(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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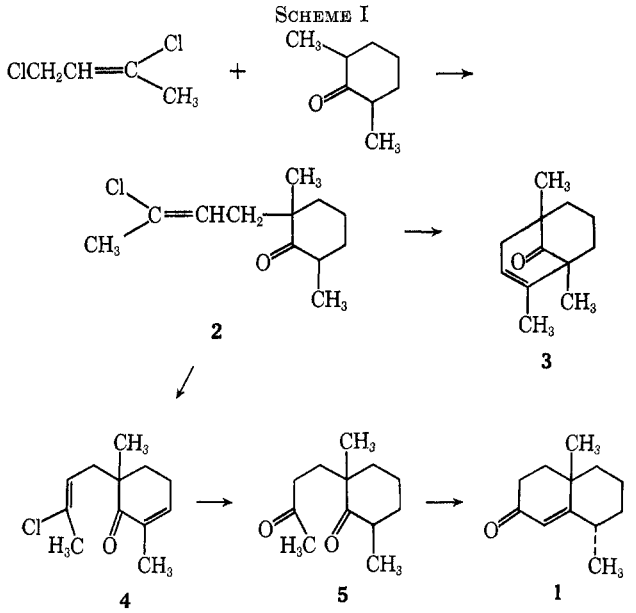
Recently, Marshall and Schaeffer[1] have discussed the difficulties associated with the usual synthetic approaches to *trans*-8,10-dimethyl-1(9)-octal-2-one (**1**) and have developed the first efficient synthesis of this compound. These workers found that a normal Wichterle scheme[2] involving alkylation 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



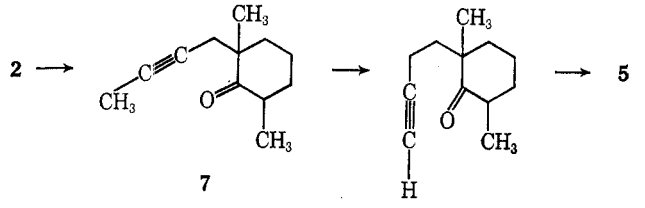
In connection with other research we were interested in the synthesis of **1** and have developed an alternative method which involves modification of the γ-chlorocrotyl side chain for conversion of **2** into **5**. It was felt that, if **2** could be converted into the ketoacetylene

(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**.

6 by dehydrohalogenation[4] and isomerization of the triple bond to the terminal position,[5] hydration of the triple bond could be carried out under sufficiently mild conditions so that 5 could be isolated and then cyclized to 1 under basic conditions.



7 6

Treatment of 2 with 2 equiv of sodium amide[6] in liquid ammonia for 4 hr gave the internal acetylene derivative 7 in quantitative yield.[7] Further reaction of 7 with 3 equiv of sodium amide in refluxing toluene for 12 hr led to the isolation of 6 in 73% yield.[8] On treatment of 6 with approximately 2% sulfuric acid in methanol–water containing a catalytic amount of mercuric sulfate for 1.5 hr at room temperature, hydration of the triple bond occurred to give 5 in 96% yield. Diketone 5 was then cyclized to 1 in 73% yield using sodium ethoxide in ethanol according to the conditions of Marshall and Schaeffer.[1]

The results of the attempted preparation of 6 by treatment of 2 with 5 equiv of sodium amide in refluxing toluene for 12 hr appear to be worthy of comment. Compound 6 was formed but the nmr spectrum of the distilled material showed that it was contaminated with a considerable amount of another product. This compound had a vpc retention time[9] identical with that of one of the isomers of 6.[7] However, hydration of the mixture as described above converted 6 into 5 and the contaminant was separated from 5 by preparative gas chromatography. This material showed a vpc retention time[9] and spectral properties identical with those of an authentic sample of 3 prepared according to the procedure of Marshall and Schaeffer.[1] The exact mode of formation of 3 on treatment of 2 with sodium amide in toluene is not known. It is possible that internal addition of C-6 of the sodium enolate of 2 to the γ position of the side chain followed by elimination of chloride ion is involved. Apparently in liquid ammonia this reaction does not compete to a significant extent with the direct dehydrohalogenation reaction.

Using the sequence described above the yield of 1 from 2 is comparable with that reported by Marshall and Schaeffer.[1] Although strongly basic conditions are required in the scheme, it appears to be applicable to the synthesis of certain octalones related to 1 but having functional groups which might be reactive under the conditions employed in the previous synthesis. The demonstration that a γ-chlorocrotyl ketone such as 2 can be readily converted into a 1,5 diketone by dehydrohalogenation, triple-bond isomerization, and hydration appears to broaden considerably the utility of 1,3-dichloro-2-butene as a methyl vinyl ketone equivalent in annelation reactions.[10]

(4) Since commercially available 1,3-dichloro-2-butene was used in the synthesis of 2, this material probably consists of geometric isomers with the side chain both *cis* and *trans* (see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N Y., 1967, p 214). However, in view of the work of L. F. Hatch and R. F. Perry, Jr. [*J. Amer. Chem. Soc.*, **77**, 1136 (1955)] on the isomeric 1,3-dichloro-2-butenes, both of these isomers should undergo relatively facile dehydrohalogenation.

(5) T. L. Jacobs, *Org. Reactions*, **5**, 1 (1949).

(6) We found it absolutely necessary to freshly prepare the sodium amide for use in this sequence. When commercially available sodium amide was employed, erratic results and much lower yields were obtained.

(7) As pointed out by Marshall and Schaeffer,[1] chlorocrotylation of 2,6-dimethylcyclohexanone gives an approximately 50:50 mixture of two stereoisomers with the four-carbon side chain at C-2 *cis* and *trans* to the C-6 methyl group. In the sequence 2 → 7 → 6 → 5 mixtures of isomers were obtained and used at each stage.

(8) The two steps could be combined with comparable over-all yield by treating 2 with 5 equiv of sodium amide in liquid ammonia for 4 hr, removing the ammonia and replacing it with toluene, and refluxing the mixture for 12 hr.

(9) A 10 ft × 0.25 in. column containing silicone SE-30 on firebrick was employed for the analysis.

(10) For recent references to the development and use of various methyl vinyl ketone equivalents, see G. Strok, *Pure Appl. Chem.*, **9**, 131 (1964), and G. Stork, S. Danishefsky, and M. Ohashi, *J. Amer. Chem. Soc.*, **89**, 5459 (1967).

(11) Boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 457 infrared spectrophotometer. Nmr spectra were determined at 60 Mc with a Varian A-60 spectrometer. Vapor phase chromatography was performed using an Aerograph A-90-P3 with helium as the carrier gas. Mass spectra were determined using a Varian M-66 spectrometer. Microanalyses were obtained by Galbraith Laboratories, Inc., Knoxville, Tenn.

(12) These spectral properties correspond closely to those reported for related acetylenic ketones [see M. Tanabe, D. F. Crowe, R. L. Dehn, *Tetrahedron Lett.*, 3943 (1967), and P. Wieland, H. Kaufmann, and A. Eschenmoser, *Helv. Chim. Acta*, **50** (7), 2108 (1967)].

Experimental Section[11]

2,6-Dimethyl-2-(2-butynyl)cyclohexanone (7).—Sodium amide (0.06 mol) was prepared by adding 1.38 g of freshly cut sodium to 150 ml of liquid ammonia containing about 0.1 g of anhydrous ferric chloride and the reaction mixture was stirred until the sodium amide precipitate was completely formed. A solution of 6.42 g (0.03 mol) of 2,6-dimethyl-2-(γ-chlorocrotyl)cyclohexanone (2)[1] in 25 ml of anhydrous ether was added with stirring and followed by an additional 25 ml of ether. The resulting suspension was stirred for 3 hr at reflux and stirring was continued while the ammonia was allowed to evaporate. When the reaction mixture reached room temperature, 30 ml of 10% aqueous hydrochloric acid was added slowly and the mixture was stirred for 10 min. The layers were then separated, and the aqueous layer was saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined etheral portions were washed with brine and dried over sodium sulfate. Concentration under reduced pressure gave a pale yellow oil which on distillation yielded 5.31 g of 7 (99%): bp 63–65° (0.04 mm); λ_{max}^{film} 5.86 (CO), 6.88, 7.27, 7.36, 7.60, 7.92, 8.90 and 10.00 μ; $\delta_{TMS}^{CCl_4}$ 0.93 (C_6-methyl, doublet, J = 6.4 cps), 1.02 and 1.20 (angular methyl, singlets), 1.72 ppm ($CH_3C\equiv$, triplet, J = 2.6 cps); mass spectrum m/e 178 (molecular ion).

Anal. Calcd for $C_{12}H_{18}O$; C, 80.83; H, 10.28. Found: C, 80.71; H, 10.35.

2,6-Dimethyl-2-(3-butynyl)cyclohexanone (6).—Sodium amide (0.06 mol) was prepared using 1.38 g of sodium and 20 ml of liquid ammonia as described previously. Dry toluene (30 ml) was added and the ammonia was removed by distillation. A solution of 3.56 g (0.02 mol) of 7 in 30 ml of dry toluene was added and the mixture was heated to reflux. The black suspension was refluxed with stirring for 12 hr and allowed to cool to room temperature. Aqueous hydrochloric acid (30 ml, 10%) was added slowly and the mixture was stirred for 10 min. The layers were separated, and the aqueous layer was saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined organic portions were washed with brine and dried over sodium sulfate. Concentration under reduced pressure gave a light yellow oil which on distillation yielded 2.61 g of 6 (73%): bp 65–67° (0.04 mm); λ_{max}^{film} 3.03 ($HC\equiv$), 4.72 ($-C\equiv C-$), 5.88 (CO), 6.89, 7.26, 7.61, 8.89, 9.48, and 9.92 μ; $\delta_{TMS}^{CCl_4}$ 0.93 (C_6-methyl, doublet, J = 6.4 cps), 0.96 and 1.18 ppm (angular methyl, singlets); mass spectrum m/e 178 (molecular ion).[12]

Anal. Calcd for $C_{12}H_{18}O$: C, 80.83; H, 10.28. Found: C, 80.61; H, 10.24.

2,6-Dimethyl-2-(3-oxobutyl)cyclohexanone (5).—A mixture composed of 6.8 ml of water, 0.5 g of concentrated sulfuric acid, 0.1 g of mercuric sulfate, 12.5 ml of methanol, and 2.0 g of 6 was stirred at room temperature under nitrogen for 1.5 hr. The

reaction mixture was then poured into 75 ml of water and extracted with 30 ml of ether. The aqueous layer was saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined ethereal extracts were washed with brine and dried over sodium sulfate. Concentration under reduced pressure gave a colorless oil which on distillation yielded 2.11 g (96%) of **5**: bp 86–88° (0.05 mm) [lit.[1] bp 76–77° (0.1 mm)]. The spectral properties of this material were identical with those reported for **5**.[1]

Registry No.—**1**, 17990-00-0; **6** (*cis*), 18019-46-0; **6** (*trans*), 17990-02-2; **7** (*cis*), 17990-01-1; **7** (*trans*), 17990-03-3.

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Cyclohexadienyl Cations. I. Protonation of Cyclohexadienones

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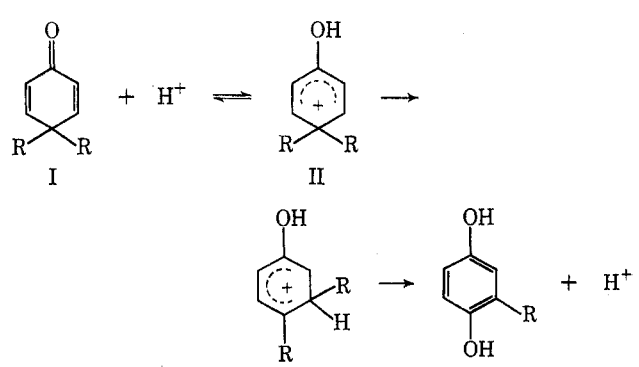
The formation of phenols from cyclohexa-2,5-dienones in the presence of an acid catalyst is a well-known reaction.[2] While many of the mechanistic details of this reaction remain unclear, there appears to be general agreement that the first step involves protonation (or coordination) of the carbonyl oxygen to form a cyclohexadienyl cation.[2b] Whereas the ultimate fate of this first intermediate depends critically on many factors, the second step seems to involve the migration of a group (usually aryl or alkyl) to a neighboring electron-deficient carbon atom.[2b,c] Subsequent expulsion of a proton furnishes the stable phenol product. This sequence is illustrated below for a simple 4,4-disubstituted cyclohexa-2,5-dienone.

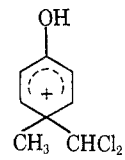


It is apparent that both the rate- and product-determining steps (which may be the same) are inextricably related to the basicity of the dienone and the distribution of charge in the first intermediate II.

(1) Address all inquiries to the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044.

(2) (a) H. H. Inhoffen, *Progr. Org. Chem.*, **2**, 146 (1953). (b) N. L. Wendler, *Mol. Rearrangements*, **2**, 1028 (1964). (c) A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 207 (1966).

A few years ago Bloom[3a] and Budzikiewicz[3b] noted that certain cyclohexadienones such as 4-dichloromethyl-4-methylcyclohexa-2,5-dienone formed stable complexes in sulfuric acid. These complexes were formulated as "delocalized ions."[3b]



IIa

We felt that these stable ions[5] would provide excellent models for the first intermediate II in the dienone–phenol rearrangement. Our investigations had a two-fold purpose. First, we wished to elucidate as completely as possible the structure and charge distribution of these stable complexes. Nmr spectroscopy seemed admirably suited to this task. Secondly, we wished to evaluate the acidity dependence for this protonation reaction to quantitatively assess the effect of substituents on the basicity of the carbonyl group.

At the time this work was completed, Friedrich[5] reported the nmr and uv spectral properties of several neutral and protonated cyclohexadienones. Friedrich's nmr and uv spectra for neutral and protonated 4-dichloromethyl-4-methylcyclohexa-2,5-dienone are essentially identical with the spectra detailed in the present work.

Results and Discussion

4-Dichloromethyl-4-methylcyclohexa-2,5-dienone (Ia) and 4-dichloromethyl-3,4,5-trimethylcyclohexa-2,5-dienone (Ib) were prepared by the reaction of sodium hydroxide and chloroform with *p*-cresol and 3,4,5-trimethylphenol, respectively.[6] These materials dissolved readily in 90.5% sulfuric acid forming stable solutions.

A complete tabulation of the nmr data for both Ia and Ib in deuteriochloroform and sulfuric acid can be found in Table I.

TABLE I

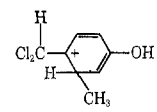
NMR SPECTRAL DATA[a] FOR Ia AND Ib IN $CDCl_3$ AND 90.5% H_2SO_4 AT 35°

Dienone	Solvent	2,6 H	3,5 H	4 CH_3	3,5 CH_3	$CHCl_2$
Ia	$CDCl_3$[b]	6.38 (d)[c]	7.00 (d)[c]	1.52		5.87
Ia	H_2SO_4[d]	7.36 (d)[e]	8.33 (d)[e]	1.65		6.20
Ib	$CDCl_3$[b]	6.26		1.55	2.22	6.10
Ib	H_2SO_4[d]	7.14		1.73	2.69	6.32

[a] Varian A-60A spectrometer, reported in parts per million from TMS. [b] Tetramethylsilane internal standard. [c] Doublet, J = 10 cps. [d] Tetramethylammonium ion internal standard. [e] Doublet, J = 9.5 cps.

(3) S. M. Bloom, *Tetrahedron Lett.*, **21**, 7 (1959); (b) H. Budzikiewicz *ibid.*, **7**, 12 (1960).

(4) The stability of IIa to rearrangement may reflect the difficulty in forming the next intermediate which would have a partial positive charge adjacent to a $CHCl_2$ group, *e.g.*



(5) E. C. Friedrich, *J. Org. Chem.*, **33**, 413 (1968).

(6) K. Von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902). See also A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 146 (1966), and H. Wynberg, *Chem. Rev.*, **60**, 169 (1960).