single reduction observed is that of the ethyl or that of the phenyl radical. Further work on other phenylammonium ions should be carried out. It is probable that all these reductions result in the formation of an amine and a hydrocarbon in the case of the tetraalkylammonium ions, ethyl alcohol in the case of choline, ethyl acetate in the case of acetylcholine, etc.

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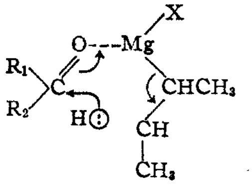
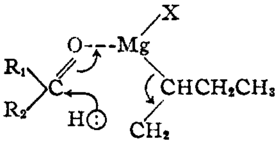
The Butenes from the Reduction of Isobutyraldehyde by *s*-Butylmagnesium Bromide

BY WILLIAM G. YOUNG AND JOHN D. ROBERTS[1]

Whitmore and George[2] have shown that the reduction of diisopropyl ketone by a Grignard reagent involves hydrogen atoms attached to the beta-carbon atom of the Grignard reagent. If the Grignard reagent had no hydrogen atoms on the β-carbon, as with neopentylmagnesium chloride, no reduction was detected. It was pointed out that a correlation exists between the extent of reduction of diisopropyl ketone and the number and primary, secondary or tertiary character of the β-hydrogens of the Grignard reagents. It is difficult, however, to determine the relative reduction rates of the different classes of β-hydrogen atoms from data obtained with several Grignard reagents because the competing reactions of addition and enolization are also markedly influenced by structure.

The relative reducing tendencies of primary and secondary β-hydrogens should be directly obtainable, independent of the addition and enolization reactions, from the ratios of 1- to 2-butene in the butenes resulting from the reduction of carbonyl compounds by *s*-butylmagnesium halides. The reduction reactions undoubtedly involve concerted cyclic processes[3] of the types





In the present work the butenes have been isolated from the reaction of *s*-butylmagnesium bromide with isobutyraldehyde. Infra-red spectroscopic analysis showed the butene mixture to consist of 1-butene (34%), *cis*-2-butene (8%) and *trans*-2-butene (58%). The 1- to 2-butene ratio was hence 34:66 or about 1:2. Since *s*-butylmagnesium bromide carries two secondary and three primary β-hydrogens, the relative tendency of primary and secondary β-hydrogens to be involved in reduction is thus about one to three.

Similar experiments with isopropylmethylcarbinylmagnesium bromide and isopropylethylcarbinylmagnesium bromide should give the relative rates of reduction of tertiary *vs.* primary and tertiary *vs.* secondary β-hydrogens, respectively.

Experimental

Isobutyraldehyde (54 g., 0.75 mole) dissolved in an equal volume of ether was added dropwise to a solution of *s*-butylmagnesium bromide prepared from 18 g. (0.75 gram atom) of magnesium, 102 g. (0.75 mole) of *s*-butyl bromide and 300 ml. of ether. The effluent gases were condensed in a Dry Ice cooled trap. The condensate was distilled into cold ether and the butenes converted to the dibromobutenes by treatment with bromine while cooling in an ice-hydrochloric acid bath. The ether was evaporated, the dibromides purified[4] and the butenes regenerated[4] and collected in an ampoule.

An infrared spectroscopic analysis was made of the butene mixture by Dr. O. Beeck of the Shell Development Company. An infrared analysis of a check sample was in satisfactory agreement with an analysis obtained by another method.[5] The Grignard complexes were decomposed with iced ammonium chloride solution and the higher-boiling products isolated in the usual way. Fractionation gave 12 g. (22%) of isobutyraldehyde, 19 g. (37%) of isobutyl alcohol, 31 g. (31%) of impure isopropyl-*s*-butylcarbinol and 12 g. of high-boiling residue. Refractionation of the addition product gave 23 g. (23%) of pure isopropyl-*s*-butylcarbinol, b. p. 81.9° (50 mm.), n^{20}_{D} 1.4325.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.80; H, 14.2.

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[4] Young, Winstein and Prater, THIS JOURNAL, **58**, 289 (1936).

[5] Dillon, Young and Lucas, *ibid.*, **52**, 1949 (1930).

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[1] Abbott Laboratories Research Fellow, 1943–1944.

[2] Whitmore and George, THIS JOURNAL, **64**, 1240 (1942).

[3] Whitmore and George, paper presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1941.

Derivatives of N,N'-Dicyclohexyl-ethylenediamine

BY F. B. ZIENTY AND R. C. THIELKE[1]

Since certain diacyl derivatives of N,N'-dicyclohexyl-ethylenediamine[2,3] had been shown to possess good solvent power for polyvinyl acetal resins and other plastic compositions, it seemed desirable to extend the study of these acyl derivatives.[4]

N,N'-Dicyclohexyl-ethylenediamine (I), prepared in 90% yield from cyclohexylamine and ethylenedichloride,[2,5] was easily acylated by reaction with acid chlorides and acid anhydrides. In the case of the formyl derivatives, however, (I) reacted with formic acid and the formate was dehydrated to the amide. Depending on the conditions of reaction, either a mixture of the monoformyl (II) and diformyl (III) derivatives

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[1] Present address: Emmett, Idaho.

[2] Kyrides, U. S. Patent 2,126,560 (Aug. 9, 1938).

[3] Kyrides, U. S. Patent 2,267,685 (Dec. 23, 1941).

[4] Lob, *Rec. trav. chim.*, **55**, 859 (1936), made a comprehensive investigation of the derivatives and reactions of a related amine, N,N'-dibenzyl-ethylenediamine.

[5] Clifford, U. S. Patent 2,126,620 (Aug. 9, 1938).

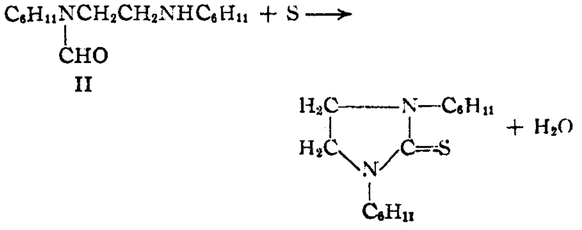
TABLE I

Derivative	M. p., °C.[a]	Formula	% Nitrogen Calcd.	% Nitrogen Found
N,N′-Dicyclohexyl-ethylenediamine (I)	B. p. 184–186 (25 mm.)[b]	$C_{14}H_{28}N_2$	12.5	12.3
(I) Monohydrate	102–103[c]	$C_{14}H_{30}N_2O$	H_2O, 7.4	7.6
(I) Dithiocarbamate	167–168[d]	$C_{15}H_{28}N_2S_2$	9.3	9.4
N-Formyl-(I)	B. p. 200–205 (8 mm.)	$C_{15}H_{28}N_2O$	11.1	11.2
N,N′-Diformyl-(I)[e]	165–166	$C_{16}H_{28}N_2O_2$	10.0	10.2
N-Formyl-N′-benzoyl-(I)	121–122	$C_{22}H_{32}N_2O_2$	7.9	7.7
N,N′-Dipropionyl-(I)	114–115	$C_{20}H_{36}N_2O_2$	8.3	8.2
N,N′-Dibutyryl-(I)	98–99	$C_{22}H_{40}N_2O_2$	7.7	7.6
N,N′-Dibenzoyl-(I)	226–227	$C_{28}H_{36}N_2O_2$	6.5	6.4
N,N′-Di-(*p*-toluenesulfonyl)-(I)	190–191	$C_{28}H_{40}N_2O_4S_2$	5.3	5.5
1,3-Dicyclohexyl-ethylenethiourea[f]	225–226	$C_{15}H_{26}N_2S$	10.5	10.3

[a] All melting points are corrected. [b] Ref. 2, b. p. 154–155° (8 mm.); ref. 5, b. p. 136–147° (2 mm.). [c] Ref. 5 gives m. p. 96–98°. [d] With effervescence. [e] Ref. 3. [f] Calcd.: C, 67.6; H, 9.8; S, 12.0. Found: C, 67.8; H, 9.6; S, 11.9

of (I), or predominantly the monoformyl derivative, could be obtained. Addition of formic acid to (I), followed by dehydration of the formate, gave a mixture of (II) and (III), while feeding of the amine (I) into the formic acid at reflux resulted in a good yield of the monoformyl derivative (II),[6] and only a small yield of the diformyl derivative (III).

N-Formyl-N,N′-dicyclohexyl-ethylenediamine, a basic compound, can be converted into (III) by further reaction with formic acid and dehydration of the formate. The reaction of (II) with sulfur at 130–150° produced a 71% yield of 1,3-dicyclohexyl-ethylenethiourea (IV)


II

IV

It was possible to obtain (IV) in 50% yield by thermal decomposition of the dithiocarbamate of (I) at 160–165°. Carbon disulfide and hydrogen sulfide were split off in this pyrolysis, so that an appreciable quantity of the original amine (I) was recovered.[7]

Experimental

N,N′-Dicyclohexyl-ethylenediamine Hydrate.—(I) very readily forms a water-insoluble monohydrate, m. p. 102–103°, which can be recrystallized from alcohol unchanged, and which can be decomposed above 125°.

N-Formyl-N,N′-dicyclohexyl-ethylenediamine (II).—Technical 85% formic acid (108 g. or 2 moles) was heated with stirring at reflux in a flask placed in a bath held at 130°, and 112 g. (0.5 mole) of (I) was fed in from a dropping funnel in the course of three hours. The reaction temperature rose from 102 to 124°. The mixture was cooled to 30°, poured into 500 cc. of water, and the solid (III) filtered off and dried (9 g.). The filtrate was alkalinized by the addition of excess 50% sodium hydroxide solution and the oily product was separated and distilled *in vacuo*; yield, 110 g. (87%) of (II).

N-Formyl-N′-benzoyl-N,N′-dicyclohexyl-ethylenediamine.—Eighteen grams of benzoyl chloride was added to 50.4 g. (0.2 mole) of (II) with stirring. A considerable amount of heat was evolved and the mixture solidified to a light brown mass which was dissolved in 20 cc. of acetone and the product precipitated by the addition of water. The solid was filtered off, washed with water and air-dried; yield, quantitative. After purification by dissolving in acetone followed by the addition of water, the product melted at 121–122°.

1,3-Dicyclohexyl-ethylenethiourea.—(1) A mixture of 100.4 g. (0.4 mole) of (II) and 16.0 g. (0.5 mole) of powdered sulfur was stirred and heated at 135°. At the end of fifteen minutes the evolution of gas had ceased and the dark brown mixture was cooled to about 50°, treated with 150 cc. of methanol, cooled with stirring to 5° and the crystals were filtered off, washed with methanol and dried; yield, 51 g. (47%) of 1,3-dicyclohexyl-ethylenethiourea. The filtrate, on evaporation and reaction with 10 g. of sulfur, yielded 25 g. more of the thiourea; total crude yield, 76 g. or 71%. The product was recrystallized from a mixture of benzene and methanol, using decolorizing charcoal, as colorless, shiny plates, m. p. 225–226°.

(2) A sample of N,N′-dicyclohexyl-ethylenediamine dithiocarbamate was heated in the range of 160–195° during thirty minutes. The cooled product, after crystallization from benzene, melted at 225–226° and did not depress the m. p. of 1,3-dicyclohexyl-ethylenethiourea prepared by Method 1.

Acknowledgments.—Many of the analyses reported were performed by Mrs. J. D. Nevins and Mr. F. N. Stewart of the Monsanto Analytical Laboratory.

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(6) Bischoff and Nastvogel, *Ber.*, **22**, 1784 (1889), prepared N-acetyl-N,N′-diphenyl-ethylenediamine by the action of one mole of acetic anhydride on N,N′-diphenyl-ethylenediamine at 120–130°.

(7) Ethylenethioureas have been prepared by decomposition of ethylenediamine dithiocarbamates [Hofmann, *Ber.*, **5**, 242 (1872); Newman, *ibid.*, **24**, 2191 (1891); Ruiz and Libenson, *C. A.*, **24**, 5726 (1930); Lob, ref. 4; van Alphen, *Rec. trav. chim.*, **58**, 544 (1939); Buchman, Reims, Skei and Schlatter, THIS JOURNAL, **64**, 2700 (1942); Johnson and Edens, *ibid.*, **64**, 2707 (1942)], from thiocyano derivatives [Newman, *loc. cit.*; Sergeev and Kolycbev, *J. Gen. Chem.* (U. S. S. R.), **7**, 1390 (1937)], and by reaction of the diethyl ester of thionothiobisformic acid with ethylenediamine [Guha and Dutta, *J. Indian Chem. Soc.*, **6**, 65 (1929)].