203–204.5°). These compounds retain solvent very tenaciously and this accounts for the variation in melting points observed. However, the infrared and nmr spectra verify the structures: ν_{max}^{KBr} 3425, 2941, 1770 and 1709 cm^{-1}. Treatment of V with ethereal diazomethane gave the above-mentioned V methyl ester.

Epoxidation of Lactone VII.—To a mixture of 0.82 g of VII[10] (mp 90–91°) and 2.8 g of anhydrous sodium sulfate in 50 ml of methylene chloride was added a solution of trifluoroperacetic acid prepared, as described above, from 1.25 ml of trifluoroacetic anhydride and 0.25 ml of 90% H_2O_2 in 10 ml of methylene chloride. After addition was complete, the solution was refluxed for 30 min. Filtration followed by removal of solvent gave 0.9 g of product, the glpc of which showed 25% unreacted VII and 75% *exo*-epoxide. Slow recrystallization from ether gave pure *exo* epoxide: mp 175–176°; ν_{max}^{KBr} 1755, 1185 cm^{-1}; nmr [CD_3-C(=O)CD_3], δ 1.08 (bd, J = 10 cps, H_{7a},H_{8a}), 1.50 (d, J = 10 cps, H_{7s},H_{8s}).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.72; H, 6.72. Found: C, 66.59; H, 6.54.

Sample Epoxidation Experiment as Used in Table I.—The following typical experimental procedure was used for those experiments recorded in Table I because under these conditions a quantitative recovery of organic material was obtained. When disodium hydrogenphosphate was used, a quantitative recovery of organic material could never be obtained despite repeated washings of the solid disodium hydrogenphosphate precipitate with methylene chloride. When *m*-chloroperbenzoic acid was used as an epoxidizing agent the gas chromatographic analysis was complicated by by-products, presumably arising from the *m*-chloroperbenzoic acid, which, however, gave esssentially the same ratio of *exo*:*endo* epoxides with III as obtained from trifluoroperacetic acid as determined by nmr analysis of the corresponding methyl esters.

To a mixture consisting of 1.78 g of III (0.01 mol) and 5.7 g of anhydrous sodium sulfate in 50 ml of methylene chloride, there was added slowly a solution of trifluoroperacetic acid prepared from 2.5 ml of trifluoroacetic anhydride, 0.5 ml of 90% hydrogen peroxide, and 15 ml of methylene chloride prepared as described above. After addition was complete, the solution was refluxed for 30 min, cooled to room temperature, and filtered, the precipitate was washed with methylene chloride, and the combined filtrate was concentrated on the rotary evaporator. To the residue 25 ml of dry benzene was added and removal of this solvent with the rotary evaporator gave 1.94 g of product. This product was dissolved in methanol and treated with excess etheral diazomethane. The resulting mixture was analyzed by glpc and gave the results indicated in the first line of Table I.

Registry No.—$C_{10}H_{10}O_4$ (*exo*-epoxide), 5826-30-2; VIII, 17989-97-8; $C_{10}H_{10}O_4$ (*endo*-epoxide), 17989-98-9; dimethyl ester of $C_{10}H_{10}O_4$ (*endo*-epoxide), 18019-45-9; VII (*exo*-epoxide), 17989-99-0.

Acknowledgment.—We thank the University System of Georgia for Quality Improvement Funds in support of this research. We also thank Dr. M. V. Kulkarni for initial experiments.

(10) S. F. Birch, N. J. Hunter, and D. T. McAllan, *J. Org. Chem.*, **21**, 970 (1956).

Reduction of 6-Dichloromethyl-2,6-dimethylcyclohexa-2,4-dien-1-one

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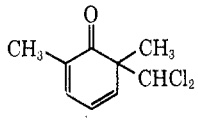
The chlorinated cyclic ketones available by the "abnormal" Reimer–Tiemann reaction[2] of substituted phenols offer a potentially useful and direct method for the preparation of alicyclic ketones and their derivatives. Yet there has been very little use made of such compounds, perhaps partly owing to difficulties encountered in their reduction.[3] Recently, the reduction of two dichloromethylmethylcyclohexanones has been reported.[4] We sought to apply this method to the preparation of 2,2,6-trimethylcyclohexanone, a useful synthetic intermediate, from 6-dichloromethyl-2,6-dimethylcyclohexa-2,4-dien-1-one, and report our results herewith.

Results and Discussion.—When the dichloromethyldienone **1** is hydrogenated in the presence of 15% KOH–methanol and with 10% Pd–C, two neutral products are isolated. The expected 2,2,6-trimethylcyclohexanone is produced in 12% yield and a monochloro ketone is produced in 14% yield. This ketone is not the expected 2-chloromethyl-2,6-dimethylcyclohexanone **2**, however, but the bicyclic ketone **3**. This



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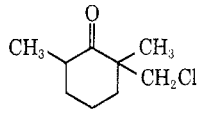

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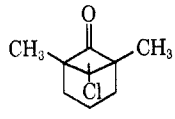

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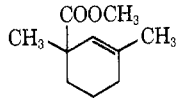
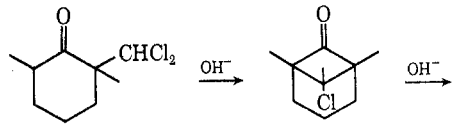


4

structure is supported by the infrared carbonyl absorption at 5.63 μ, characteristic of four-membered ketones.[5] While lactones also absorb in this region, the elemental analysis precludes this structure. The nmr spectrum also supports this structure (see Experimental Section).

Further confirmation of this structure was found in a product isolated from the aqueous extracts of the original hydrogenation mixture. Upon acidification, a mixture of acids was obtained. These, after esterification with methanol, yielded as a major component the cyclohexene derivative **4**. The structure of this ester is assigned on the basis of its analysis, as well as absorption in the infrared region at 12.4 μ (trisubstituted olefin,[5] but more particularly on the basis of its nmr spectrum (see Experimental Section). A plausible mechanism interrelating these products is the attack



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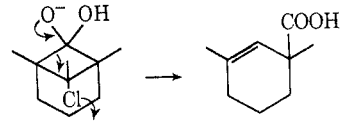


by base on intermediate 2-dichloromethyl-2,6-dimethylcyclohexanone **5**, followed by base-catalyzed ring

(1) National Science Foundation Undergraduate Research Participant.
(2) H. Wynberg, *Chem. Rev.*, **60**, 169 (1960).
(3) M. Busch and H. Stove, *Ber.*, **49**, 1063 (1916).
(4) M. G. Reinecke, *J. Org. Chem.*, **29**, 299 (1964).
(5) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966.

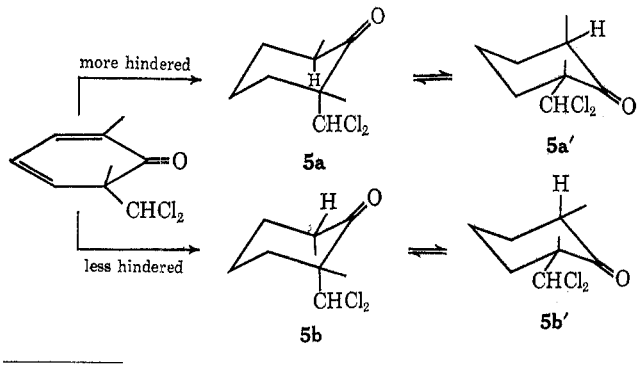
opening and expulsion of chloride ion. In accord with the proposed mechanism, ketone **3**, after treatment with methanolic KOH and esterification with diazomethane, is cleanly converted into the methyl ester **4**.

As the direct hydrogenation produced an inferior yield of the trimethylcyclohexanone, the two-step procedure, neutral hydrogenation, followed by basic hydrogenation, was utilized. Neutral hydrogenation, utilizing 10% Pd–C, proceeded without incident, to give a good yield of the tetrahydro compound **5a**. This was obtained as a liquid. Upon hydrogenation under basic conditions, 2,2,6-trimethylcyclohexanone was obtained in improved yield (54%), along with the bicyclic ketone **3**. In addition, gas chromatography and infrared analysis showed the presence of a small amount of chloromethyl ketone **2**. A solid was also isolated of mp 88.5–90.5, whose infrared spectrum closely resembled that of the liquid tetrahydro isomer **5a**, previously obtained by neutral hydrogenation. The nmr spectrum, as well as the analysis, makes it clear that this is also a 2-dichloromethyl-2,6-dimethylcyclohexanone.

It appears then that the two isomeric forms of this ketone may be separately obtained. To establish the stereochemistry of the two isomers, the products were separately subjected to treatment with alcoholic KOH. It is to be expected that isomer **5a** would react more rapidly to form the four-membered ketone. It was in fact found that the liquid ketone formed the four-membered ketone almost completely after treatment for 20 min with 15% alcoholic KOH. The solid isomer **5b**, according to infrared analysis, under the same conditions, forms mostly an equilibrium mixture of the two ketones. Upon subjecting either of the ketones **5a** or **5b** to gas chromatography (180°, *ca.* 30 min), the same mixture of isomers is formed, according to infrared analysis.

The interesting conclusion to be drawn from this experiment is that hydrogenation under neutral conditions proceeds by approach to the more hindered side of the dienone, as shown below, to give **5a**, rather than the expected isomer **5b**, which would be formed by steric approach control *via* hydrogenation from the least hindered side.[6] A possible explanation is that the dichloromethyl group is more strongly adsorbed on the catalyst than a methyl group, thereby facilitating hydrogenation from the more hindered side (Scheme I). While it is clear that isomer **5b** (**5b'**) is not excluded from formation of the bicyclic ketone,

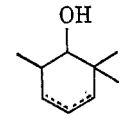
SCHEME I



this reaction must be preceded by isomerization of the α hydrogen to give **5a** (**5a'**).

A further conclusion, derived from the base-catalyzed hydrogenation, is that liquid isomer **5a** is hydrogenated more rapidly than solid **5b**.

Other methods of reduction were briefly investigated. $LiAlH_4$[7] and diphenyltin dihydride[8] failed to remove halogen from the dienone. Reduction with sodium in alcohol[9] gave a poor yield of a mixture of alcohols of type **6**.



6

The catalytic reduction of 6-dichloromethyl-2,6-dimethylcyclohexa-2,4-dien-1-one then provides a good method for the preparation of 2,2,6-trimethylcyclohexanone, as well as for the bicyclic ketone, 6-chloro-1,5-dimethylbicyclo[3.1.1]heptan-7-one (**3**), and of *cis*- and *trans*-dichloromethyl-2,6-dimethylcyclohexanones.

Experimental Section[10]

6-Dichloromethyl-2,6-dimethylcyclohexa-2,4-dien-1-one (1).[2]—2,6-Xylenol, 250.0 g, was dissolved in a solution of 750 g of KOH in 1500 ml of H_2O. Chloroform, 500 ml, was added slowly with heating initially, then at a rate to maintain reflux. After the addition was complete, the mixture was gently refluxed for an additional 5 hr. The resultant mixture was extracted with ether. The ether layer was thoroughly extracted with 10% KOH solution, washed with water, dried over anhydrous K_2CO_3, and concentrated *in vacuo*. The residual oil was distilled under reduced pressure to give 112.0 g (26.6%) of 6-dichloromethyl-2,6-dimethylcyclohexadien-1-one, bp 111–113° (6 mm).

One-Step Catalytic Reduction.—6-Dichloromethyl-2,4-dimethylcyclohexa-2,4-dien-1-one, 5.0 g, was hydrogenated in a solution of 170 ml of 15% KOH–methanol with 2.5 g of 10% Pd–C, utilizing a Paar apparatus, and an initial pressure of 60 psi of H_2. Approximately 3 equiv of H_2 was absorbed in 16 min. The catalyst was removed by filtration, the solvent evaporated under reduced pressure, and the residue poured into water. The products were extracted with ether, washed with water, and dried over $MgSO_4$. The ether solution was evaporated under reduced pressure yielding 1.79 g of product which was analyzed by gas chromatography using a 10 ft × 0.25 in. column packed with 20% Apiezon L (5 ft) and 20% DEGS (5 ft)/60–80 Chromosorb W at 182°. The following products were detected: 2,2,6-trimethylcyclohexanone (33.0%), 6-chloro-1,5-dimethylbicyclo-[3.1.1]heptan-7-one (40.0%), unidentified (27.0%).

Neutral Hydrogenation.—6-Dichloromethyl-2,6-dimethylcyclohexa-2,4-dien-1-one (**1**), 110.0 g, was hydrogenated in 175 ml of methanol, using 1.0 g of 10% Pd–C, in a Paar apparatus with 40.7-psi initial pressure. After 2 equiv had been absorbed, the catalyst was removed by filtration, the solvent evaporated, and the product taken up in ether and washed with water. Distillation under reduced pressure gave 106 g (94.5%) of 2-dichloromethyl-2,6-dimethylcyclohexanone, **5a**: bp 116–118° (8 mm): ir 3.39 (s), 3.49 (m), 5.85 (s), 6.87 (m), 7.24 (m), 7.30 (w), 8.09 (w), 8.90 (m), 10.36 (m), 11.92 (m), 13.00 (s), 13.36 (m), 13.65

(6) H. E. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 1.

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

(8) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964).

(9) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, **82**, 5377 (1960).

(10) The melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. The boiling points are uncorrected. Infrared spectra were determined as liquid films unless otherwise indicated. Nmr spectra were determined with a Varian A-60 spectrometer, 10% solutions in CCl_4, with TMS internal reference. Analyses were made by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(m), and 14.25 μ (m); nmr singlet τ 3.82 (1 H), multiplet *ca.* 8.0, singlet 8.67 (3 H), doublet 8.97 (3 H). *Anal.* Calcd for $C_9H_{14}OCl_2$: C, 51.67; H, 6.70; Cl, 33.97. Found: C, 51.75; H, 6.59; Cl, 33.87.

Basic Hydrogenation of 2-Dichloromethyl-2,6-dimethylcyclohexanone (5).—2-Dichloromethyl-2,6-dimethylcyclohexanone, 90.0 g, was hydrogenated in two portions, each in 175 ml of 15% KOH–methanol, utilizing a Paar apparatus and 5.0 g of 10% Pd–C. The work-up was identical with that previously described. Crude product (54.6 g) was obtained which was analyzed by gas chromatography, as above. The following products were identified: 2,2,6-trimethylcyclohexanone (61.0%), ketone **3** (27.0%), and 2-dichloromethyl-2,6-dimethylcyclohexanone, **5** (2.0%). The material was distilled to give the following fractions: 2,2,6-trimethylcyclohexanone [bp 56–60° (9 mm); 55% yield; lit.[11] bp 66–67° (10 mm)]; 6-chloro-1,5-dimethylbicyclo[3.1.1]heptan-7-one (**3**) [bp 100–101° (9 mm); 25% yield; mp 27°; ir 3.41 (s), 3.50 (m), 5.63 (s), 5.79 (m), 6.89 (m), 7.23 (m), 7.85 (w), 8.01 (w), 9.38 (w), 9.63 (w), 10.31 (w), 10.57 (m), 10.95 (m), 11.29 (w), 12.68 (w), 13.26 μ (w); nmr singlet τ 5.94 (1 H), triplet 7.73 (4 H), quintuplet 8.34 (2 H), singlet 8.90 (6 H) (*Anal.* Calcd for $C_9H_{13}OCl$: C, 62.69; H, 7.68; Cl, 20.58. Found: C, 62.61; H, 7.58; Cl, 20.53)]; 2-dichloromethyl-2,6-dimethylcyclohexanone (**5b**) [bp 111–116° (9 mm); mp 88.5–90.5° after three recrystallizations from ether; ir 3.36 (w), 3.39 (s), 3.49 (m), 5.88 (s), 6.88 (m), 7.26 (m), 10.43 (m), 10.77 (w), 11.31 (w), 11.52 (m), 11.84 (w), 12.05 (m), 13.08 (s), 13.36 (s), 14.16 (w), 14.80 μ (w); nmr singlet τ 3.62 (1 H), singlet 8.77 (3 H), doublet 8.99 (3 H) (*Anal.* Calcd for $C_9H_{14}OCl_2$: C, 51.67; H, 6.70; Cl, 33.97. Found: C, 51.58; H, 6.67; Cl, 33.79)].

3-Carboxymethyl-1,3-dimethylcyclohexene (4).—A portion of the filtered aqueous extract was acidified with concentrated hydrochloric acid. The oily precipitate was extracted with ether and converted into methyl ester by treatment with 5% methanolic HCl. The ester mixture was analyzed by gas chromatography (10 ft × 0.25 in. 20% Apiezon L + 20% DEGS/60–80 Chromosorb W, 140°). The major component was analyzed: ir 3.41 (s), 5.77 (s), 6.96 (s), 7.27 (w), 7.36 (w), 7.46 (w), 8.63 (m), 8.99 (s), 10.10 (w), 11.60 (w), 11.91 (w), 12.37 (w), 13.02 μ (w); nmr singlet τ 4.69 (1 H), singlet 6.40 (3 H), quintuplet 8.20 (2 H), singlet 8.34 (3 H), singlet 8.83 (3 H). *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.32; H, 9.61. Found: C, 71.43; H, 9.51.

Reaction of Stereoisomers 5a and 5b with Base.—The liquid isomer of 2-dichloromethyl-2,6-dimethylcyclohexanone (**5a**) and solid isomer **5b** were treated separately with 10% KOH–methanol for 20 min at room temperature. The products were isolated as previously described under the hydrogenation experiments. Analysis by infrared spectroscopy (2.5% solution of CS_2) indicated that the liquid isomer was almost completely converted into the bicyclic ketone **3** (band at 5.63 μ). The solid isomer showed lesser amounts of ketone **3**, and an almost equal mixture of ketones **5a** and **5b** (bands at 11.92 and 12.05 μ, respectively).

Sodium–Alcohol Reduction.—6-Dichloromethyl-2,6-dimethylcyclohexa-2,4-dien-1-one, 30.0 g, was dissolved in 150 ml of absolute ethanol. Sodium, 18.0 g, was added in pieces as rapidly as possible, and with vigorous stirring. A black, viscous mixture resulted. After all of the sodium reacted, the solution was cooled and poured into ice water. The products were extracted with petroleum ether (bp 30–60°) and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Fractional distillation yielded an oil with a distinct camphoraceous odor: yield 2.7 g (13%); bp 72–80° (10 mm). A gas chromatographed sample was analyzed: ir 2.98 (s), 3.32 (m), 3.40 (s), 3.42 (s), 6.05 (w), 6.89 (m), 7.30 (m), 9.80 (s), 14.10 μ (m). *Anal.* Calcd for $C_9H_{16}O$: C, 77.14; H, 11.43. Found: C, 77.07; H, 11.67.

Registry No.—**1**, 14789-76-5; **3**, 18386-55-5; **4**, 18386-56-6; **5a**, 18386-57-7; **5b**, 18386-58-8.

Acknowledgment.—This research was partly supported by a grant from the Petroleum Research Fund, American Chemical Society, and is gratefully acknowledged.

(11) O. Wallach and B. Kempe, *Ann.*, **329**, 86 (1903).

An Alternative Synthesis of *trans*-8,10-Dimethyl-1(9)-octal-2-one

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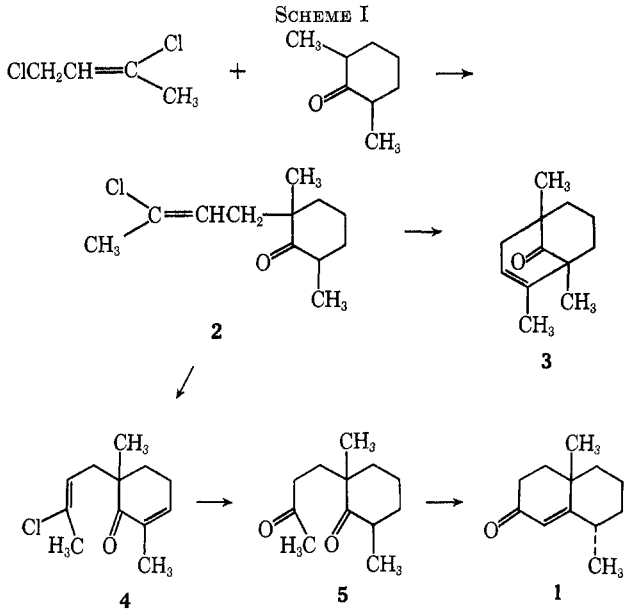
Received June 24, 1968

Recently, Marshall and Schaeffer[1] have discussed the difficulties associated with the usual synthetic approaches to *trans*-8,10-dimethyl-1(9)-octal-2-one (**1**) and have developed the first efficient synthesis of this compound. These workers found that a normal Wichterle scheme[2] involving alkylation of 2,6-dimethylcyclohexanone with 1,3-dichloro-2-butene followed by hydrolysis of the γ-chlorocrotyl ketone **2** in concentrated sulfuric acid gave only the bicyclo[3.3.1]nonene **3** and none of the desired octalone **1**. The complete failure of the Wichterle scheme in this case resulted from the fact that, under the strongly acidic conditions required for hydrolysis of the vinyl chloride system, the intermediate diketone **5** was rapidly cyclized to **3**.[1,3] However, by a modification of the Wichterle scheme involving bromination and dehydrobromination **2** was converted into the γ-chlorocrotylenone **4** which was hydrolyzed and then reduced catalytically to **5**. Cyclization of **5** under basic conditions then gave **1** in excellent yield (Scheme I).[1]

SCHEME I



In connection with other research we were interested in the synthesis of **1** and have developed an alternative method which involves modification of the γ-chlorocrotyl side chain for conversion of **2** into **5**. It was felt that, if **2** could be converted into the ketoacetylene

(1) J. A. Marshall and D. J. Schaeffer, *J. Org. Chem.*, **30**, 3642 (1965).

(2) O. Wichterle, J. Prochaska, and J. Hoffman, *Collect. Czech. Chem. Commun.*, **13**, 300 (1948).

(3) See ref 1 and S. Julia, *Bull. Soc. Chim. Fr.*, **21**, 780 (1954); W. G. Dauben and J. W. McFarland, *J. Amer. Chem. Soc.*, **82**, 4245 (1960); and E. J. Corey and S. Nozoe, *ibid.*, **87**, 5728 (1965), for other examples of the formation of bridged systems in acid-catalyzed cyclizations of 1,5 diketones related to **5**.