1-(Chloromethylene)-3,3,5,5-tetramethylcyclohexane (IIa) had infrared C=C peaks at 1670 (w), 911 (m), 892 (m), 877 (w), and 867 cm^{-1} (w); CCl at 695 cm^{-1} (s). Nmr showed 0.98, $C(CH_3)_2$, *trans* (6.5); 0.93, $C(CH_3)_2$, *cis* (6.5); 1.28, CCH_2C (2.0); 1.78, $CH_2C(=CHCl)CH_2$, *trans* (1.9); 3.84, $CH_2C(=CHCl)CH_2$, *cis* (1.8); 5.30 ppm, =CH (0.69).

Anal. Calcd for $C_{11}H_{19}Cl$: C, 70.74; H, 10.27; Cl, 18.99. Found: C, 71.00; H, 10.29; Cl, 18.90.

Compound IIb had infrared C=C peaks at 3080 (w), 1650 (m), 900 (m), 885 (m), and 875 cm^{-1} (m); CCl at 760 (m), 772 (s), 795 (s), and 814 cm^{-1} (s).

Anal. Calcd for $C_{11}H_{19}Cl$: C, 70.74; H, 10.27. Found: C, 71.02; H, 10.16.

2,2,6,6-Tetramethyl-4-chloromethyl-3-heptene (IIIa) had infrared C=C peaks at 3100 (w), 1649 (m), 920 (s), and 900 cm^{-1} (s); CCl at 765 (s), 791 (s), and 895 cm^{-1} (s). Nmr showed 0.99, methyl protons of neopentyl group (8.8); 0.94, methyl protons of *t*-butyl group (8.8); 1.97, CH_2 of neopentyl group (2.0); 4.02 (a doublet), CH_2Cl (2.1); 5.20 ppm, =CH (1.2).

Anal. Calcd for $C_{12}H_{23}Cl$: C, 71.08; H, 11.43. Found: C, 71.16; H, 11.71.

1-Chloro-2,4,4-trimethyl-2-pentanol (IVa) had infrared OH at 3480 (s) and 3580 cm^{-1} (s); CO, tertiary alcohol at 1085 (s) and 1115 cm^{-1} (s). Nmr showed 1.07, $C(CH_3)_3$ (8.80); 1.48, CH_3C-OH (2.95); 1.57, CH_2 (2.13); 1.96, OH (1.13); 3.50 ppm CH_2Cl (2.06).

Anal. Calcd for $C_8H_{17}ClO$: C, 58.51; H, 10.35; Cl, 21.36. Found: C, 58.22; H, 10.53; Cl, 21.43.

2-Chloromethyl-4,4-dimethyl-1-pentene (IVb) had infrared C=C peaks at 3080 (w), 1640 (m), and 920 cm^{-1} (s); CCl at 655 (s), 751 (s), and 840 cm^{-1} (s). Nmr showed 0.92, $C(CH_3)_3$ (9.19); 2.10, CH_2 (1.90); 4.05 (a doublet), CH_2Cl (1.90); 4.94, =CH (0.99); 5.28 ppm, =CH (0.99).

Anal. Calcd for $C_8H_{15}Cl$: C, 65.50; H, 10.33; Cl, 24.17. Found: C, 65.73; H, 10.43; Cl, 24.26.

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Selectivity in Hydride Reductions of Tropone. A Mechanism for Apparent Double Hydride Transfer

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A few years ago, Chapman, Pasto, and Griswold[1] reported that reduction of tropone (1) with lithium aluminum hydride for short periods of time gives a mixture of 3,5-cycloheptadienone (2) and 3,5-cycloheptadienol (3) in a 2:3 ratio. We were interested in this reaction not only for the preparation of 2 and 3, but also because of the unusual nature of a reaction which gave a mixture of products involving ultimately single and double hydride transfer to tropone in a medium containing excess hydride. A number of previous examples of conjugate addition of lithium aluminum hydride are known (*e.g.*, benzoylethylenes, perinaphthenone, tetracyclone, etc.),[2] but this reaction showed features which seemed to warrant some further study. Accordingly, we investigated hydride reductions of tropone under a variety of conditions, varying the hydride reagent, the solvent, and, the most important, the method of work-up.

The results are given in Table I.

TABLE I

PRODUCTS OF HYDRIDE REDUCTIONS OF TROPONE

No. of equiv of hydride[a] per mole of tropone[b]	Quenching reagent	Relative yields of ketone **2** and alcohol **3**, %
3.5 (A)	Water[c]	60, 40
7.0 (A)	Satd aqueous NH_4Cl[c]	45, 55
8.0 (A)	Satd aqueous NH_4Cl[c]	13, 87[d]
3.0 (A)	Wet Na_2SO_4[e,c]	53, 47
4.0 (A)	Wet Na_2SO_4[e,c]	40, 60
1.0 (A)	Wet Na_2SO_4[e,c]	40, 60
3.0 (A)	Glacial acetic acid[f]	90, 10
2.0 (A)	Glacial acetic acid[f]	90, 10
1.0 (A)	Glacial acetic acid[f]	90, 10
4.0 (A)	50% aqueous acetic acid	90, 10
3.0 (A)	20% aqueous NaOH[f]	78, 22
2.0 (A)	20% aqueous NaOH[f]	77, 23
3.0 (A)	5% aqueous H_2SO_4[f,g]	62, 38
3.0 (A)	5% aqueous H_2SO_4[f,g]	68, 32
3.0 (A)	3% aqueous H_2SO_4[f,g]	85, 15
1.0 (A)	3% aqueous H_2SO_4[f,g]	83, 17
3.0 (A)	1% aqueous H_2SO_4[f,g]	75, 25
3.0 (B)	Water	<1, >99[d]
4.0 (C)	Aqueous acetic acid[c]	<1, >99
3.0 (C)	Aqueous acetic acid[c]	<1, >99

[a] A = $LiAlH_4$ in dry ethyl ether; B = $NaBH_4$ in absolute methanol; C = $NaBH_4$ in 85% methanol–water. [b] 5% excess hydride used in each run over quantity listed in table. [c] Quencher added to hydride mixture. [d] Considerable tropone was recovered. [e] Procedure of ref 1. [f] Hydride mixture added slowly to quencher solution with rapid stirring. [g] Ketone **2** is unstable to strong acid and may well have been partially consumed under these hydrolyzing conditions.

The products of the reaction, **2** and **3**, were identified by comparison of retention times (glpc) and spectra with authentic samples, and by preparation of derivatives. The ketone 2 had been prepared previously in our laboratory[3] by the procedure of Parham,[4] and the alcohol **3** was prepared by sodium borohydride reduction of ketone 2.[5] The physical and spectral properties of 2 and 3 (as obtained by both routes) and of their N-phenylmaleimide adducts agreed with those previously reported.[1,3-5]

Table I gives the relative yields of 2 and 3 obtained under various conditions, based on glpc analysis. The results of the lithium aluminum hydride reductions demonstrate a strong dependence of the yield of ketone 2 on the method of quenching. When the hydride re-

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[2] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

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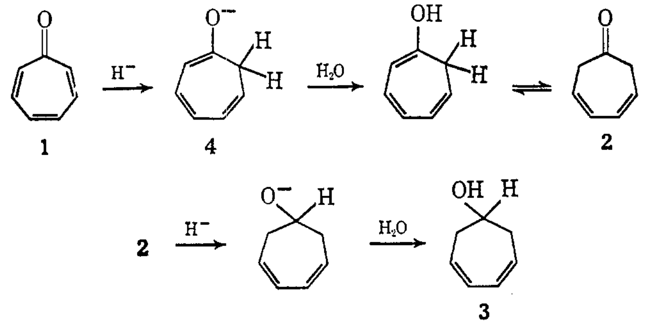
[4] W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Am. Chem. Soc.*, **84**, 1755 (1962); W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *ibid.*, **87**, 321 (1965).

[5] J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *ibid.*, **77**, 4401 (1955).

action mixture was slowly added to rapidly stirred aqueous or glacial acetic acid, the ratio of **2**:**3** was approximately 10:1 and was independent of the number of equivalents of hydride used. Even with a large excess of hydride, the principal product is ketone **2**, indicating that the alcohol **3** is predominantly if not totally produced during the hydrolysis step. The initial step appears to be conjugate addition to tropone to give the enolate **4** which is not reduced further in ether solution. Protonation of the enolate ion **4** on hydrolysis gives ketone **2** which is rapidly reduced to alcohol **3** by any residual or partially hydrolyzed LiAlH$_4$. Rapid stirring during hydrolysis would clearly minimize the second reduction step, as observed. The procedure used by Chapman and co-workers,[1] and other hydrolysis procedures which did not involve dropwise addition to a rapidly stirred hydrolysis solution, gave comparatively high yields of alcohol **3** (Table I). In accord with this scheme, sodium borohydride reduction of tropone in methanol-water gave excellent yields of alcohol **3** and only traces of ketone **2**, since in this medium conjugate addition of hydride to give **4** is followed directly by hydrolysis to ketone **2** and reduction to alcohol **3**.



For preparative work, it is therefore possible to obtain either **2** or **3** from reduction of tropone by proper choice to conditions, without having to resort to tedious separation by preparative glpc. The best procedures found in this work are given in the Experimental Section, although these probably do not represent conditions for obtaining optimum yields of products. Some cycloheptatriene detected in the product was probably an impurity in the tropone, although it could conceivably be a reduction product.[2]

These results also indicate that some caution may have to be observed in interpretations of other apparent double hydride transfers in lithium aluminum hydride reactions,[2] since the possibility of some reduction at the work-up stage seems not to have been previously considered.[6]

Experimental Section

Tropone was prepared (20-25% yield) by selenium dioxide oxidation of 1,3,5-cycloheptatriene (Shell Chemical Co.),[7] according to the procedure of Radlick.[8]

Reduction of tropone according to the procedure of Chapman[1] gave a mixture of alcohol and ketone, according to its infrared spectrum. Analysis by gas-liquid partition chromatography on a 20% THEED on Chromosorb P column showed two peaks with retention times of 10.2 and 12.8 min (column temperature 100°, He flow rate 180 cc/min) in approximately equal amounts. From analysis of various distillation fractions, the component of retention time 10.2 min was identified as 3,5-cycloheptadienone (**2**) and the 12.8-min component as 3,5-cycloheptadienol (**3**). While most of the glpc analyses were carried out on the THEED column, separation of tropone and the products could also be achieved on a silicone gum rubber SE-30 column at 75°.

The results of varying the agent used in quenching the hydride reaction mixture are given in Table I. In runs in which the lithum aluminum hydride reaction mixtures were hydrolyzed using wet sodium sulfate[1] or saturated ammonium chloride solution, the quenching agents were added slowly directly to the hydride mixtures. In the other lithium aluminum hydride reactions, the following procedure was used. The hydride reduction was carried out in a three-necked flask equipped with a high-speed stirrer, a reflux condenser, and an addition funnel with a pressure-equalizing side arm. The flask had an outlet at the bottom with a connecting tube and a Teflon stopcock. After the reaction was complete (usually 2 hr), the hydride mixture was slowly added through the connecting tube to another three-necked flask, also equipped with a high-speed stirrer and a condenser, containing the hydrolyzing agent. When hydrolysis was completed, the mixture was neutralized and separated into aqueous and ethereal layers. The aqueous layer was extracted several times with ether, the combined ether extracts were dried over anhydrous magnesium sulfate and then concentrated under reduced pressure, and the residue was analyzed by glpc (Table I).

The best procedures found for isolating high purity ketone **2** and alcohol **3** are given below.

3,5-Cycloheptadienone (2).—To a suspension of 1.41 g (0.15 equiv) of lithium aluminum hydride in 200 ml of anhydrous ether was added dropwise 5.00 g (0.047 mole) of tropone in 100 ml of ether with vigorous stirring. The mixture was stirred rapidly at room temperature for 2 hr and was then added through a connecting tube equipped with a Teflon stopcock (see above) to 50 ml of glacial acetic acid, with rapid stirring. After 10 min the mixture separated into two layers and was then neutralized with aqueous sodium bicarbonate. The layers were separated and the organic layer was washed with a 10% solution of sodium bicarbonate, dried over magnesium sulfate, and concentrated. Distillation through a microapparatus gave 2.9 g (58%) of 3,5-cycloheptadienone, bp 40-45° (4 mm) [lit. bp 45° (5 mm),[5] 43.5-46° (4.6 mm)[4]].

The infrared spectrum of this material was identical with that obtained[3] for ketone **2** prepared by the method of Parham[1] featuring sharp maxima at 1600 and 1710 cm^{-1}. The nmr spectrum agrees with that previously reported[4] except for peaks due to a trace of alcohol **3**, also detected by glpc. The N-phenylmaleimide adduct was prepared[5] and had mp 199-202° (lit. mp 204-205°,[4] 200-200.5°,[1] 199-202°[5]).

3,5-Cycloheptadienol (3).—To 3 g (0.028 mole) of tropone in 60-70 ml of methanol and 10 ml of distilled water was slowly added 2.0 g (0.053 mole) of sodium borohydride with vigorous stirring. Gas evolution occurred immediately. The mixture was stirred vigorously for 2 hr and any remaining hydride was then decomposed by the dropwise addition of 10 ml of glacial acetic acid. After neutralization with sodium bicarbonate, the mixture was extracted with three 30-ml portions of ether, the ethereal extracts were dried over magnesium sulfate, and the resulting solution was concentrated under reduced pressure and distilled. The product, 3,5-cycloheptadienol, had bp 50-55° (4 mm) [lit. bp 73° (25 mm),[5] 45-52° (6 mm)[4]] and amounted to 1.9 g (65%). This material contained less than 1% of ketone **2** according to analysis by glpc.

The infrared spectrum of **3** agreed exactly with that reported previously,[1,5] and the unexceptional nmr spectrum was in accord with the structure. Preparation[5] of the N-phenylmaleimide adduct gave material with mp 188-190° (lit. mp 185.5-187.0°,[1] 185-188°[5]).

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[7] We gratefully acknowledge generous gifts of 1,3,5-cycloheptatriene from the Shell Chemical Co.

[8] P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).