Anal. Calcd for $C_{12}H_{31}O_3NSi_2$: C, 49.15; H 10.58; Si, 19.11; N, 4.78; mol wt, 293. Found: C, 49.59, 48.66; H, 10.69, 10.60; Si, 18.09, 17.80; N, 5.30, 5.03; mol wt, 293 (mass spectrometry).

The residue, vacuum distilled, gave 27 g of N,N-bis(trimethylsilyl)-3-aminopropyltriethoxysilane, bp 108–110° (0.5 mm). Its identity was confirmed by ir and glpc retention time which was identical with that of the sample obtained from expt IA.

III. Alkylation of 1,1-Diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane.—A butyllithium solution (139 cc, 0.23 mol) was added slowly in a stream of N_2 to a solution of 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane (28 g, 0.113 mol) and 100 ml of anhydrous ether. After addition, the solution was stirred at room temperature for 2 hr. The white solid was filtered off and washed with hexane. The filtrate and wash solution were combined and distilled, giving 22.8 g of colorless liquid [bp 75–80° (0.1 mm)]. Glpc analysis indicated two components separated by gas chromatography. Compound I (21.8%) was assigned as 1-ethoxy-1-butyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane.

Anal. Calcd for $C_{12}H_{29}NOSi_2$: C, 55.59; H, 11.20; Si, 21.62; N, 5.41; mol wt, 259. Found: C, 56.08, 55.84; H, 11.52, 11.40; Si, 20.78, 20.58; N, 5.60, 5.41; mol wt, 259 (mass spectrometry).

Compound II (54.9%) was assigned as 1,1-dibutyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane.

Anal. Calcd for $C_{14}H_{33}NSi_2$: C, 61.99; H, 12.18; Si, 20.66; N, 5.17; mol wt, 271. Found: C, 61.73, 61.73; H, 12.33, 12.09; Si, 20.54, 20.47; N, 5.44, 5.31; mol wt, 271 (mass spectrometry).

IV. Attempts to Synthesize 1,1-Diethoxy-1-sila-2-azacyclopentane.—3-Aminopropyltriethoxysilane (94 g, 0.32 mol) and ammonium sulfate (9 g) were heated to reflux under N_2 for 2 hr. Upon vacuum distillation, 40 g of 3-aminopropyltriethoxysilane was recovered. Further distillation decomposed the reaction mixture to ethyl alcohol and an unidentified polymer. The ethyl alcohol was identified by its ir spectrum.

Registry No.—A, 21297-72-3; N-(trimethylsilyl)-3-aminopropyltriethoxysilane, 21297-73-4; 1-ethoxy-1-butyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane, 21-297-74-5; 1,1-dibutyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane, 21297-75-6; N,N-bis(trimethylsilyl)-3-aminopropyltriethoxysilane, 17940-89-5.

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Preparation of Cycloheptanone *via* a Lewis Acid Catalyzed Cyclization of 6-Heptenoyl Chloride to β-Chlorocycloheptanone

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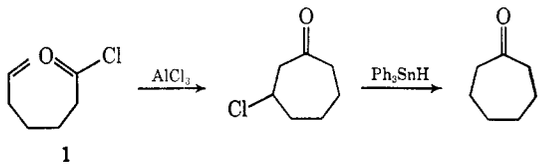
We have found that cycloheptanone can be prepared in fair yield by triphenyltin hydride reduction[2] of β-chlorocycloheptanone, which was obtained from the aluminum trichloride catalyzed cyclization of 6-heptenoyl chloride. For three runs which used 0.3 g of



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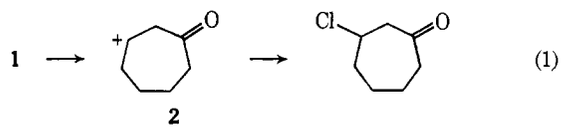
6-heptenoyl chloride, the yield of cycloheptanone was 53 ± 4% based on glpc analysis using cyclohexanone as an internal standard. The identity of the cycloheptanone was proved by nmr, ir, and glpc analyses of the colorless oil which was obtained by vacuum distillation of the crude product from a run which used 3 g of 6-heptenoyl chloride. Glpc analysis showed that the distilled product contained >80% cycloheptanone and <2% 2-methylcyclohexanone.

Kuivila[2] has clearly shown that the triphenyltin hydride reduction of an alkyl chloride usually goes without any carbon skeleton rearrangements. Therefore the cycloalkanones obtained from the triphenyltin hydride reduction should possess the same carbon structures as the chlorocycloalkanones from the cyclization reaction. Further confirmation that the crude product from the aluminum trichloride catalyzed cyclization of 6-heptenoyl chloride was mainly β-chlorocycloheptanone was obtained by nmr and ir analyses. Cyclization of the olefin to form a carbonium ion followed by attack of a chloride ion on this cation



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should lead to β-chlorocycloheptanone. Comparison of the nmr spectrum of an authentic sample of α-chlorocycloheptanone with that of the crude product provided convincing evidence for the absence of the α isomer.

The formation of the cyclooctanone by triphenyltin hydride reduction of the products of the aluminum trichloride catalyzed cyclization of 7-octenoyl chloride was attempted. Under conditions similar to those used for the cyclization of 6-heptenoyl chloride and even under conditions 50 times more dilute, the 7-octenoyl chloride formed mainly tars. Attempts using carbon disulfide–stannic chloric, benzene–stannic chloride, carbon disulfide–aluminum trichloride, and ether–stannic chloride with high dilution met with similar results. Glpc analysis of the triphenyltin reduction of the products from the aluminum trichloride treatment of 7-octenoyl chloride showed that less than 0.1% cyclooctanone or methylcycloheptanones was produced.

Discussion

Most olefin cyclization reactions, either under solvolytic conditions,[3,4] acid-catalyzed conditions,[3,5] or other conditions that generate cations,[6] lead to five- and six-membered rings. Recently several groups of workers have reported the formation of seven-membered rings

(1) U. S. Public Health Service Fellow, 1966–1967.

(2) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 77 (1964).

(3) W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968), and references cited therein.

(4) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, **32**, 150 (1967), and references cited therein.

(5) (a) M. F. Ansell and M. H. Palmer, *Quart. Rev.* (London), **18**, 211 (1964); (b) J. C. Bardhan and K. C. Bhattachargya, *Chem. Ind.* (London), 800 (1951); (c) O. Riobe, *Compt. Rend.*, **248**, 2774 (1959); (d) J. J. Beereboom, *J. Org. Chem.*, **30**, 4230 (1965); (e) W. F. Erman and H. C. Kretschmar, *ibid.*, **33**, 1545 (1968).

(6) (a) G. Büchi, E. Koller, and C. W. Perry, *J. Amer. Chem. Soc.*, **86**, 5646 (1964); (b) E. E. Van Tamelen and E. J. Hessler, *Chem. Commun.*, 411 (1966); (c) R. Breslow, J. T. Groves, and S. S. Olin, *Tetrahedron Lett.*, 4717 (1966); (d) L. Cassar, G. P. Chiusoli, and M. Foa, *ibid.*, 285 (1967); (e) T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 869, 872 (1967).

by olefin cyclization.[7-10] High yields of seven-membered rings have been obtained from the treatment of unsaturated aldehydes or epoxides with Lewis acids in benzene.[7,8] However, in these cases, cyclization to a seven-membered ring was favored by the presence of a 6-methyl group which resulted in a tertiary carbonium ion during cyclization to a seven-membered ring. 6-Heptenoic acid has been reported to give 10% cyclohept-2-enone by cyclization with trifluoroacetic anhydride.[9] Cyclization of this unsaturated acid by polyphosphoric acid has been reported to give six-membered ring products.[5a] We recently reported the formation of seven-membered ring compounds in 10% yield and six-membered ring compounds in 4% yield by solvolysis of 6-heptenyl *p*-nitrobenzenesulfonate in 2,2,2-trifluoroethanol.[10] The low yield and mixture of cyclic materials suggest that in general seven-membered ring compounds cannot be synthesized in acceptable yields by solvolysis of 6-heptenyl derivatives in 2,2,2-trifluoroethanol.

The cyclization of 6-heptenoyl chloride reported in this paper is the first example of an acid-catalyzed cyclization of a simple 6-heptenoyl derivative that gives a seven-membered ring compound in fair yield. Our results suggest that the triphenyltin hydride reduction of the β-chlorocycloheptanone obtained from the aluminum trichloride catalyzed cyclization of a substituted 6-heptenoyl chloride may be a good synthetic sequence for the preparation of cycloheptanones that would be difficult to obtain by other routes. It should be noted that the aluminum trichloride catalyzed cyclization of 6-heptenoyl chloride to β-chlorocycloheptanone probably goes in 76% yield, since the triphenyltin hydride reduction of a chlorocycloalkane is reported to give the corresponding cycloalkane in 70% yield.[2]

The failure of 7-octenoyl chloride to lead to cyclooctanone or methylcycloheptanones in a similar series of reactions indicates that the additional methylene group makes ring closure of a simple 7-octenoyl derivative too slow[11] to compete with polymerization reactions. It is still possible, however, that substituted 7-octenoyl derivatives would lead to cyclic products under the present reaction conditions.

Analysis of the minor products from the larger scale run showed that <1% 2-methylcyclohexanone was produced, which means that the major pathway for the olefin cyclization must be that given by eq 1, namely the formation of a seven-membered ring cation followed by reaction of that cation to give β-chlorocycloheptanone.

Experimental Section

General.—Routine equipment and methods have been previously described.[12] All reagents, solvents, and chemicals except those described below were obtained from commercial sources and purified by distillation or recrystallization when necessary.

6-Heptenoyl Chloride (1).—5-Hexenyl methanesulfonate was prepared in 95% yield from 5-hexenol and methanesulfonyl chloride in pyridine by the method of Streitwieser and Schaeffer.[13] To 4.17 g (0.234 mol) of 5-hexenyl methanesulfonate in 200 ml of 70% aqueous acetonitrile was added 33.0 g (0.506 mol) of potassium cyanide. After the mixture was refluxed and stirred for 9 hr, an additional 15 g of potassium cyanide was added. The mixture was refluxed for 20 hr and cooled. Ether (50 ml) was added to the two dark layers and the ethereal solution was washed with water five times. The washings were extracted twice with ether and the combined ethereal solutions were washed twice with saturated sodium bicarbonate, dilute hydrochloric acid, and water. The ethereal solution was dried ($MgSO_4$) and the ether was removed, yield 80%. The nitrile (19.0 g, 0.2 mol) and 17.7 g (0.3 mol) of potassium hydroxide in 210 ml of 60% aqueous ethanol were refluxed for 26 hr. To the cooled mixture was added *ca.* 150 ml of cold 3 *M* hydrochloric acid. The mixture was extracted with ether twice; the combined ether extracts were washed twice with water, dried ($MgSO_4$), concentrated, and distilled, giving 21.8 g (85%) of a colorless liquid: bp 118–120° (10 mm) [lit.[14] bp 125° (15 mm)]; nmr (CCl_4) δ 12.08 (s, 1, –COOH), 6.20–4.80 (m, 3, CH_2=CH–), 2.34 (t, 2, J = 6.5 Hz, $-CH_2COOH$), 2.08 (q, 2, J = 6 Hz, CH_2=$CHCH_2$–), and 1.85–1.15 (m, 4).

Treatment of the acid with thionyl chloride in pyridine gave the chloride, 71%, bp 63–64° (8 mm) [lit.[14] bp 70° (20 mm)], nmr (CCl_4) same as 6-heptenoic acid except that the acid peak was absent and the $-CH_2O-$ triplet was at δ 2.87 (J = 7 Hz).

α-Chlorocycloheptanone was prepared by the method of Newman,[15] nmr (neat) δ 4.9–4.6 (q,[16] 1, –CHCl–) and 2.9–1.3 (m, 10).

7-Octenyl Chloride.—5-Hexenol was converted into 7-octenoic acid by a malonic ester synthesis similar to that used by Bartlett,[11] bp 100–101° (0.8 mm) [lit.[17] bp 136° (15 mm)]. The acid was converted into the acid chloride with oxalyl chloride by the method of Goldsmith and Cheer.[18]

Conversion of 6-Heptenoyl Chloride into Cycloheptanone.—A quantity of 0.29 g (2.0 mmol) of 6-heptenoyl chloride in 8 ml of methylene chloride was added over a period of 20 min to a stirred mixture of 0.40 g (3.0 mmol) of aluminum trichloride in 8 ml of methylene chloride at 25° under a nitrogen atmosphere. After the mixture was stirred for 2 hr, 15 ml of methylene chloride was added and the mixture was washed with 10% hydrochloric acid, water, and saturated sodium bicarbonate. After the methylene chloride solution was dried ($MgSO_4$) and filtered, the solvent was removed by distillation with the last traces of solvent being removed under vacuum. The nmr and ir spectra of the product were consistent with those of β-chlorocycloheptanone: nmr ($CDCl_3$) δ 4.6–4.1 (quintet, 1, ClCH–) and 3.1–1.3 (m, 10); ir (CCl_4) 1705 cm^{-1} (C=O). The crude product was reduced by triphenyltin hydride in toluene by the method of Kuivila.[2] A known quantity (*ca.* 1.0 mmol) of cyclohexanone was added to the solution after the hydride reduction and the solution was analyzed directly by glpc. The yield of cycloheptanone was determined by comparison of the cycloheptanone peak with that of the cyclohexanone with the assumption that the thermal conductivities of the two ketones are equal.

A larger scale run using 3.05 g (20.8 mmol) of 6-heptenoyl chloride was carried out in a similar fashion. After the hydride reduction, the toluene was distilled at atmospheric pressure and 0.70 g of a product that distilled at 55–62° (9 mm) was collected. The nmr and ir spectra of this fraction were essentially those of cycloheptanone. Glpc analysis using an 8 ft × 0.25 in. column of 20% Carbowax 20M on Chromosorb P at 140° showed that this fraction contained >80% cycloheptanone, <2% 2-methylcyclohexanone, <11% 3-methylcyclohexanone, no 4-methylcyclohexanone, and *ca.* 5% of an unknown. These products were identified by peak enhancement with authentic samples.

Attempted cyclizations of 7-octenoyl chloride were carried out by the method described above for the cyclization of 6-heptenoyl

(7) J. A. Marshall and N. H. Anderson, *Tetrahedron Lett.*, 1219 (1967).
(8) P. J. Goldsmith and B. C. Clark, Jr., *ibid.*, 1215 (1967).
(9) M. F. Ansell, J. C. Emmett, and R. V. Coombs, *J. Chem. Soc., C*, 217 (1968).
(10) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968).
(11) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1314 (1965).
(12) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).
(13) A. Streitwieser and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 6233 (1957).
(14) P. Graubert, R. P. Linstead, and H. N. Rydon, *J. Chem. Soc.*, 1971 (1937).
(15) M. S. Newman, M. D. Farbman, and H. Hipsher, "Organic Synthesis," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., p 188.
(16) This peak is a quartet and is similar to the nmr signals of the α protons of some α-halocyclohexanones that have been reported by E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **86**, 1780 (1964).
(17) A. S. Von Dozent, *Fette, Seifen Anstrichmittel*, **58**, 1077 (1956).
(18) D. J. Goldsmith and C. J. Cheer, *J. Org. Chem.*, **30**, 2264 (1965).

chloride and by modified procedures using 20–130 times more solvent and the following systems: CS_2–$SnCl_4$; benzene–$SnCl_4$; CS_2–$AlCl_3$; ethyl ether–$SnCl_4$.

Registry No.—1, 21430-12-6; cycloheptanone, 502-42-1; β-chlorocycloheptanone, 21430-13-7.

Attempted Ring Cleavage and Closures of the Norbornane Skeleton by Organometallic Routes

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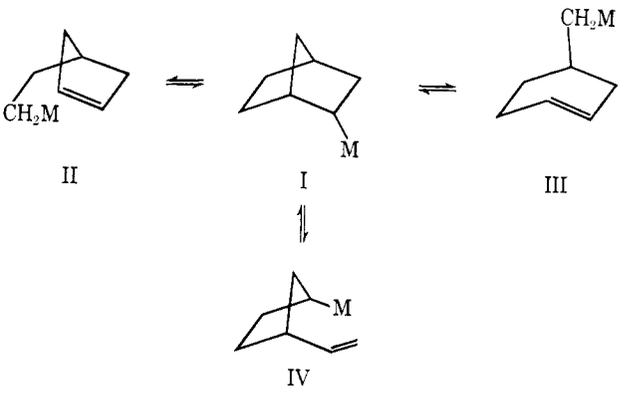
In earlier studies, it has been found that carbon–carbon bond cleavage with ring rupture occurs in cyclobutylmethyl Grignard reagents and other polar organometallics in which the metal is on a carbon atom adjacent to a strained ring.[2] In some systems, the reverse, an intramolecular addition to the carbon–carbon double bond, is observed.[2b,3]

Another strained cyclic system of interest is the bicyclo[2.2.1]heptyl system. Freeman and coworkers have found that reactions of 5-chloro- and 5-chloromethylnorbornene with sodium lead to ring-cleavage products, but that the saturated analogs show no such rearrangement.[2f,4] Most likely, a great deal of the driving force in these cases derives from formation of allylic carbanions or organosodium compounds, and possibly from the increased strain of norbornene over norbornane.[5] A similar lack of ring cleavage was noted in the norbornyllithium compound formed by addition of *t*-butyllithium to norbornene.[6]

We find, as did Freeman, that the reaction of norbornyl chloride with sodium produces no cleavage attributable to transient organosodium compounds. Furthermore, no evidence for ring cleavage is found on heating the Grignard reagent in tetrahydrofuran to 130° for 100 hr or 170° for 40 hr. In both cases, attack on solvent leads to destruction of the organometallic. Similar lack of ring cleavage is found with norbornyllithium in hydrocarbon or ethers under a variety of conditions.

Failure to observe cleavage in the norbornyl system might, in principle, be due either to the slowness of the reaction relative to other reaction pathways open to the organometallic, or to thermodynamic stability of the norbornyl skeleton relative to the various alternative ring-cleaved systems (eq 1). For this reason, halides

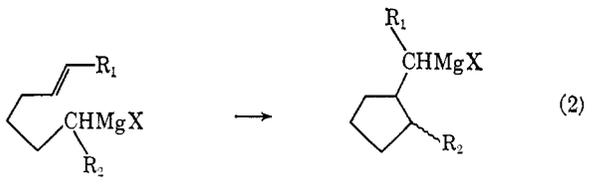


II I III IV

corresponding to organometallics II and III were prepared. It may be noted that the former carbonium ion cyclizes readily to norbornyl,[7] which suggests that such a cyclization of the organometallic *might* be energetically feasible.

The Grignard reagent from Δ³-cyclohexenylmethyl bromide was heated to 140–180°. The only products found were 4-methylcyclohexene and toluene. Similar results were obtained on heating the lithium reagent until it had pyrolized completely or on treating the bromide with sodium. Results are somewhat less conclusive with 2-(Δ³-cyclopentenyl)ethyl organometallics, owing to the strong tendency toward carbonium-ion cyclization. Hydrolysis of the Grignard reagent prepared from the bromide yielded 4-ethylcyclopentene and about 6% norbornene. After heating until most of the Grignard reagent had been destroyed by attack on solvent, about 9% norbornane was found. This may result from a small amount of cyclization under drastic conditions or simply from preferential norbornane formation by the norbornyl Grignard on reaction with the solvent. The original bromide contained about 5% norbornyl bromide. Formation of the lithium reagent, and reaction of the chloride with sodium likewise produced about 2–3% norbornane. At any rate, it may be concluded that, if cyclization of the cyclopentenylethyl system to norbornyl does occur by an organometallic route, the reaction is slow even under the most drastic conditions.

Recently, Richey[3] has reported that the Grignard reagent Vb from 6-bromo-1-heptene undergoes a facile ring closure to a mixture of *cis*- and *trans*-2-methylcyclopentylmethyl Grignard reagents (VIb) (eq 2). We



(2)

Va, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$

VIa, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$

(1) (a) To whom inquiries should be addressed: Department of Chemistry, University of Wisconsin—Milwaukee. (b) Acknowledgment is made to the donors of Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (c) Taken in part from the Ph.D. Thesis of R. J. T., University of Minnesota, 1966. (d) Taken in part from the M. S. Thesis of A. D., University of Minnesota, 1963.

(2) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964); (b) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963). (c) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 264 (1960). (d) P. T. Lansbury, *ibid.*, **85**, 1886 (1963). (e) E. A. Hill, R. J. Theissen, and K. Taucher, *J. Org. Chem.*, **34**, 3061 (1969). (f) P. K. Freeman, V. N. M. Rao, D. E. George, and G. L. Fenwick, *ibid.*, **32**, 3958 (1967).

(3) H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966).

(4) P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, **29**, 1682 (1964).

(5) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

(6) J. E. Mulvaney and Z. G. Garlund, *J. Org. Chem.*, **30**, 917 (1965).

(7) (a) R. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (c) C. F. Wilcox and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).