

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

**Reduction of Multiple Carbon Bonds. V. The Reduction of Aromatic Hydrocarbons and Dialkylacetylenes by Calcium Ammonia<sup>1,2</sup>**BY KENNETH N. CAMPBELL AND JOHN P. McDERMOTT<sup>3</sup>

A general study of the reduction of unsaturated hydrocarbons by various chemical reducing agents has been in progress in this Laboratory for some time, with the object of finding the limitations of each method, and of formulating, if possible, a satisfactory mechanism to explain the reactions. As a part of this study the reduction of dialkylacetylenes and of some aromatic hydrocarbons by calcium ammonia was investigated.

Benzene and its simple homologs are very resistant to most chemical reducing agents. Dumanskii and Zvyereva<sup>4</sup> found, however, that when dry ammonia gas was passed into a mixture of benzene and calcium at room temperature, the benzene was reduced. They identified the product as a dihydrobenzene, since it formed a tetra-bromide melting at 172–173°. Kazanskii and his students<sup>5,6</sup> later made a more detailed study of the reaction, and obtained results which differed from those of Dumanskii. Kazanskii and his co-workers treated calcium with dry ammonia to form the complex  $\text{Ca}(\text{NH}_3)_6$ ; this was then allowed to react at 0° or room temperature with the aromatic hydrocarbon. They found that under these conditions the product was a tetrahydro and not a dihydro derivative, and in the case of mono-alkylbenzenes they believed it to have the 1-alkyl-1-cyclohexene structure, although they offered no rigorous proof for this. The physical constants of their products, however, do not agree well with those given in the literature for the pure cyclic mono-olefins, and indicate contamination with material of higher index of refraction.

We have reinvestigated the reduction of benzene and toluene by calcium ammonia, using both the procedure of Dumanskii and that of Kazanskii. The composition of the product was the same in both cases, but the Kazanskii procedure, using pre-formed calcium ammonia, gave the better yields (as there was less loss of product by entrainment). The product was found to be a mixture, and could not be separated into the pure components by fractional distillation; therefore a combination of chemical and physical methods

was used to identify the components. In the case of benzene the physical constants and hydrogenation data showed the substantial absence of dienes, and indicated that the product contained approximately 75% of cyclohexene and 25% of benzene. Raman spectra measurements<sup>7</sup> confirmed these results, showing the presence of 70–75% of cyclohexene and 25–30% of benzene, and the absence of other compounds.

In the case of toluene, the physical constants indicated that the product contained 20–30% of toluene and that the balance was a mono-olefin. When, however, quantitative hydrogenation and bromination experiments were carried out on this material, the results showed the presence of but 0.35–0.4 double bond per molecule. This discrepancy was resolved by Raman spectra data; Dr. Murray reported that "practically every (Raman) line can be accounted for if the material is assumed to be a mixture of 30% toluene, 40% 1-methyl-1-cyclohexene and 30% 4-methyl-1-cyclohexene."<sup>8</sup> Lozovoi and D'yakova<sup>9</sup> have also found a steric hindrance to hydrogenation of 1-methyl-1-cyclohexene; this olefin is also apparently resistant to saturation by bromine. This steric hindrance of 1-methyl-1-cyclohexene and related olefins is now being investigated in more detail. Kazanskii and his co-workers<sup>5,6</sup> were in error in assuming that alkylbenzenes yielded solely the 1-alkyl-1-cyclohexenes.

It was not found possible to obtain any identifiable amount of a dihydrobenzene. When either benzene or toluene was treated with a deficiency of calcium ammonia, the product was a mixture of aromatic hydrocarbon and mono-olefin, with a larger proportion of the aromatic compound than when more reducing agent was used.

The Russian workers did not investigate the action of calcium ammonia on dialkylacetylenes. It would be predicted, however, that acetylenes would be reduced by this reagent, since they are, in general, more easily attacked than aromatic hydrocarbons. Since the mechanism is probably similar to that proposed for other chemical reductions,<sup>10</sup> the *trans* olefins should be formed. This was found to be the case: dipropyl, dibutyl and butylethylacetylenes were readily reduced by calcium ammonia, and in each case the product was shown to be the corresponding *trans* olefin,

(1) A portion of this work was presented before the Organic Division at the Cleveland meeting of the American Chemical Society, April, 1944.

(2) Previous paper in this series; Campbell and Young, *THIS JOURNAL*, **65**, 965 (1943). Paper XLVIII on alkyl acetylenes; previous paper, *ibid.*, **66**, 1289 (1944).

(3) Present address: Esso Laboratories, Bayway, New Jersey.

(4) Dumanskii and Zvyereva, *J. Russ. Phys.-Chem. Soc.*, **48**, 994 (1916); *C. A.*, **11**, 787 (1917).

(5) Kazanskii and Smirnova, *Bull. acad. sci. U. R. S. S., Classe sci. math. nat.*, **547** (1937); *C. A.*, **32**, 2090 (1938).

(6) Kazanskii and Glushnev, *J. Gen. Chem. (U. S. S. R.)*, **8**, 642 (1938); *C. A.*, **33**, 1279 (1939).

(7) We wish to express our thanks to Dr. M. J. Murray of the Illinois Institute of Technology for making these measurements for us.

(8) Private communication from Dr. Murray.

(9) Lozovoi and D'yakova, *J. Gen. Chem. (U. S. S. R.)*, **10**, 1 (1940); *C. A.*, **34**, 4728 (1940).

(10) Campbell and Campbell, *Chem. Rev.*, **31**, 77 (1942).

by comparison with the *trans* olefins synthesized earlier by Campbell and Eby.<sup>11,12</sup>

TABLE I  
REDUCTION OF DIALKYLACETYLENES BY CALCIUM AMMONIA

Olefin formed	Yield, %	B. p.		$n_D^{20}$	$d_4^{20}$	F. p., °C.
		°C.	mm.			
<i>trans</i> 3-octene	67	122	739	1.4122	0.7156	-106
		122.4 <sup>a</sup>	741 <sup>a</sup>	1.4124 <sup>a</sup>	.7163 <sup>a</sup>	-108 <sup>a</sup>
<i>trans</i> 4-octene	65	121.5 <sup>a</sup>	740	1.4113	.7144	-93
		121.4 <sup>a</sup>	739 <sup>a</sup>	1.4116 <sup>a</sup>	.7147 <sup>a</sup>	-94 <sup>a</sup>
<i>trans</i> 5-decene	91	170	740	1.4235	.7406	-73
		170.2 <sup>a</sup>	739 <sup>a</sup>	1.4235 <sup>a</sup>	.7401 <sup>a</sup>	-73 <sup>a</sup>

<sup>a</sup> These were obtained by Campbell and Eby<sup>11,12</sup> on *trans* olefins prepared by reducing dialkylacetylenes with sodium in liquid ammonia.

We are continuing our work on the chemical reduction of unsaturated hydrocarbons, including aromatic hydrocarbons.

### Experimental

**Reduction by Calcium Ammonia—Method A.**—Fifteen grams of calcium turnings was placed in a 500-ml. flask equipped with an inlet tube, separatory funnel and reflux condenser, and protected from moisture. The flask was placed in a bath of liquid ammonia, and dry ammonia gas (distilled from sodium) was admitted to the reaction flask under a slight positive pressure. When all the calcium was used up (this required two to two and one-half hours) the cooling bath was removed and the excess ammonia was allowed to evaporate. The last traces of ammonia were removed by pumping the system at 100 mm. and 22°. (The vapor pressure of calcium ammonia,  $\text{Ca}(\text{NH}_3)_6$ , is 100 mm. at 22°.<sup>13</sup>) The unsaturated hydrocarbon, dissolved in two to three volumes of sodium-dried ether, was then added to the solid residue, and the reaction mixture was allowed to stand for twenty-four hours. The pasty mass was extracted with several portions of anhydrous ether, and the extracts were filtered under slight suction to remove calcium amide.<sup>14</sup> The ether extract was washed with water, dilute hydrochloric acid and dilute sodium carbonate solution. It was dried over potassium carbonate and distilled through a small helix-packed column of the Fenske-Whitmore type.

**Method B.**—The hydrocarbon, in anhydrous ether solution, was placed in a 3-neck flask containing calcium. The flask, which was equipped with a gas inlet tube, reflux condenser and mercury-sealed stirrer, was cooled in a bath of liquid ammonia and dry ammonia gas (distilled from sodium) was passed into the reaction mixture slowly for about four hours. The cooling bath was then removed,

(11) Campbell and Eby, *THIS JOURNAL*, **63**, 216 (1941).

(12) Campbell and Eby, *ibid.*, **63**, 2683 (1941).

(13) Kraus, *ibid.*, **30**, 653 (1908).

(14) Care must be used to keep the calcium amide on the filter moist with ether, as it is spontaneously inflammable in air. At the end of the filtration the calcium amide was added cautiously, in small portions, to a large amount of cracked ice.

and the mixture was allowed to stand overnight. It was then worked up as described under Method A.

**Reduction of Benzene.**—When 0.25 mole of benzene and 0.87 mole of calcium reacted, using either Method A or Method B, the product had b. p. 81°,  $n_D^{20}$  1.4500,  $d_4^{20}$  0.8134. A 0.01-mole sample absorbed 0.0077 mole of hydrogen over Raney nickel at room temperature and 3 atmospheres pressure. The material did not give an addition compound with maleic anhydride, and no tetrabromide could be obtained, showing the substantial absence of dienes. It did yield a dithiocyanate, m. p. 57–58°, which did not depress the melting point of cyclohexene dithiocyanate, m. p. 58°. The hydrogenation data, and the index of refraction and density, indicated a composition of approximately 75% of cyclohexene and the balance of benzene. Raman spectra measurements showed the composition to be about 25–30% of benzene and 70–75% of cyclohexene, and showed that no appreciable amounts of other substances were present.

The yield by Method A was 65%. by Method B, 32%; in this case there was considerable loss of hydrocarbon by entrainment with ammonia.

**Reduction of Toluene.**—In this case also substantially the same results were obtained by either method. In a typical experiment 0.87 mole of calcium and 0.25 mole of toluene reacted by Method A. The product, obtained in 15-g. yield, had b. p. 105–107°,  $n_D^{20}$  1.4540,  $d_4^{20}$  0.8135. A 0.01-mole sample absorbed 0.0035 mole of hydrogen over Raney nickel. In the dark, at 0°, a 0.1 mole sample absorbed 0.04 mole of bromine. No solid bromine derivative could be isolated. The hydrogenation and bromination data thus obtained were not in accord with the physical constants, which indicated about 70% of mono-olefin. Practically every line of the Raman spectra can be accounted for if the sample is assumed to be a mixture of toluene (30%), 4-methyl-1-cyclohexene (30%) and 1-methyl-1-cyclohexene (40%). Since the spectrum of 3-methyl-1-cyclohexene has not been reported, it is not possible to say whether any of this isomer was present.

**Reduction of Dialkylacetylenes.**—With these substances Method B gave much better results than Method A. Usually 0.12 mole of the dialkylacetylene, and 15 g. of calcium were used. The results are summarized in Table I.

### Summary

1. The reduction of benzene, toluene and three dialkylacetylenes by calcium ammonia has been investigated.

2. Benzene has been found to give cyclohexene as the sole reduction product, contaminated with unreduced benzene.

3. Toluene has been found to yield a mixture of two mono-olefins, identified by Raman spectra as 1-methyl-1-cyclohexene and 4-methyl-1-cyclohexene.

4. Dialkyl acetylenes are reduced by calcium ammonia to the corresponding *trans* olefins.

NOTRE DAME, INDIANA

RECEIVED OCTOBER 28, 1944

(15) Dermer and Dysinger, *THIS JOURNAL*, **61**, 750 (1939)