Waugh and Fessenden,[3] indicates that the aliphatic chain is part of a ring, which is situated over the aromatic nucleus.

This new class of *ansa* compounds is of extraordinary interest for several reasons. The physical and chemical properties may serve as criteria for estimating interatomic distances, electronic effects, ring strain, and other steric effects. Compounds of the type **4** are useful models for macrocyclic ring tautomers[4] and for macrolide antibiotics.[5] We are currently investigating other properties of **4** and the synthesis of lower and higher homologs.

Experimental Section[6]

ω-(*p*-Toluoyl)nonanoic Acid.—To a mixture of 15 g (0.065 mole) of methyl hydrogen sebacate and 125 ml of dry ligroin, heated to 70°, was added 31 g (0.26 mole) of thionyl chloride in several portions. Then the mixture was heated at 70–75° for 7 hr, and excess thionyl chloride and ligroin were removed by distillation at atmospheric pressure. The residual viscous, dark brown liquid was distilled: bp 124–127° (0.6 mm), yield 15.2 g (47%). In several experiments the yield of ω-carbomethoxynonanoyl chloride varied from 59 to 83%.

To a solution of 130 g (0.55 mole) of ω-carbomethoxynonanoyl chloride and 500 ml of dry, freshly distilled toluene, cooled to 3°, was added, with stirring, 150 g (1.13 moles) of anhydrous aluminum chloride so as to maintain the temperature at 5–10°. The mixture was stirred in the cold for 1 hr, then heated on the steam bath for 8 hr. After decomposition with ice–dilute hydrochloric acid, the organic layer was removed and combined with two ether washings of the water layer. The organic phase was steam distilled until no more toluene could be collected. Then the residue was extracted with ether. The ether solution was washed four times with saturated sodium bicarbonate and twice with water, dried over anhydrous sodium sulfate, and concentrated to yield 148 g of crude product. This was distilled up to 340° (21 mm). The distillate (123 g) was heated under reflux with aqueous, methanolic KOH for 3.5 hr. The solution was cooled and the 1,8-di-*p*-toluoyloctane was removed by filtration and recrystallized from ligroin: mp 100–101°, yield 27.5 g (14%), $\bar{\nu}_{CO}$ 1680 cm^{-1}, λ_{max} 251 mμ (log ϵ 4.50).

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.12; H, 8.39.

The **semicarbazone** had mp 223–224°.

Anal. Calcd for $C_{26}H_{36}N_6O_2$: C, 67.21; H, 7.81; N, 18.09. Found: C, 67.29; H, 7.82; N, 18.32.

The filtrate from above was acidified to yield ω-(*p*-toluoyl)-nonanic acid (**1**), which was recrystallized from ligroin: mp 92–93°, yield 71.8 g (47%), $\bar{\nu}_{CO}$ 1720 and 1695 cm^{-1}.

Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.06; H, 8.79.

Ultraviolet showed λ_{max} 251 mμ (log ϵ 4.16); nmr peaks (CCl_4) at 1–2 (broad multiplet), 2.28 (triplet), 2.38 (singlet), 2.88 (triplet), and 7.44 ppm (quartet).

The **semicarbazone** of **1** had mp 155–156° (ethanol–water).

Anal. Calcd for $C_{18}H_{27}N_3O_3$: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.19; H, 8.44; N, 12.68.

Oxidation of 1.—A mixture of 1 g of acid **1**, 7 g of potassium dichromate, 10 ml of concentrated sulfuric acid, and 40 ml of water was heated under reflux for 2 hr. It was poured into 50 ml of water and the solid was collected. The solid was purified by trituration in warm 5% sulfuric acid, dissolution in 10% potassium hydroxide, acidification of the alkaline filtrate, and recrystallization of the resulting solid from ethanol–water, mp 295–300° dec. The infrared spectrum was identical with one of terephthalic acid.

ω-(*p*-Bromoethylbenzoyl)nonanoic Acid (2).—A mixture of 5 g (0.018 mole) of acid **1**, 3.23 g (0.018 mole) of N-bromosuccinimide, a few crystals of "Vazo" (azobisisobutyronitrile, E. I. du Pont de Nemours and Co.), and 100 ml of carbon tetrachloride was heated at reflux for 2 hr. It was filtered while still hot, and the filtrate was allowed to cool. The solid was recrystallized several times from benzene–pentane, mp 103–104°, and finally once from acetone–water, mp 105–106°. Its nmr spectrum exhibited a singlet at 4.53 ($ArCH_2Br$) and none at 2.38 ppm ($ArCH_3$).

Anal. Calcd for $C_{17}H_{23}BrO_3$: C, 57.50; H, 6.54; Br, 22.46. Found: C, 57.65; H, 6.45; Br, 22.29.

In several experiments the yield of **2** ranged from 30 to 70%.

ω-(*p*-Hydroxymethylbenzoyl)nonanoic Acid (3).—A mixture of 1 g of bromo acid **2**, 2 g of potassium hydroxide, and 100 ml of 50% aqueous methanol was heated at reflux for 3 hr. After acidification, concentration, ether extraction, and removal of the ether, there remained a dark yellow semisolid. Repeated recrystallization from ether–pentane raised the melting point to 90–91°: $\bar{\nu}_{OH}$ 3500–3700 cm^{-1}, a singlet in the nmr (chloroform) at 5.50 ppm, λ_{max} 251 mμ (log ϵ 4.31).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.64; H, 8.29.

ω-(*p*-Hydroxymethylbenzoyl)nonanoic Acid Lactone (4).—A 5-l., round-bottomed flask, containing 2 l. of tetrahydrofuran, was fitted with two reflux condensers, each topped with a dropping funnel. One contained a solution of 0.5 g of ω-(*p*-bromomethylbenzoyl)nonanoic acid (**2**) in 250 ml of tetrahydrofuran; the other, a solution of 0.08 g of potassium hydroxide, 25 ml water, and 100 ml of tetrahydrofuran. The solutions were added dropwise and simultaneously to the refluxing solvent over a period of 6 hr, while magnetic stirring was maintained. The supernatant solution was removed from a white solid by decantation and concentrated to an oily solid. The crude product, dissolved in chloroform, was separated into two fractions by thick layer chromatography (1:1 benzene–chloroform eluent) in several batches. The faster moving component was recovered as a white solid: mp 78–79.5°; $\bar{\nu}_{CO}$ (deuteriochloroform) 1685 and 1720 cm^{-1}; nmr peaks at 7.68 (doublet), 5.19 (singlet), 2.88 (triplet), 2.15 (triplet), 1.2–1.7 (broad multiplet), and 0.95 ppm (broad); λ_{max} 246 mμ (log ϵ 4.14). The mass spectrum[7] contains peaks at 274 (molecular ion), 256, 228, 216, 189, 134, 118, 90, with metastable peaks at about 239, 204, and 191.

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.25; H, 8.11.

Acknowledgment.—We are greatly indebted to Dr. J. J. Uebel for helpful discussions during the course of this investigation.

---

[3] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[4] P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).

[5] M. Berry, *Quart. Rev.* (London), **17**, 343 (1963); H. Griesbach and W. Hofheinz, *J. Roy. Inst. Chem.*, **88**, 332 (1964).

[6] Infrared spectra were determined as halocarbon and Nujol mulls (unless otherwise stated) with a Perkin-Elmer 337 grating spectrophotometer; ultraviolet spectra were measured in methanol either with a Perkin-Elmer Model 4000 Spectracord or a Cary 14 spectrophotometer. Nmr spectra were determined in deuteriochloroform (unless otherwise stated) with a Varian A-60 instrument and are reported in parts per million (ppm) relative to tetramethylsilane. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points and boiling points are uncorrected.

[7] We are grateful to Dr. Kenneth L. Rinehart, Jr., and associates, University of Illinois, Urbana, Ill., for determination of the mass spectrum.

Reactions of Hypochlorous Acid with Hindered Olefins[1]

SOLOMON MARMOR[2] AND JOHN G. MAROSKI

Chemistry Department, New Mexico Highlands University, Las Vegas, New Mexico

Received November 29, 1965

The reaction of *unsym*-dineopentylethylene oxide with anhydrous hydrogen chloride in ether or with other acids leads to the formation of dineopentylacetal-

---

[1] (a) Taken in part from the M.S. thesis submitted by J. G. M.; (b) presented at the Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov. 18, 1965.

[2] To whom correspondence should be addressed: California State College, Dominguez Hills, Gardena, Calif.

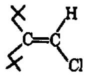
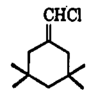
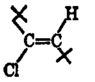
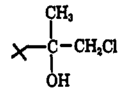
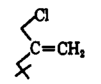
dehyde[3,4] rather than the corresponding chlorohydrin. The observed rearrangement can be explained on the basis of the steric inhibition of the approach of the chloride ion following the protonation of the oxygen atom. It became of interest to determine the nature of the reaction of hypochlorous acid with dineopentylethylene and other hindered olefins, the supposition being that no chlorohydrin should be formed because of the same steric factors.

Preliminary results of the heterogeneous reactions of alkenes with HOCl indicated that homogeneous conditions would be preferable, from the point of view of reducing reaction time. Acetone was selected as a mutual solvent for the hydrocarbon and the aqueous reagent. Solutions of hypochlorous acid in acetone were found to be stable for at least 3 hr at 25°, and the HOCl decomposed only very slowly thereafter. Furthermore, it was ascertained that the acetone did not interfere with the normal reaction of HOCl with the double bond of cyclohexene, which resulted in the formation of the expected chlorohydrin.[5]

The reactions of chlorine-free hypochlorous acid with four hindered alkenes led, in all cases but one, to mixtures of products (Table I).

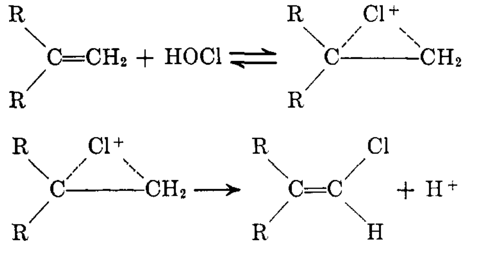
TABLE I

PRODUCTS[a] OF REACTIONS OF ALKENES WITH HYPOCHLOROUS ACID

Alkene	Products
unsym-Dineopentylethylene (I)	 Ia, 48% of product mixture[b]
3,3,5,5-Tetramethylmethylenecyclohexane (II)[c]	 IIa $C_{11}H_{19}Cl$ 115b[d]
2,2,4,6,6-Pentamethyl-3-heptene (III)	 IIIa
2,4,4-Trimethyl-1-pentene (IV)	 IVa, 34% of mixture  IVb, 46% of mixture[e]

[a] See the Experimental Section for infrared and nmr spectral data which permitted identification of products. [b] A minimum total of eleven products was detected on the gas chromatogram. Two other chlorine-containing products were isolated but not identified. [c] The addition of HOCl to methylenecyclohexane has been reported: see J. G. Traynham and O. S. Pascual, *Tetrahedron*, **7**, 165 (1959); *J. Org. Chem.*, **21**, 1362 (1956); *J. Am. Chem. Soc.*, **79**, 2341 (1957). [d] Insufficient material precluded complete identification. [e] A third product, 20% of the mixture, was isolated but not positively identified.

That no oxygen-containing functional groups were detected in any of the products of the reactions of the hindered olefins I, II, and III is of particular significance. The formation of 1-chloroalkenes from I and from II can be accounted for by analogy with the reaction of dineopentylethylene oxide with an acid such as hydrogen chloride. In the reaction of HOCl with the alkene the formation of a cyclic chloronium ion[6] may be proposed. The structure of this intermediate is analogous to the protonated oxirane structure. Since some



chlorohydrin was produced in the reaction of 2,4,4-trimethyl-1-pentene with HOCl, it is obvious that the normal reaction path was followed to some extent. With only one neopentyl group and a much smaller methyl group surrounding the olefinic linkage there is less steric interference with the step following the introduction of the positive chlorine.

It is perhaps somewhat more difficult to account for the products in which a chlorine atom has substituted for hydrogen. The substitution of halogen atoms for paraffinic hydrogen atoms during the course of halogen addition to olefinic bonds has been observed in many instances.[7] An ionic mechanism which involves rearrangement has been proposed[8] to account for the apparent substitution of chlorine at the allylic position. However, such a mechanism would not be applicable to reactions wherein products are formed in which the double bond is in its original position. Since direct halogenation of alkanes is believed to occur *via* a free-radical process, in which the first step is initiated by light, heat, or a chemical initiator, it is reasonable to expect that the substitution accompanying addition in reactions of alkenes with halogens is also due to a free-radical process. However, the conditions usually employed for addition reactions are not conducive to free-radical mechanisms, as they are generally understood. Recently, Poutsma[9] applied the concept of "molecule-induced homolysis," which had been advanced by other workers[10] to explain other free-radical reactions, to account for observed substitution of chlorine on a nonallylic carbon in cyclohexene. Poutsma further established that cyclohexane, which had been incorporated in a reaction mixture of cyclohexene and chlorine, also underwent substitution by chlorine. Cyclohexane alone, on the other hand, remained unaffected by chlorine under the same conditions.

---

[3] W. J. Hickinbottom and D. G. M. Wood, *J. Chem. Soc.*, 1600 (1951).

[4] P. D. Bartlett, G. L. Fraser, and R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 495 (1941).

[5] The preparation of 2-chlorocyclohexanol by reaction of HOCl (prepared *in situ*) with cyclohexene under heterogeneous conditions is described in G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p 158.

[6] P. B. de la Mare and A. Salama, *J. Chem. Soc.*, 3337 (1956); P. Ballinger and P. B. de la Mare, *ibid.*, 1481 (1957).

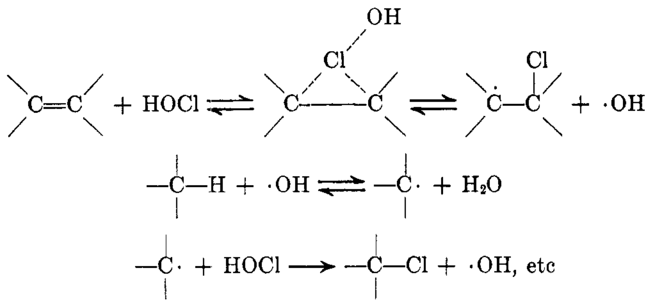
[7] See, for example, P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955); H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939); see also ref 4 of this paper.

[8] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

[9] M. L. Poutsma, *ibid.*, **85**, 3511 (1963).

[10] J. C. Martin and E. H. Drew, *ibid.*, **83**, 1232 (1961); G. Fraenkel and P. D. Bartlett, *ibid.*, **81**, 5582 (1959).

We wish to propose that the concept of "molecule-induced homolysis" is apparently operative in reactions of hypochlorous acid with alkenes. The HOCl molecule is believed to be largely undissociated in water solution. As such it is analogous to a chlorine molecule. Furthermore, it has been established[11] that HOCl can and does react with unsaturated ketones, in the presence of peroxides, *via* a free-radical mechanism. It is being assumed, therefore, that some of the HOCl undergoes homolysis, with the generation of chain-propagating radicals. The fact that no C–OH structures are formed is explained on the basis of the greater stability of the OH radical as compared with the Cl radical. (In the free-radical reaction of HOCl with quinones and unsaturated ketones,[11] no hydroxy compounds were observed in the products either.) A possible mechanism is represented by the following scheme.



Following the approach used by Poutsma, the reaction of hypochlorous acid with a mixture of dineopentylethylene and cyclohexane was studied. The formation of chlorocyclohexane, which was identified on the basis of gas chromatography, indicated that free radicals were indeed generated, if we are to assume that substitution of H by Cl proceeds *via* a free-radical mechanism only. In addition, reactions run in the dark and under a nitrogen atmosphere, using purified (peroxide-free) alkene, led to the same product mixture as obtained in reactions in which no special precautions were taken.

Experimental Section

Analytical Methods.—The infrared spectra were taken on the Beckman IR-9. The Beckman GC-2 gas chromatograph was used for all analytical and preparative gas chromatography. Helium was used as the carrier gas, with a thermal conductivity cell as the detector. Approximate relative yields were determined by the method of internal normalization of the chromatograms. Area ratios were determined either by polar planimeter or by weighing. Nuclear magnetic resonance spectra were taken on the Varian A-60 by Dr. Audrey M. Small at the University of Connecticut. The spectra obtained are of neat samples or $CDCl_3$ solutions. All elemental analyses were performed by Galbraith Labratories, Inc., Knoxville, Tenn.

Materials.—Hypochlorous acid was prepared by the reaction of chlorine with an aqueous suspension of mercury(II) oxide.[12] The approximately 1 *M* solutions that were obtained were stored in the cold and found[13] to be stable for several weeks. *unsym*-Dineopentylethylene was prepared from triisobutylene[4] or purchased from Humphrey Chemical Co., North Haven, Conn. 2,2,4,6,6-Pentamethyl-3-heptene is commercially available from Humphrey Chemical Co. 2,4,4-Trimethyl-1-pentene was obtained from Phillips Petroleum Co., Special Products Division, Bartlesville, Okla. 3,3,5,5-Tetramethylmethylenecyclohexane, a new compound, was prepared as described below.

3,3,5,5-Tetramethylmethylenecyclohexane.—The Wittig reagent was prepared by a standard procedure.[14] An ether or hexane solution of *n*-butyllithium[15] (0.1 mole) was added to 200 ml of anhydrous ether contained in a 500-ml four-necked flask equipped with a reflux condenser and drying tube, mechanical stirrer, pressure-equalized dropping funnel, and gas inlet tube. The system was flushed with nitrogen and a cover of the inert gas maintained throughout the reaction. While the solution was stirred 56 g (0.1 mole) of methyltriphenylphosphonium iodide was added from an erlenmeyer flask which was attached to one of the necks with a piece of Gooch tubing. The resulting solution was stirred for 4 hr at 23°.

Fifteen grams (0.1 mole) of 3,3,5,5-tetramethylcyclohexanone (Aldrich Chemical Co.) was added dropwise to the solution of methylenetriphenylphosphorus. As the addition continued, a white precipitate (triphenylphosphine oxide) formed with evolution of considerable heat. The solution was then refluxed for 11 hr, following which the mixture was filtered. The filtrate was washed and then dried over anhydrous calcium chloride. After removal of the ether by distillation, an infrared spectrum of the crude product was obtained and showed a carbonyl absorption band at 1720 cm^{-1}. A gas chromatogram of the crude mixture also indicated (by comparison of retention times) the presence of unreacted ketone.

The olefin was best separated from the ketone by means of column chromatography. The mixture was chromatographed on a 34 × 4 cm column packed with 250 g of Woelm alumina neutral (activity grade I), using petroleum ether (bp 60–110°) as eluent. The progress of the separation was monitored by gas chromatography of the elutates. A total of 1.5 g of olefin (10% yield) was obtained.

Anal. Calcd for $C_{11}H_{20}$: C, 86.74; H, 13.26. Found: C, 86.79; H, 13.12.

The infrared spectrum showed peaks (C=C) at 3070, 1650, 890, and 879 cm^{-1}. Bands in the nmr spectrum, their assignments, and peak areas follow: 0.90, $C(CH_3)_2$ (11.9); 1.21, CH_2 (2.4); 1.81, CH_2CCH_2 (4.0); 4.51 ppm, $=CH_2$ (2.0).

General Procedure for the Reaction of Hypochlorous Acid with Olefins.—All reactions were run either in a darkened room or the apparatus was covered with an opaque black cloth. A flat-bottomed, three-necked flask equipped with magnetic stirrer, thermometer, reflux condenser, and pressure-equalized addition funnel was the reaction apparatus.

The hypochlorous acid solution was added to a solution of the olefin[16] in acetone (or dioxane in one case), while cooling the reaction mixture as necessary with an ice-water bath to maintain the temperature between 25 and 30°. When the reaction was complete, as determined by analysis of 1-ml samples withdrawn from the reaction mixture, the solution was extracted with ether three times. The ether extracts were combined, washed with water until neutral and then dried over anhydrous magnesium sulfate. After filtering, the ether solution was stripped of solvent under reduced pressure. In each case the infrared spectrum of the crude residue was obtained immediately. The separation of the components of the mixture was effected by gas chromatography, using a 10 ft × 0.25 in. column packed with 20% Carbowax 1540 on Chromosorb W 45–60.

Analytical data for compounds isolated are as follows.

1-Chloro-2-neopentyl-4,4-dimethyl-1-pentene (Ia) had infrared C=C peaks at 3080 (w), 1625 (m), and 920 cm^{-1} (m); CCl peaks at 770 (m), 791 (m), and 809 cm^{-1}. Nmr (area ratios in parentheses) showed 0.88, $C(CH_3)_3$ (9.0); 0.93, $C(CH_3)_3$ (9.0); 1.96, CH_2 (2.0); 2.13, CH_2 (2.0); 5.65 ppm, =CH (1.0).[17]

Anal. Calcd for $C_{12}H_{23}Cl$: C, 71.08; H, 11.43; Cl, 17.48. Found: C, 70.85; H, 11.10; Cl, 17.80.

---

[11] S. Marmor, *J. Org. Chem.*, **30**, 3556 (1965).

[12] A. Chung and C. G. Israel, *J. Chem. Soc.*, 2667 (1955).

[13] "Scott's Standard Methods of Analysis," Vol. I, N. H. Furman, Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, p 274.

[14] G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960). Methyl iodide was used in place of methyl bromide and a 98% yield of methyltriphenylphosphonium iodide was obtained.

[15] R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 352 (1951). *n*-Butyllithium in hexane was also obtained from Foote Mineral Co., Exton, Pa., and was found to be as satisfactory as the ether solution of *n*-butyllithium prepared according to the procedure in the reference cited.

[16] It was found that a 50–100% excess of olefin over HOCl, in the reactions with dineopentylethylene, gave fewer products as compared with those reactions in which equimolar amounts of reactants were employed.

[17] In the nmr spectrum of I absorption of the vinylic protons was observed at 4.65 ppm. The difference of 1.00 ppm between the absorption assigned to the vinylic hydrogens of the starting materials and that of the product is consistent with data reported in the literature. See, for example, R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 86.

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, $C\mathit{H}_2C(=CHCl)CH_2$, *trans* (1.9); 3.84, $CH_2C(=CHCl)C\mathit{H}_2$, *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, $C\mathit{H}_3C$-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.

Acknowledgement.—The authors are indebted to Dr. Audrey M. Small, University of Connecticut, for the nmr spectra and for assistance in their interpretation. Mr. Max Rivera is to be credited for his efforts in some of the preliminary experiments. We are also indebted to Dr. R. E. Partch for his aid in our discussions.

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

DAVID I. SCHUSTER, JOEL M. PALMER, AND
S. CARLTON DICKERMAN

*Department of Chemistry, New York University,
University Heights, Bronx, New York 10453*

Received June 20, 1966

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-

---

(1) O. L. Chapman, D. J. Pasto, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1213 (1962).

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

(3) F-T. Lee, Ph.D. Dissertation, New York University, 1966.

(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).