was the alkylbenzene (Table III). This result was expected since the intermediate anion

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(20) The approximate time required for the complete consumption of the metal was estimated from the pressure profile of the reaction. When all the metal had reacted, the pressure within the autoclave ceased to increase from concurrent hydrogen formation.

(21) Benkeser and co-workers were able to increase the selectivity for 1-methylcyclohexene to 76% by using a mixture of methylamine and dimethylamine rather than neat methylamine as the solvent.[15]

(22) Part of the material listed as $\Delta^{1,9}$-octalin could be other double-bond isomers.

TABLE III

REDUCTION OF AROMATIC HYDROCARBON MIXTURES[a]

Expt	Substrate mixtures, mmoles	Product composition,[b] mmoles				Total yield of monoolefins,[c] %
		Benzene	Cyclohexene	Alkylbenzene	Alkylcyclohexene	
21	Benzene, 50 Toluene, 50	25.3	24.7	36.6	13.4	38
22	Benzene, 50 *t*-Butylbenzene, 50	Trace	~50	43.3	6.7	57
23	Benzene, 50 *p*-Xylene, 50	20.7	29.3	34.3	15.7	45
24	Benzene, 75 *t*-Butylbenzene, 25	28.7	46.3	17.5	7.5	54
25	Benzene, 75 Cumene, 25	31.5	43.5	18.6	7.4	50

[a] Potassium, 0.4 mole; methylamine solvent, 2.0 moles; reaction time, 2.0 hr; temperature, ~55–75°. All of the metal was consumed in each experiment. [b] The aromatic hydrocarbons were reduced to the corresponding cyclohexenes; no dienes were formed. Material balances were >90%. The product composition has been normalized to 100%. [c] Based on the metal.

radicals of alkylbenzenes should form less readily than the anion radical of benzene. Consequently, benzene should reduce more rapidly in a common environment where the two substrates compete for the unreacted metal. It is noteworthy that the total yield of cyclic monoolefins, based on the metal, was usually greater than was the yield of cyclohexene (39.2%) obtained from benzene alone (compare expt 5, Table I, with expt 22–25, Table III).

An interesting result was obtained when the aromatic compounds were reduced individually in separate experiments (~60°, ArH, 0.1 mole; K, 0.4 g-atom; CH_3NH_2, 2.0 mole). The conversions were benzene 39.2% (expt 5), toluene 48% (expt 13), cumene 62% (expt 14), and *t*-butylbenzene 75.5% (expt 15).[23] These conversions are a measure of the relative quantities of the metal which reacted with the aromatic hydrocarbon and with the solvent to produce hydrogen. Therefore, it appears that the metal–methylamine reaction is more competitive with the reduction of benzene than it is with the reduction of the alkylbenzenes. This was not the case for sodium reductions in neat ammonia where the conversion of benzene was greater than that of an alkylbenzene.[7]

Aprotic solvents containing ammonia in quantities stoichiometric or less to the metal also are suitable media for the reduction of aromatic compounds. Aprotic media used were *n*-dodecane, excess of the aromatic substrate, tetrahydrofuran, diethyl ether and trimethylamine. For example, benzene (0.1 mole) in 40 ml of tetrahydrofuran containing 0.4 mole of ammonia and 0.4 g-atom of potassium was reduced (1.5 hr, 55°) to cyclohexene in 58% yield, based on the metal. Similar experiments in *n*-dodecane (50 ml) or excess benzene (0.5 mole, 45 ml) produced cyclohexene in 30 and 48% yields, respectively. Whereas potassium and rubidium in excess benzene produce cyclohexene, cyclohexadienes are obtained with lithium. Alkyl-substituted benzenes are reduced by potassium under these conditions in lower yields than is benzene.

Experimental Section

Reagents.—The aromatic compounds and aprotic solvents were of high purity and were usually distilled from lithium aluminum hydride. Anhydrous, reagent grade methylamine, and ethylamine were obtained from the Matheson Co. and Eastman Kodak, respectively. Reagent grade potassium and lithium metals were obtained from Mallinckrodt Chemical Works and Lithium Corp. of America, respectively. Cesium and rubidium were purchased from Alpha Inorganics, Inc. Sodium–potassium and sodium–rubidium alloys were prepared *in situ* by fusing the two appropriate metals. Ethylenediamine was distilled from sodium–potassium alloy.

General Procedure.—A 300-ml, stainless steel Magnadrive autoclave was loaded inside a nitrogen-flushed drybox with the reactant metal, aromatic compound to be reduced, and, when appropriate, an aprotic liquid. Outside of the drybox, methylamine or ammonia was distilled before being introduced into the autoclave from a weighed stainless steel vessel of ~250-ml capacity. Ethylamine was introduced into the evacuated and cooled autoclave from vials as purchased without prior distillation.

The autoclave was then heated to the desired temperature and stirred at a paddle speed of ~1000 rpm. After the reaction was complete, the system was cooled to room temperature and the excess amine or ammonia (when present) was allowed to evaporate through a suitable solvent scrubber, *e.g.*, toluene when benzene was reduced. A vacuum was applied through the scrubber to the autoclave and the organic product distilled into the solvent. This distillation procedure worked well for substrates such as benzene, toluene, *o*-xylene, and *t*-butylbenzene. However, for tetralin, the organic product was separated by filtration and solvent washing of the resultant metal amide. The results of most of these experiments are listed in the text tables. The weights of the coproduct metal amides were usually 95–100% of theory. The following is a typical analysis of the white, powdery potassium methylamide isolated when neat methylamine was the solvent and potassium the reducing metal.

Anal. Calcd for $KNHCH_3$: C, 17.37; H, 5.83; N, 20.26; K, 56.54. Found: C, 16.3; H, 6.0; N, 20.6; K, ~54.

Caution! Metal alkylamides may explode when exposed to air.[19]

Analyses and Identification of Organic Products.—The products from the reduction of benzene and toluene were analyzed as reported previously.[7] 1-Isopropylcyclohexene was resolved quantitatively from 3- and 4-isopropylcyclohexenes by glpc with a 20-ft polyphenyl ether–Carbowax column at 170°. Mass spectrometric analyses confirmed the assigned molecular weight of the products and showed that cyclic dienes were not present. The 60-Mc/sec nmr spectrum (Varian Associates, A-60) of the isolated (Wilkins Autoprep glpc) 1-isopropylcyclohexene was consistent with the proposed structure. That is, absorptions were centered at δ 5.5 ppm from tetramethylsilane (TMS) which indicates the presence of only one vinylic (olefinic) hydrogen. Also, absorptions were centered at 1.4–2.5 ppm from TMS for nine hydrogens and a doublet was centered at ~1.1 ppm from TMS for six hydrogens.

1,2-Dimethylcyclohexene resulting from *o*-xylene was resolved quantitatively from 1,6-, 3,4-, and 4,5-dimethylcyclohexenes by glpc with a 20-ft polyphenyl ether–Carbowax column at 150°. Mass spectrometric analyses confirmed the assigned molecular weights of the products and showed that dienes were not present. The 60-Mc/sec nmr spectrum of the isolated 1,2-dimethylcyclohexene was consistent with the proposed structure. That is, no vinylic hydrogens were present since absorptions at δ ~5.5

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[23] See footnote *b* of Table II.

ppm from TMS were absent. Absorptions for the 14 hydrogens of the molecule occurred at 1.4–2.3 ppm from TMS.

A glpc analysis (polyphenyl ether–Carbowax column) indicated that the 1,3,5-trimethylbenzene content of this reactant substrate was $\sim$95%. The remaining material apparently consisted of other isomeric trimethylbenzenes. The product was resolved quantitatively on the above glpc column. A mass spectrometric analysis showed that the main product was 1,3,5-trimethylcyclohexene. No cyclic dienes were formed.

The product from the reduction of tetralin was resolved from tetralin by glpc with a 20-ft polyphenyl ether–Carbowax column at 250°. The mass spectrum of the product showed it to be octalin, $C_{10}H_{16}$. The infrared spectrum corresponded closely to that $\Delta^{9,10}$-octalin,[24] but weak bands at 10.8 and 11.5 μ and the enhancement of the 12.5-μ band might be due to minor amounts of $\Delta^{1,9}$-octalin. The 60-Mc/sec nmr spectrum indicated the product to be $\sim$95% $\Delta^{9,10}$-octalin. That is, from the area under the absorption centered at δ $\sim$5.3 ppm from TMS for vinylic hydrogens, the amount of $\Delta^{1,9}$-octalin must be $\sim$5%. If the double bond were located in one of the other nonsymmetrical positions so that two vinylic hydrogens per double bond were present, the calculated amount of octalins other than $\Delta^{9,10}$-octalin would be even less than 5%.

1-*t*-Butylcyclohexene was resolved by glpc from the other olefin isomers and unreacted *t*-butylbenzene. Mass spectrometric, infrared, and nmr analyses confirmed assigned structures of the products. The 60-Mc/sec nmr spectrum of 1-*t*-butylcyclohexene showed absorption centered at 5.65 ppm from TMS for one vinylic hydrogen, at 2.2 ppm for four allylic hydrogens, at 1.78 ppm for four other hydrogens, and a singlet at 1.2 ppm for the nine equivalent *t*-butyl hydrogens.

Isomerization of 4-Methylcyclohexene.—According to the general procedure described above, 0.4 mole of potassium methylamide (isolated from a reaction of potassium with toluene in methylamine at 100°), 0.1 mole of 4-methylcyclohexene (Aldrich Chemical Co.), and 59 g of anhydrous methylamine were stirred in a 300-ml, stainless steel Magnadrive autoclave for 1.0 hr at 60°. In a second experiment, 4-methylcyclohexene was treated similarly with 0.4 mole of lithium methylamide (prepared in the same manner as potassium methylamide). Analyses (glpc) of the methylcyclohexene before and after treatment with the metal methylamides showed the compositions given in Table IV.

TABLE IV

	4-Methylcyclohexene, %	3-Methylcyclohexene, %	1-Methylcyclohexene, %
Olefin before isomerization	95		5
Olefin after CH_3NHK treatment	8[a]		92
Olefin after CH_3NHLi treatment	91.5[a]		8.5

[a] Sum of 4-methyl- and 3-methyl-cyclohexenes.

Registry No.—Potassium methylamide, 13427-02-6; 1-isopropylcyclohexene, 4292-04-0; 1,2-dimethylcyclohexene, 1674-10-8; 1-*t*-butylcyclohexene, 3419-66-7; $\Delta^{9,10}$-octalin,493-03-8.

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Peracetic Acid Oxidation of Hydrazones. II. Aliphatic Ketone and Aldehyde Alkylhydrazones[1-3]

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The oxidation of aliphatic ketone monoalkylhydrazones $R_1R_2C{=}NNHR_3$ with peracetic acid furnished azoacetates and azoxyacetates of the types $R_1R_2C(O_2CCH_3)N{=}NR_3$ (**1**) and $R_1R_2C(O_2CCH_3)N(O){=}NR_3$ (**2**), respectively. The latter compounds were shown by an independent synthesis to be formed in the reaction by the peracetic acid oxidation of the corresponding **1**. The aliphatic aldehyde monoalkylhydrazones $R_1CH{=}NNHR_3$ were oxidized by peracetic acid to acetylalkylhydrazides of the type $R_1CONHN(COCH_3)R_3$ (**6**). These products were postulated to form by an O → N acyl migration in an intermediate hydrazimino anhydride, the tautomer of an azoacetate of type **1**, where R_2 = H. The type-**2** compounds were found labile to acid, liberating nitrogen, $R_1R_2C{=}O$, and R_3OH.

The peracetic acid oxidation of aromatic aldehyde monoalkylhydrazones had been investigated previously and reported to yield simple azoxy compounds.[3] The present investigation was undertaken in an attempt to extend this reaction to aliphatic ketone and aldehyde monoalkylhydrazones.

When cyclohexanone methylhydrazone was oxidized with peracetic acid using a 1:1 ratio, two products, 1-(methylazo)cyclohexanol acetate (**1a**) and 1-(methylazoxy)cyclohexanol acetate (**2a**)[4] were isolated in 41 and 15% yield, respectively. When a 2:1 ratio of peracetic acid to hydrazone was used, a greater amount of decomposition was noticed from which a 17.5% yield of **2a** was obtained and no **1a** was isolated. These results were undoubtedly due to the complete oxidation of **1a** by peracetic acid and to the labile nature of **2a** toward acid. The structures of **1a** and **2a** were demonstrated by independent synthesis and spectral studies. Oxidation of cyclohexanone methylhydrazone by the method of Iffland, *et al.*,[5] using lead tetraacetate furnished authentic **1a**. This material was then oxidized with peracetic acid to yield authentic **2a** in 55% yield (Scheme I).

Oxidation of cyclohexanone phenylhydrazone with 1 equiv of peracetic acid yielded 29% of 1-(phenylazo)cyclohexanol acetate (**1b**) and 6% of 1-(phenylazoxy)cyclohexanol acetate[4] (**2b**). When a 2:1 ratio of per acid to hydrazone was used, the large amount of

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[2] Abstracted from the Ph.D. Dissertation of K. F. Schimmel, Duquesne University, 1961.

[3] Previous paper: B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **27**, 413 (1962).

[4] The nomenclature used herein is consistent with that used in ref 3.

[5] D. C. Iffland, L. Salisbury, and W. R. Schaffer, *J. Am. Chem. Soc.*, **83**, 747 (1961).