undepressed when mixed with an authentic sample of 3-methyl-6-pyridazone.[7]

Reaction of Diethyl Acetylsuccinate with Semicarbazide.—A solution of semicarbazide hydrochloride (11.2 g., 0.1 mole) and hydrated sodium acetate (13.6 g., 0.1 mole) in 100 ml. of water was mixed with a solution of diethyl acetylsuccinate (25.6 g., 0.1 mole) in 100 ml. of ethanol. There was no heat evolved on mixing and the mixture was then heated at reflux for one hour, after which the solvents were removed under vacuum. The residue was crystallized from 300 ml. of water to give 16 g. (59% yield) of material melting at 115–116°. Recrystallization did not raise this melting point.

Anal. Calcd. for $C_{11}H_{19}N_3O_5$: C, 48.35; H, 6.97; N, 15.38. Found: C, 48.69; H, 7.13; N, 15.64.

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NOTES

Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines. II. Stereochemistry. Chemical Reduction of an Isolated Non-terminal Double Bond

BY ROBERT A. BENKESER, GENE SCHROLL AND DALE M. SAUVE

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It was demonstrated in a previous publication[1] from this Laboratory that lithium, dissolved in methyl, ethyl- and *n*-propylamine, constitutes a powerful reducing medium for aromatic hydrocarbons. In every case thus far investigated this reagent has been found to effect far more extensive reductions than had previously been noted with sodium in liquid ammonia.[2]

It had been established conclusively by Campbell[3] that reduction of acetylenes by sodium in liquid ammonia involved a *trans* addition of hydrogen. Reductions carried out in the lithium–amine system were so markedly different from those effected by sodium in ammonia that it was deemed expedient to determine the stereochemistry of this new reducing medium. An approach similar to that employed by Campbell was utilized successfully in the present study.

When samples of 3-octyne and 5-decyne were reduced at −78° by lithium dissolved in ethylamine, good yields of *trans*-3-octene and *trans*-5-decene were obtained. The configuration of the products was established by comparing their freezing points and infrared spectra with authentic samples of both *cis*- and *trans*-3-octene and 5-decene. These were prepared either by catalytic hydrogenation of the corresponding acetylenes (*cis* product), or by reducing these acetylenes with sodium in liquid ammonia (*trans* product).

During the course of reducing 5-decyne at +17° it was observed that appreciable quantities of *n*-decane were obtained, particularly if lithium in large excess of two equivalents was employed. This was in sharp contrast to the same reduction by sodium in liquid ammonia which stopped cleanly at the olefin stage. Obviously the lithium–amine reagent is capable of reducing a non-terminal unsaturated center. To our knowledge this is the first instance of a chemical reduction not involving a terminal double bond.[4]

This reduction was extended to the olefin series where it was found that cyclohexene could be reduced to cyclohexane, and 1-ethylcyclohexene to ethylcyclohexane.

It obviously could be argued that the reductions observed in the above instances were not actually chemical in nature but rather were brought about by the hydrogen produced from the reaction of lithium with the solvent. Admittedly the latter reaction is much more pronounced with amine solvents than with ammonia. To test this possibility, the quantity of lithium absorbed per mole of cyclohexene reduced was determined. The average uptake of metal in three such determinations was 1.8 gram atoms per mole of cyclohexene. This indicated that reduction of the olefin was proceeding by some type of chemical addition of metal. Such an addition requires two equivalents of metal per equivalent of olefin. If the reduction was being effected simply by hydrogen generated from reaction of lithium with solvent, no constant ratio of metal to olefin would exist.

Experimental

Preparation of 3-Octyne and 5-Decyne.—Reaction of 1-hexyne (b.p. 71°, $n^{20}\text{D}$ 1.3989) with sodium amide in liquid ammonia and subsequently with butyl bromide gave a 70% yield of 5-decyne,[3] b.p. 176° at 748 mm., $n^{25}\text{D}$ 1.4311. When ethyl bromide was used in the reaction sequence, a 50% yield of 3-octyne[3] (b.p. 132° at 751 mm., $n^{20}\text{D}$ 1.4258) was obtained.

Reduction of 5-Decyne with Lithium in Ethylamine. A. At −78°.—A Dry Ice–carbon tetrachloride–chloroform slush was placed around a 500-cc. flask which contained a blue solution of 1.73 g. (0.25 g. atom) of lithium in 300 cc. of ethylamine. To the chilled solution was added 13.8 g. (0.1 mole) of 5-decyne over several minutes. The stirred solution turned gray after four hours; nine grams of methanol was then added and the cooling bath was removed after the hydrolysis of the excess lithium was completed. The solvent was permitted to evaporate partially, petroleum ether (b.p. 35–40°) as well as water was added, and the two-phase system was filtered through Celite. The hydrocarbon layer was separated, washed with water and dilute acid, and dried over calcium chloride. The solvent was distilled off and the residue was fractionally distilled with a Vigreux column (6 mm. outside diameter, three feet long) to give 7.8

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[1] R. A. Benkeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, THIS JOURNAL, **77**, 3230 (1955).

[2] For excellent reviews on this topic see G. W. Watt, *Chem. Revs.*, **46**, 317 (1949), and A. J. Birch, *Quart. Revs.*, IV, **69**, (1950).

[3] K. N. Campbell and L. T. Eby, THIS JOURNAL, **63**, 216 (1941).

[4] Sodium in the presence of ammonia and methanol has been used to reduce simple terminal olefins. Apparently the reaction fails completely with non-terminal olefins. See T. J. King, *J. Chem. Soc.*, 898 (1951), and H. Greenfield, R. A. Friedel and M. Orchin, THIS JOURNAL, **76**, 1258 (1954).

g. (55% yield) of *trans*-5-decene. The infrared spectrum of the main fraction of the product (b.p. 170° at 746 mm., $n^{20}\mathrm{D}$ 1.4247, f.p. −71 to −72° cor.) was identical to that of a sample of authentic *trans*-5-decene; characteristic peaks of *cis*-5-decene were entirely absent.

B. **At +17°.**—Two-tenths of a mole of 5-decyne was added dropwise over two hours to a solution of 5.5 g. (0.8 g. atom) of lithium in 300 cc. of ethylamine in a flask equipped with a stirrer, a dropping funnel and a Dry Ice condenser. A Drierite tube was used to exclude water; no insulation or cooling baths were placed around the flask. Stirring was continued for ten hours. The blue reaction mixture was then packed in Dry Ice overnight and then permitted to warm up to 17° the next day. More lithium (1.94 g.) was added; the color of the solution changed from colorless through a pink to a permanent blue in one hour. After four more hours of stirring, the remaining pieces of lithium were removed and solid ammonium chloride was added until the solution was colorless. The product was then taken up in low-boiling petroleum ether, as in the reduction at −78°. The petroleum ether solution was treated with an excess of bromine dissolved in carbon tetrachloride, washed with sulfurous acid and water, and dried. The solvent was evaporated and the residue was distilled. The distillate (b.p. 60–70° at 18 mm., $n^{20}\mathrm{D}$ 1.4149) was treated with sodium at 110° for two hours. The hydrocarbon was separated from the sodium by vacuum distillation to give 5.5 g. (19% yield) of pure *n*-decane,[5] b.p. 66–67° (18 mm.), $n^{20}\mathrm{D}$ 1.4120, f.p. −30° cor.

C. **At +17°.**—One-tenth mole of 5-decyne was added dropwise over one hour to a stirred solution of 2.08 g. (0.3 g. atom) of lithium in 300 cc. of ethylamine. Ten grams of methanol was added after 2.3 hours more of stirring. The product was isolated and purified as in the reduction at −78°. Eight grams of impure product (assumed to be a mixture of *n*-decane and *trans*-5-decene) was obtained upon fractional distillation; the boiling points of the fractions varied from 168 to 170.9° at 747 mm. while the refractive indices varied from $n^{20}\mathrm{D}$ 1.4219 to 1.4200. The infrared spectrum indicated that *trans*-5-decene was the only olefin isomer present in the mixture.

Reduction of 3-Octyne with Lithium in Ethylamine at −78°.—Twenty-two grams (0.2 mole) of 3-octyne was treated with 3.45 g. (0.5 g. atom) of lithium in 300 cc. of ethylamine for two hours at about −78° and then methanol was added to destroy the excess lithium. The yield of *trans*-3-octene was 52% (11.65 g.), b.p. 122.2° at 754 mm., $n^{20}\mathrm{D}$ 1.4130, initial f.p. −110.4°, purity 98.2 mole %. Its infrared spectrum was identical to that of an authentic sample of *trans*-3-octene; peaks characteristic of *cis* 3-octene were absent entirely.

Preparation of Authentic Samples of the *cis* and *trans* Isomers of 5-Decene and 3-Octene.[3]—The corresponding dialkylacetylenes were hydrogenated in the presence of Raney nickel to give the *cis*-olefins and reduced with sodium in ammonia to give the *trans*-olefins: *trans*-5-decene, yield 60%, b.p. 170–170.5° at 753 mm., $n^{20}\mathrm{D}$ 1.4240, f.p. −72° cor.; *cis*-5-decene, yield 72%, b.p. 170° at 752 mm., $n^{20}\mathrm{D}$ 1.4256, f.p. −113° cor.; *trans*-3-octene, yield 71%, b.p. 122.5° at 751 mm., $n^{20}\mathrm{D}$ 1.4132, initial f.p. −109.09°, purity 99.5 mole %; *cis*-3-octene, yield 59%, b.p. 121–121.5° at 748 mm., $n^{20}\mathrm{D}$ 1.4137, very wide freezing point range.[6]

Attempted Isomerization of *cis*-5-Decene.—Benzene (6.85 g.) was added dropwise to a solution of 2.43 g. of lithium in ethylamine.[1] After the lithium had been completely consumed in the reduction, *cis*-5-decene was added. The mixture was stirred for four hours, methanol was added and the decene was isolated in the usual way; $n^{20}\mathrm{D}$ 1.4252. The recovered decene then was added to a solution of lithium in ethylamine which was kept at Dry Ice temperature. The solid lithium was removed after 2.5 hours and methanol was added. The decene was isolated in the usual manner: b.p. 169° (753 mm.), $n^{20}\mathrm{D}$ 1.4250. The infrared spectra before and after attempted isomerization were identical.

Freezing Points.—The freezing points of the *trans*-3-octenes were secured with the aid of a platinum resistance thermometer[7] and may therefore be considered very accurate. The other freezing points were obtained with the aid of a pentane thermometer which had been calibrated with powdered Dry Ice; their probable accuracy was considered to be ±1°.

Reduction of Cyclohexane by Lithium in Ethylamine. A. **At 17°.**—Treatment of 16.4 g. (0.20 mole) of cyclohexene with 4.2 g. (0.6 g. atom) of lithium in 200 cc. of ethylamine resulted in 8.50 g. (51%) of cyclohexane, b.p. 79–80° (743 mm.), $n^{20}\mathrm{D}$ 1.4260. The solution decolorized bromide only slowly in carbon tetrachloride and slowly gave a red color with fuming sulfuric acid indicating only a trace of cyclohexene if any.

B. **At −78°.**—The treatment of 16.4 g. (0.2 mole) of cyclohexene with 4.2 g. (0.6 g. atom) of lithium in ethylamine at −78° after working up the reaction mixture resulted in the recovery of the cyclohexene essentially unchanged.

Determination of Absorption of Lithium by Cyclohexene in Ethylamine.—Employing the technique previously described,[8] the metal to hydrocarbon ratio between lithium and cyclohexene was determined in order to distinguish between an addition mechanism or reduction by "nascent" hydrogen for the isolated double bond. Triplicate determinations indicated an uptake of 2.0, 1.5 and 1.9 equivalents of lithium per mole of hydrocarbon.

Reduction of 1-Ethylcyclohexene by Lithium in Ethylamine.—The reduction of 16.9 g. (0.154 mole) of 1-ethylcyclohexene by 3.2 g. (0.46 g. atom) of lithium in 250 cc. of ethylamine resulted in 11.6 g. (68%) of a mixture of 1-ethylcyclohexene and ethylcyclohexane, $n^{20}\mathrm{D}$ 1.4482. The mixture was analyzed refractometrically and found to contain 62% olefin and 38% ethylcyclohexane.

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(5) K. N. Campbell and L. T. Eby, THIS JOURNAL, **63**, 2684 (1941).

(6) A similar observation on the f.p. of this compound was made by A. L. Henne, see *ibid.*, **65**, 2020 (1943).

(7) The authors wish to thank Mr. H. Podall of the Purdue Chemistry Department for his assistance in this matter.

(8) R. A. Benkeser, R. E. Robinson and H. Landesman, THIS JOURNAL, **74**, 5701 (1952).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

Dealkylation of Diisopropyl Phosphite by Hydrogen Chloride[1]

BY C. H. CAMPBELL[2] AND D. H. CHADWICK[2]

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Gerrard and Whitbread have reported a study of the dealkylation by hydrogen halide of the *n*-butyl phosphites.[3] They examined their data with a view to calculating specific rates. They concluded, and we agree, that study over a much more extensive field of conditions is necessary before precise statements can be made about the details of mechanism. Toward this end, it appears worth while to report pertinent data obtained by us in connection with another problem.

Solutions of hydrogen chloride of 4 to 7% by weight in diisopropyl phosphite were prepared, and the rate of dealkylation at room temperature and at 40° followed by titrating aliquots of the solutions for ionic chloride by the modified Volhard method. The data obtained, presented in Table I, are in excellent agreement with second-order kinetics in respect to hydrogen chloride. The data are not in agreement with first-order kinetics in respect to

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(1) This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C., in the Research Laboratory of the Former Phosphate Division, Monsanto Chemical Co., Anniston, Alabama.

(2) Organic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

(3) W. Gerrard and E. G. G. Whitbread, *J. Chem. Soc.*, 914 (1952).