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REDUCTION OF ORGANIC COMPOUNDS BY LITHIUM IN LOW MOLECULAR WEIGHT AMINES. HIGHLY SELECTIVE LITHIUM-AMINE REDUCING SYSTEMS

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WE have shown[1] that lithium dissolved in certain low molecular weight amines is a unique and potent reagent for reducing aromatic compounds selectively to monoolefins.

We are hereby reporting that even a greater selectivity can be achieved in these reductions by carrying out the reactions in a mixture of solvents rather than in the pure amine. It will be noted from Table 1, that the addition of materials like dimethylamine, isopropylamine and morpholine to the usual solvents for these reductions (methylamine, ethylamine and ethylenediamine), increases quite markedly, in most instances, the percentage of the more thermodynamically stable 1-alkylcyclohexene. An equally important advantage to this new technique is that it enables one to carry out the reductions in a much less volatile solvent system than was heretofor possible.

The presence of at least small amounts of methylamine, ethylamine, or ethylenediamine seems essential. In the presence of pure morpholine or

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[1] See R.A. Benkeser, J.J. Hazdra, R.F. Lambert and P.W. Ryan, J. Org. Chem. 24, 854 (1959) for reference to the previous papers in this series.

dimethylamine, the reductions shown in Table 1 do not occur at any appreciable rate. On the other hand, cumene is reduced quite selectively to 1-isopropylcyclohexene in a solvent mixture containing 93 per cent dimethylamine and only 7 per cent methylamine by volume (entry 6 in Table 1).

It should be noted that not all the additives we tested showed the effects illustrated in Table 1. While reductions did occur in the presence of diluents like trimethylamine, ethyl ether and t-octylamine, the isomer ratios were essentially unaffected.

TABLE 1

Reduction of Aromatic Hydrocarbons by Lithium in Various Amines

		Per cent olefin distribution[a]	
Hydrocarbon reduced	Solvent	1-Alkylcyclohexene	3+4-Alkylcyclohexene
Toluene	methylamine	59	41
Toluene	CH_3NH_2 - Me_2NH(90)[b]	82	18
Cumene	methylamine	46	54
Cumene	CH_3NH_2 - i- $PrNH_2$(50)	65	19
Cumene	CH_3NH_2 - morpholine (75)	88	12
Cumene	CH_3NH_2 - Me_2NH(93)	82	18
Cumene	ethylenediamine[c]	76	19
Cumene	NH_2 -$(CH_2)_2NH_2$-morpholine (67)	87	13
Cumene	ethylamine	66	34
Cumene	$EtNH_2$ - Me_2NH(52)	85	15
t-Butylbenzene	ethylenediamine	70	30
t-Butylbenzene	$H_2N(CH_2)_2NH_2$-morpholine(66)	86	14
t-Butylbenzene	$EtNH_2$ - Me_2NH(52)	86	14

[a] The olefin mixtures were analyzed by vapor phase chromatography.

[b] The values in parentheses indicate percentage by volume in which the diluents were present.

[c] L. Reggel, R.A. Friedel and I. Wender, J. Org. Chem. **22**, 891 (1957).

We have undertaken a broad program designed to assess the types of additives which affect the selectivity of these reductions, as well as to determine the cause of this effect. The latter is particularly intriguing, since the ultimate explanation may be intimately connected with the classical problem of the constitution of the "blue solutions" resulting from the solubility of metals in ammonia or amines.

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