anhydride in 40 ml. of alcohol-free[26] chloroform was refluxed for 48 hr. and then subjected to the previously described isolation procedure. The crude product, 715 mg. of yellow prisms melting at 160–165°, contained[27] the alcohol **7b** and the ester **10c**. Two crystallizations from ether–methanol mixtures afforded 449 mg. (55%) of the ester **10c**, m.p. 169–170.5°, identified with an authentic sample by a mixture melting point determination and by comparison of infrared spectra.

Synthesis of Bicyclo[4.4.0]decanones and Bicyclo[3.3.1]nonanones *via* the Wichterle Reaction

JAMES A. MARSHALL AND DAVID J. SCHAEFFER

Department of Chemistry, Northwestern University, Evanston, Illinois

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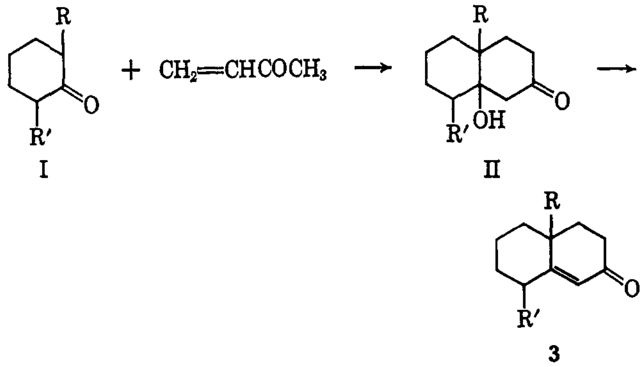
The preparation of *trans*-8,10-dimethyl-1(9)-octal-2-one (**3c**) utilizing the Wichterle reaction was explored. The sequence initially investigated involved alkylation of 2,6-dimethylcyclohexanone with 1,3-dichloro-*cis*-2-butene to give 2,6-dimethyl-2-(γ-chlorocrotyl)cyclohexanone (**1c**). Hydrolysis of this γ-chlorocrotylcyclohexanone under mild conditions in sulfuric acid afforded none of the desired dione, 2,6-dimethyl-2-(3-oxobutyl)cyclohexanone (**2c**); instead, the bridged product, 1,2,5-trimethylbicyclo[3.3.1]non-2-en-9-one (**4c**), was exclusively formed. Changes in the reaction conditions gave no useful result and therefore the sequence was modified. To this end, 2,6-dimethyl-2-(γ-chlorocrotyl)-5-cyclohexenone (**5b**), obtained from 2,6-dimethyl-2-(γ-chlorocrotyl)cyclohexanone (**1c**) by bromination and dehydrobromination, gave the corresponding dione, 2,6-dimethyl-2-(3-oxobutyl)-5-cyclohexenone (**6b**), upon hydrolysis in sulfuric acid. The desired octalone **3c** was prepared by catalytic hydrogenation of unsaturated dione **6b** followed by base-catalyzed aldol cyclization of the resulting saturated dione **2c**. The same sequence of reactions was investigated using 2-methylcyclohexanone as the starting material. In contrast to the aforementioned 2,6-dimethyl-2-(γ-chlorocrotyl)cyclohexanone (**1c**) case, conditions were found whereby 2-methyl-2-(γ-chlorocrotyl)cyclohexanone (**1a**) and 2-methyl-6-(γ-chlorocrotyl)cyclohexanone (**1b**) could be converted to the respective diones, 2-methyl-2-(3-oxobutyl)cyclohexanone (**2a**) and 2-methyl-6-(3-oxobutyl)cyclohexanone (**2b**). 8,10-Dimethyl-1(9),7-hexal-2-one (**7b**) and 10-methyl-1(9),7-hexal-2-one (**7a**) were prepared from the unsaturated diones **6b** and **6a** in order to demonstrate an additional application of the reaction sequence.

We recently described a modified Robinson annelation of cyclohexanones whereby the ketol intermediates (*e.g.*, II) are isolated and purified prior to dehydration.[1] Although this modification offers distinct advantages for the preparation of octalones derived from 2-methylcyclohexanones, it fails in the case of 2,6-dimethylcyclohexanone (I, R = R′ = CH_3). In fact, all attempts to prepare *trans*-8,10-dimethyl-1(9)-octal-2-one (**3c**) *via* the Robinson annelation route were unsatisfactory; impure bicyclic material was formed in less than 20% yield.



Since a large amount of octalone **3c** was required as a starting material for synthetic studies, we considered alternative methods for its preparation. To this end, the scheme devised by Wichterle[2] presented certain desirable features. This method utilizes 1,3-dichloro-*cis*-2-butene[3] (DCB) as a methyl vinyl ketone equivalent and thus circumvents the undesirable condensations and polymerizations which often attend Michael reactions between unactivated cyclohexanones and vinyl ketones. An application of the Wichterle sequence which commanded our attention involves the alkylation of cyclohexanone with DCB followed by hydrolysis of the resulting γ-chlorocrotylcyclohexanone **1** (R = R′ = H) in sulfuric acid to give the octalone **3** (R = R′ = H)[2c] presumably *via* the dione intermediate **2** (R = R′ = H).[2b]

Julia[2c] noted an alternative reaction pathway in the hydrolysis of 2-methyl-2-(γ-chlorocrotyl)cyclohexanone (**1a**). In this case aldol condensation of the intermediate dione **2a** (not isolated) gave the bicyclo[3.3.1]nonanone **4a** rather than the bicyclo[4.4.0]decanone **3a**. Although the same reaction course is open to the precursor of octalone **3c**, we hoped to suppress the formation of the bicyclo[3.3.1]nonane **4c** by employing mild conditions for the hydrolysis step (**1** → **2**) such that dione **2c** could be isolated. Subsequent base-catalyzed aldol condensation of this intermediate would then yield the desired octalone **3c**. Diones **2a** and **2b** were of interest in connection with another problem and we therefore also planned to utilize the above route to prepare these materials.

Chlorocrotylcyclohexanones **1a** and **1b** were prepared from 2-methylcyclohexanone by alkylation with DCB using sodamide in benzene. The resulting mixture of monoalkylated 2-methylcyclohexanones contained 80% of the 2,2 isomer **1a** and 20% of the 2,6 isomer **1b** estimated by evaluation of the integrated n.m.r. spectrum. These isomers were separated by the hydroxymethylation method,[4] and the pure 2,2-

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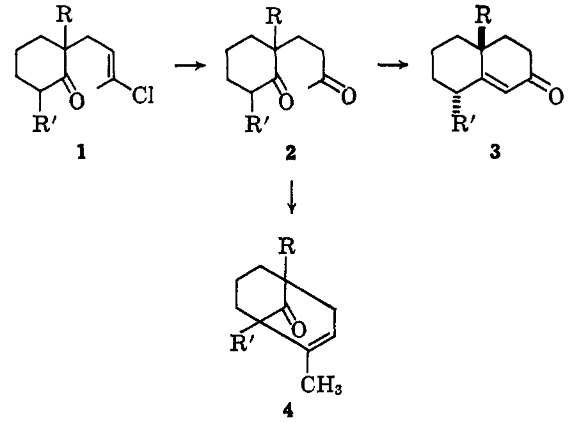
[1] J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

[2] (a) O. Wichterle, J. Prochazka, and J. Hofmann, *Collection Czech. Chem. Commun.*, **13**, 300 (1948), and earlier papers; (b) W. G. Dauben and J. W. McFarland, *J. Am. Chem. Soc.*, **82**, 4245 (1960); (c) S. Julia, *Bull. soc. chim. France*, **21**, 780 (1954); (d) V. Prelog, P. Barman, and M. Zimmerman, *Helv. Chim. Acta*, **32**, 1284 (1949).

[3] L. F. Hatch and S. G. Ballin, *J. Am. Chem. Soc.*, **71**, 1041 (1949).

[4] W. J. Bailey and M. Madoff, *ibid.*, **76**, 2707 (1954).



a, $R = CH_3$; $R' = H$
b, $R = H$; $R' = CH_3$
c, $R = R' = CH_3$

dialkylcyclohexanone **1a** was regenerated from its acidic hydroxymethylene derivative in refluxing aqueous sodium carbonate. Alkylation of 2,6-dimethylcyclohexanone proceeded smoothly and the desired γ-chlorocrotylcyclohexanone **1c** was obtained in 63% yield as a mixture of stereoisomers.

After a number of trials we found that hydrolysis of the vinyl chloride grouping of chlorocrotylcyclohexanone **1a** in sulfuric acid was complete within 30 min. at 0° and the dione **2a** was thereby obtained in about 50% yield. This finding is significant in light of the conditions reported by previous workers[2] for this phase of the Wichterle reaction. Usually the γ-chlorocrotyl compound was allowed to remain in sulfuric acid at room temperature for periods ranging from 12 hr. to 1 week. We have found that such prolonged reaction periods often give inferior yields owing to the formation of tars and water-soluble substances.[5] In fact, even under the mild conditions described above only 70–80% yields of distillable materials were realized.[6]

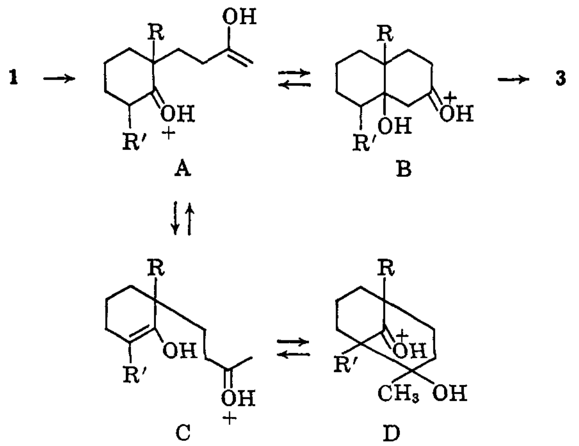
Despite numerous efforts to control conditions, the cyclization reaction leading to the bicyclo[3.3.1]-nonanone **4a** described by Julia[2c] could not be completely suppressed. This bridged ketonic substance comprised about 10% of the volatile product according to gas chromatography. However, none of the octalone **3a** was detected either in the gas chromatogram or infrared spectrum of the distilled product. Authentic bridged ketone **4a** was synthesized by allowing the γ-chlorocrotylcyclohexanone **1a** to remain in sulfuric acid for 90 min. at 0° and 45 min. at room temperature.

Hydrolysis of 2-methyl-6-(γ-chlorocrotyl)cyclohexanone (**1b**) was essentially complete within 20 min. at 0°. Dione **2b** represented the major volatile product under these conditions but, as in the previously discussed example, a significant quantity of a material which appeared to be the bridged product **4b** was formed. Again, none of the octalone **3b** could be detected. An attempt to prepare the bridged ketone **4b** by prolonging the hydrolysis reaction time gave a mixture containing principally the desired material **4b** contaminated with some octalone **3b** as evidenced by infrared and n.m.r. spectra. However, only about 10% of the reaction product could be distilled and the gas chromatogram of the distillate revealed four components. Evidently, polymerization constitutes the major reaction pathway in this case.

In sharp contrast with its above-described analogs, 2,6-dimethyl-2-(γ-chlorocrotyl)cyclohexanone (**1c**) gave no detectable amount of the expected dione **2c** upon hydrolysis in sulfuric acid at 0°. Instead, the bridged ketone **4c** was obtained in high yield. Numerous attempts to alter this result by using shorter reaction times and lower temperatures were to no avail. Either mixtures of starting material **1c** and bicyclo[3.3.1]-nonanone **4c** or the latter product alone was obtained. We could not detect dione **2c** in these reaction mixtures using n.m.r. and gas chromatographic analysis. The octalone **3c** was likewise completely absent.

Thus, not only do all three γ-chlorocrotylcyclohexanones **1a**, **1b**, and **1c** show a preference for cyclization to bridged bicyclo[3.3.1]nonanones **4a**, **4b**, and **4c** over bicyclo[4.4.0]decanones **3a**, **3b**, and **3c** in sulfuric acid, but cyclization of the dimethyl compound (presumably **2c**, see Experimental Section) occurs markedly faster than the analogous reaction of the monomethyl compounds (presumably **2a** and **2b**).

These findings provide an interesting contrast with the results obtained from 2-(γ-chlorocrotyl)cyclohexanone (**1**, R = R' = H). In this case a mixture resulted in which the bicyclo[4.4.0] and bicyclo[3.3.1] products (**3**, R = R' = H, and **4**, R = R' = H) were formed in nearly equal amount.[2c] Although any mechanistic interpretation must be regarded as speculative without additional quantitative data,[7] we present one possible explanation, because reasoning based upon these views led us to devise a means for suppressing the formation of bicyclo[3.3.1] products and thus enabled a synthesis of dione **2c** to be realized.



a, $R = CH_3$; $R' = H$
b, $R = H$; $R' = CH_3$
c, $R = R' = CH_3$

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(5) *Cf.* C. Djerassi, J. Burakevich, J. W. Chamberlin, D. Elad, T. Toda, and G. Stork, *J. Am. Chem. Soc.*, **86**, 465 (1964); G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *ibid.*, **87**, 275 (1965), for several examples where low yields are obtained using extended reaction times.

(6) If the reaction mixtures are not quenched rapidly in order to minimize the contact time of the substrate with intermediate concentrations of acid, the yield of volatile material is lowered. This technique, which is particularly important when olefins are formed, has been effectively employed by Deno, *et al.*: *cf.* N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963).

(7) *Cf.* D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4033 (1958), for the mechanism of acid-catalyzed aldol condensation.

The ease of bicyclo[4.4.0]decanone formation (A → B) will depend, in part, upon the steric environment of the cyclohexanone carbonyl grouping. Methyl groups in the 2- and 6-position of the cyclohexanone ring should retard the reaction A → B. On the other hand, both a 2- and 6-methyl group might be expected to facilitate the reaction leading to bicyclo[3.3.1] products (C → D). The energy difference between the conformer with an axial butanone side chain (needed for the formation of bridged product Da) and the equatorial side-chain conformer (where bridging is prohibited by steric effects) should be smaller in the 2-methyl-2-(3-oxobutyl)cyclohexanone intermediate Ca than in the corresponding desmethyl analog C (R = R′ = H) where the equatorial side chain should be greatly favored. Bridged product **4** might therefore be more easily formed from the former intermediate (**2a**).

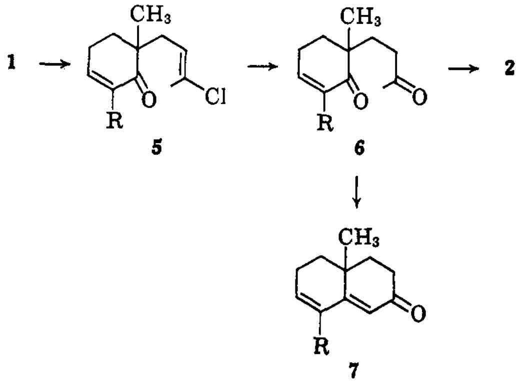
Intermediate Cb derived from dione **2b** would receive hyperconjugative stabilization of the enol double bond by the 6-methyl group. This same stabilization would, in the case of 2-(γ-chlorocrotyl)cyclohexanone, lead to the predominance of an enol form which cannot form a bridged product such as **4**. Both this factor and the previously mentioned steric retardation of the reaction leading to bicyclo[4.4.0]decanone **3b** (Ab → Bb) by a 6-methyl substituent should lead to a higher proportion of bridged ketone **4** from 2-(γ-chlorocrotyl)-6-methylcyclohexanone (**1b**) than from 2-(γ-chlorocrotyl)cyclohexanone (**1**, R = R′ = H).

Enol stability and conformational energy differences must contribute significantly to the ease with which the bicyclo[3.3.1] products **4** are formed since the cyclization rate of the presumed dimethyl intermediate Cc, where both factors are favorable, exceeds that of the monomethyl analogs Ca and Cb. This trend also suggests that reaction at the cyclohexanone carbonyl grouping (*e.g.*, A → B) is more sensitive to steric factors than reaction at the cyclohexenyl double bond (*e.g.*, C → D).

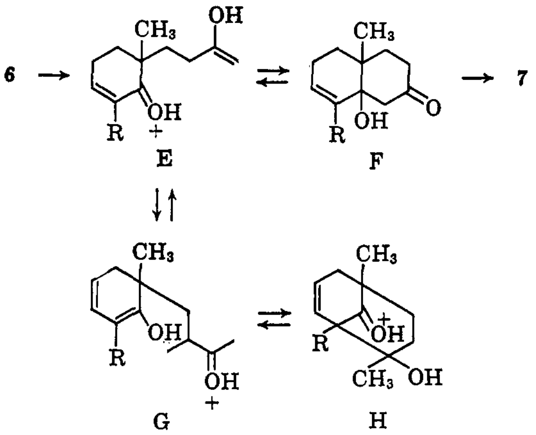
With the above arguments in mind, we reasoned that a conjugated ketone such as **6** might not cyclize readily to a bicyclo[3.3.1] product (G → H) since conjugation should diminish the nucleophilicity of the enol double bond. Furthermore, since the enol G required for such a cyclization is a *cisoid* diene, it may be less readily formed than the analogous nonconjugated enol C. Conjugation should also retard the formation of a bicyclo[4.4.0] product from dione **6** (E → F) by decreasing the electrophilicity of the ketonic function in intermediate E. Thus, there seemed to be an excellent chance that hydrolysis of the γ-chlorocrotylcyclohexenones **5a** and **5b** might give the unsaturated diones **6a** and **6b** as isolable products.

The requisite unsaturated ketones **5a** and **5b** were easily prepared by bromination of their saturated counterparts **1a** and **1c** and subsequent dehydrobromination of the crude bromo ketones. Hydrolysis of each at 0° for 1 hr. afforded the respective diones **6a** and **6b** in over 80% yield. No cyclization products of the bridged or normal type could be detected in either reaction mixture.

Diones **2a** and **2c** were readily obtained by hydrogenation of the unsaturated diones **6a** and **6b** over palladium on carbon. Dione **2a** afforded octalone **3a** upon treatment with ethanolic potassium hydroxide at room temperature. Dione **2b** was likewise converted to the isomeric octalone **3b**. Although cyclization of the homologous dione **2c** required more stringent conditions, octalone **3c** was nevertheless formed in 89% yield using ethanolic sodium ethoxide as the catalyst. The elusive 8,10-dimethyl-1(9)-octal-2-one (**3c**) is thus available from 2,6-dimethylcyclohexanone in about 40% over-all yeld.



a, R = H
b, R = CH$_3$



Procurement of unsaturated diones **6a** and **6b** gave us an opportunity to investigate the preparation of dienones **7a** and **7b**. To this end, unsaturated dione **6a** was treated with ethanolic potassium hydroxide. The resulting material contained 70% of the dienone **7a**[8] and 30% of an unidentified ketonic material (λ_{max} 5.85 μ) which could not be removed by distillation or chromatography. Cyclization of the homologous dione **6b** with ethanolic alkali was very slow at room temperature and extensive decomposition took place at elevated temperatures leading to resinous materials. However, satisfactory results were obtained with *p*-toluenesulfonic acid in refluxing toluene and a high material balance could thus be obtained. Dienone **7b** comprised the bulk of this material, but an unidentified ketonic contaminant (λ_{max} 5.87 μ) could not be removed by fractional distillation. Fortunately, crystallization at low temperature proved feasible in this case and dienone **7b**, m.p. 29°, was easily obtained in pure form.

[8] M. Yanagita and A. Tahara, *J. Org. Chem.*, **18**, 792 (1953).

Experimental Section[9]

2-Methyl-2-(γ-chlorocrotyl)cyclohexanone (1a).—A mixture containing 126 g. (1.13 moles) of 2-methylcyclohexanone and 42 g. (1.1 moles) of sodamide in 750 ml. of benzene was stirred at reflux for 5 hr. and allowed to cool overnight.[9c] A solution containing 126 g. (1.0 mole) of 1,3-dichloro-2-butene in 100 ml. of benzene was slowly added to the stirred mixture. The mixture was refluxed for 4 hr., concentrated to a volume of 400 ml., allowed to cool, and treated with 100 ml. of 1:1 aqueous hydrochloric acid. The product was isolated with ether[9b] and distilled, giving 135 g. (68%) of material, b.p. 87–91° (0.3 mm.), lit.[2c] b.p. 128–132° (13 mm.). The n.m.r. spectrum displayed peaks at 1.07 (singlet) and 0.97 p.p.m. (doublet, J = 6 c.p.s.) due to the aliphatic methyl groups of **1a** and **1b**. Integration of these peaks allowed an estimate of the composition of this mixture as 80% **1a** and 20% **1b**.

A 12.6-g. portion of the above mixture was treated with 31 g. of sodium methoxide and 21 ml. of ethyl formate in 100 ml. of benzene according to the procedure of Johnson and Posvic.[10] The mixture was cooled in ice after standing at room temperature for 19 hr., and 100 ml. of cold water was added with stirring. The mixture was diluted with ether and thoroughly extracted with cold 5% aqueous sodium hydroxide. The combined alkaline extracts were acidified with cold hydrochloric acid and the organic material was isolated with ether.[9b]

The crude hydroxymethylene derivative of ketone **1a** was refluxed in 200 ml. of 20% aqueous sodium carbonate for 3 hr.[9c] The cooled solution was saturated with sodium chloride and the product was isolated with ether[9b] and distilled to give 6.0 g., b.p. 73–83° (0.3 mm.). The analytical sample (95% pure by gas chromatography), b.p. 76–77° (0.1 mm.), was obtained after three redistillations: $\lambda_{\max}^{\text{film}}$ 5.87 (CO), 6.00 (C=C), 8.90, 9.37 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.47 [H—C=C, triplet of quartets, J (triplet) = 7 c.p.s., J (quartet) = 1.5 c.p.s.], 2.10 (vinyl CH_3, doublet, J = 1.5 c.p.s.), 1.07 p.p.m. (aliphatic CH_3).

Anal. Calcd. for $C_{11}H_{17}ClO$: C, 65.82; H, 8.54; Cl, 17.67. Found: C, 65.5; H, 8.5; Cl, 17.6.

The 2,4-dinitrophenylhydrazone derivative, m.p. 132–133° (lit.[2c] m.p. 133–135°), was prepared.

2-Methyl-6-(γ-chlorocrotyl)cyclohexanone (1b).—The neutral material from the above hydroxymethylation reaction was distilled giving 3.1 g., b.p. 89–96° (0.2 mm.). The analytical sample, b.p. 80–81° (0.1 mm.), was obtained after two redistillations: $\lambda_{\max}^{\text{film}}$ 5.84 (CO), 6.00 (C=C), 8.84, 10.13 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.58 [H—C=C, triplet of quartets, J (triplet) = 7 c.p.s., J (quartet) = 1 c.p.s.], 2.10 (vinyl CH$_3$, doublet, J = 1 c.p.s.), 0.97 p.p.m. (aliphatic CH$_3$, doublet, J = 6 c.p.s.).

Anal. Calcd. for $C_{11}H_{17}ClO$: C, 65.82; H, 8.54; Cl, 17.67. Found: C, 65.9; H, 8.6; Cl, 17.6.

2,6-Dimethyl-2-(γ-chlorocrotyl)cyclohexanone (1c).[11]—The procedure outlined above for ketones **1a** and **1b** was followed using 50.4 g. of 2,6-dimethylcyclohexanone.[12] The yield of material, b.p. 92–94° (0.2 mm.), was 54 g. (63%). The analytical sample, b.p. 94–95° (0.1 mm.), n^{24}D 1.4879, was obtained after redistillation: $\lambda_{\max}^{\text{film}}$ 5.88 (CO), 6.00 (C=C), 9.22, 9.93 μ.

Anal. Calcd. for $C_{12}H_{19}ClO$: 67.12; H, 8.92; Cl, 16.51. Found: C, 66.9; H, 9.0; Cl, 16.7.

Analysis by gas chromatography[13] indicated a 1:1 mixture of compounds having similar retention times. This mixture most likely results from C-2 epimers since subsequent transformations of the material afforded homogeneous substances in high yields.

General Procedure for Hydrolysis of Chlorocrotylcyclohexanones.—The sulfuric acid, contained in a test tube or erlenmeyer flask, was cooled to the stated temperature and a rapid stream of nitrogen was cautiously bubbled through the liquid by means of a sintered-glass gas-dispersion tube. The chlorocrotyl ketone was carefully added and after the stated time interval the mixture was slowly poured as a fine stream into 7 vol. of a rapidly stirred slurry of ice and water. The product was extracted with ether and the combined extracts were thoroughly washed with water, aqueous sodium bicarbonate, and saturated brine, and dried over anhydrous magnesium sulfate.

2-Methyl-2-(3-oxobutyl)cyclohexanone (2a). A. Hydrolysis of Chlorocrotyl Ketone 1a.—The general hydrolysis procedure described above was followed using 10 ml. of sulfuric acid and 5.1 g. of chlorocrotyl ketone **1a** at 0° for 20 min. Distillation of the product afforded 0.5 g. (11%), b.p. 66–82° (0.1 mm.) (70% bridged ketone **4a** and 30% dione **2a** according to analysis by gas chromatography[13]), and 2.2 g. (47%), b.p. 87–102° (0.1 mm.) (7% bridged ketone **4a** and 93% dione **2a**). The second fraction was redistilled twice and the material, b.p. 70–71° (0.1 mm.), was submitted for combustion analysis: $\lambda_{\max}^{\text{film}}$ 5.85 (CO), 8.89, 9.10, 10.10 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 2.10 (CH_3CO), 0.99 p.p.m. (angular CH$_3$).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.8; H, 10.0.

B. Hydrogenation of Unsaturated Dione 6a.—A 2.61-g. sample of dione **6a** was stirred with 0.4 g. of 5% palladium on carbon in 60 ml. of ethanol under 1 atm. of hydrogen whereupon the theoretical volume (360 cc.) of hydrogen was rapidly absorbed. The mixture was filtered and the filtrate was distilled giving 2.53 g. (95%) of dione **2a**. The infrared and n.m.r. spectra of this material were indistinguishable from those of dione **2a** prepared according to part A above.

2-Methyl-6-(3-oxobutyl)cyclohexanone (2b).—The general hydrolysis procedure was followed using 25 ml. of sulfuric acid and 7.0 g. of chlorocrotyl ketone **1b** at 0° for 20 min. The product was distilled giving 0.8 g., b.p. 60–70° (0.3 mm.) (15% chlorocrotyl ketone **1b**, 60% bridged ketone **4b**, and 25% dione **2b**),[13] and 3.0 g. (47%), b.p. 85–87° (0.3 mm.) (2% bridged ketone **4b** and 98% dione **2b**).[13] The analytical sample, b.p. 84° (0.2 mm.), was obtained after two redistillations of the second fraction: $\lambda_{\max}^{\text{film}}$ 5.84 (CO), 8.82, 11.63 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 2.08 (CH_3-CO), 0.95 (aliphatic CH_3, doublet, J = 6.5 c.p.s.).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.8; H, 10.0.

1,2,5-Trimethylbicyclo[3.3.1]non-2-en-9-one (4c).—The general hydrolysis procedure was followed using 10 ml. of sulfuric acid and 1.1 g. of chlorocrotyl ketone **1c** at 0° for 30 min. The product was isolated and distilled, affording 0.9 g. (93%) of ketone **4c**, b.p. 60° (bath temperature) (0.2 mm.): $\lambda_{\max}^{\text{film}}$ 5.85 (CO), 9.45, 9.97, 10.35, 11.50, 11.60 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.55 (H—C=C, broad), 1.61 (vinyl CH$_3$), 1.03, 0.95 p.p.m. (angular CH$_3$). The analytical sample, b.p. 53–54° (0.1 mm.), n^{24}D 1.4971, was obtained from material prepared in another experiment.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.0; H, 10.2.

Dione **2c** was completely converted to unsaturated ketone **4c** under the reaction conditions described above (30 min. at 0°). When the hydrolysis of chlorocrotyl ketone **1c** was allowed to proceed overnight at room temperature, a red, nonvolatile tar was the only isolable product.

2,5-Dimethylbicyclo[3.3.1]non-2-en-9-one (4a).—The general hydrolysis procedure was followed using 10 ml. of sulfuric acid and 4.8 g. of chlorocrotyl ketone **1a**. The mixture was allowed to stand at 0° for 90 min. and at room temperature for 45 min. and the product was isolated and distilled, giving 2.5 g. (60%) of ketone **4a**: b.p. 55° (0.3 mm.); $\lambda_{\max}^{\text{film}}$ 5.81 (CO), 5.97 (C=C), 9.05, 9.51, 10.05, 10.60, 12.78, 14.24 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.63 [HC=C, triplet of quartets, J (triplet) = 4 c.p.s., J (quartet) = 2 c.p.s.], 1.70 (vinyl CH$_3$, doublet, J = 2 c.p.s.), 0.95 p.p.m. (angular CH_3). This material was judged homogeneous by gas chromatography.[13]

The 2,4-dinitrophenylhydrazone derivative was prepared, m.p. 154–155° (lit.[2c] m.p. 151–153°).

2-Methyl-2-(γ-chlorocrotyl)-5-cyclohexenone (5a).—To a stirred solution of 20.0 g. of ketone **1a** in 100 ml. of acetic acid was added 57 ml. of 2 M bromine in acetic acid over a period of 1.5 hr. The mixture was stirred for an additional 0.5 hr. and 500 ml. of water was added. The mixture was extracted with ether and the combined extracts were thoroughly washed with water, aqueous sodium bicarbonate (*caution!*), and saturated brine, and dried over anhydrous magnesium sulfate.

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[9] (a) Melting points were determined on a Fisher-Johns hot stage. (b) The isolation procedure consisted of thorough extraction and back extraction with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a steam bath. (c) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere over reaction mixtures. (d) Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

[10] W. S. Johnson and H. Posvic, *J. Am. Chem. Soc.*, **76**, 2707 (1954).

[11] Experiment was performed by T. F. Mich.

[12] M. S. Newman, I. Waltcher, and H. F. Ginsberg, *J. Org. Chem.*, **17**, 968 (1952).

[13] A 10 ft. × 0.25 in. column packed with 20% Carbowax 20M on Gas Pack F was employed for gas chromatographic analyses.

The crude bromo ketone was dehydrobrominated[14] by treatment with 18 g. of calcium carbonate in 300 ml. of N,N-dimethylacetamide at reflux for 30 min. Most of the solvent was removed under reduced pressure and the residue was thoroughly triturated with hot heptane. The combined heptane solutions were washed with water and brine, dried over anhydrous magnesium sulfate, and distilled, giving 13.9 g. (70%) of unsaturated ketone **5a**: b.p. 76–90° (0.3 mm.); $\lambda_{\max}^{\text{film}}$ 5.98 (CO), 8.18, 8.92, 12.2, 12.4 μ; $\lambda_{\max}^{\text{EtOH}}$ 227 mμ (ϵ 9500); $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 6.95 [*H*C=CHCO, doublet of triplets, *J* (doublet) = 10 c.p.s., *J* (triplet) = 4 c.p.s.], 5.97 [HC=C*H*CO, doublet of triplets, *J* (doublet) = 10 c.p.s., *J* (triplet) = 2 c.p.s.], 5.50 [$CH_2C\mathit{H}=C(Cl)CH_3$, triplet of quartets, *J* (triplet) = 7.5 c.p.s., *J* (quartet) = 1.5 c.p.s.], 2.12 (vinyl CH_3, doublet, *J* = 1.5 c.p.s.), 1.07 p.p.m. (aliphatic CH_3). The analytical specimen, b.p. 70° (0.1 mm.), was obtained after redistillation.

Anal. Calcd. for $C_{11}H_{15}ClO$: C, 66.50; H, 7.61; Cl, 17.84. Found: C, 66.2; H, 7.7; Cl, 17.9.

2,6-Dimethyl-2-(γ-chlorocrotyl)-5-cyclohexenone (5b).—The bromination–dehydrobromination sequence described above was employed using 64.1 g. of ketone **1c**. The yield of unsaturated ketone **5b**, b.p. 82–90° (0.3 mm.), was 90%: $\lambda_{\max}^{\text{film}}$ 6.00 (CO), 8.38, 9.20, 9.70 μ; $\lambda_{\max}^{\text{EtOH}}$ 235 mμ (ϵ 8650); $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 6.67 [$\mathit{H}C=C(CH_3)CO$, triplet of quartets, *J* (triplet) = 4 c.p.s., *J* (quartet) = 1.5 c.p.s.], 5.47 [$CH_2C\mathit{H}=C(Cl)CH_3$, triplet of quartets, *J* (triplet) = 7 c.p.s., *J* (quartet) = 1.5 c.p.s.], 2.10 [$CH_2CH=C(Cl)C\mathit{H}_3$, doublet, *J* = 1.5 c.p.s.], 1.72 [$HC=C(C\mathit{H}_3)CO$, doublet, *J* = 1.5 c.p.s.], 1.02 p.p.m. (aliphatic CH_3). The analytical sample, b.p. 80–81° (0.3 mm.), was obtained after two redistillations.

Anal. Calcd. for $C_{12}H_{17}ClO$: C, 67.76; H, 8.06; Cl, 16.67. Found: C, 68.0; H, 8.0; Cl, 16.7.

2-Methyl-2-(3-oxobutyl)-5-cyclohexenone (6a).—The general hydrolysis procedure was followed using 25 ml. of sulfuric acid and 11.3 g. of unsaturated chlorocrotyl ketone **5a** at 0° for 1 hr. The dione was isolated and distilled, giving 8.6 g. (84%): b.p. 90–102° (0.3 mm.); $\lambda_{\max}^{\text{film}}$ 5.84 (CO), 5.98 (conjugated CO), 8.17, 8.58, 8.91 μ; $\lambda_{\max}^{\text{EtOH}}$ 227 mμ (ϵ 9000); $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 6.99 [*H*C=CHCO, doublet of triplets, *J* (doublet) = 10 c.p.s., *J* (triplet) = 4 c.p.s.], 5.85 [HC=C*H*CO, doublet of triplets, *J* (doublet) = 10 c.p.s., *J* (triplet) = 2 c.p.s.], 2.10 ($C\mathit{H}_3CO$), 1.02 p.p.m. (aliphatic CH_3). The analytical specimen, b.p. 80–81° (0.1 mm.), was obtained after two redistillations.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.5; H, 8.9.

2,6-Dimethyl-2-(3-oxobutyl)-5-cyclohexenone (6b).—The general hydrolysis procedure was followed using 140 ml. of sulfuric acid at 0° to which 47 g. of unsaturated chlorocrotyl ketone **5b** was added over 15 min. After an additional hour at 0° the product was isolated and distilled giving 36.3 g. (88%) of dione **6b**: b.p. 97–108° (0.5 mm.); $\lambda_{\max}^{\text{EtOH}}$ 237 mμ (ϵ 9000); $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 6.70 [*H*C=C, triplet of quartets, *J* (triplet) = 4 c.p.s., *J* (quartet) = 2 c.p.s.], 2.03 (CH_3CO), 1.67 (vinyl CH_3, doublet, *J* = 2 c.p.s.), 1.00 p.p.m. (aliphatic CH_3). The analytical specimen, b.p. 86–87° (0.2 mm.), was obtained after three redistillations.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.0; H, 9.4.

2,6-Dimethyl-2-(3-oxobutyl)cyclohexanone (2c).—Reduction of 9.90 g. of unsaturated dione **6b** in 140 ml. of ethanol was effected under 1 atm. of hydrogen over 0.5 g. of 5% palladium on carbon. The mixture was filtered after the theoretical volume of hydrogen was taken up and the filtrate was distilled, giving 9.16 g. (92%) of dione **2c**, b.p. 82–100° (0.2 mm.). The analytical sample, b.p. 76–77° (0.1 mm.), was prepared by two additional distillations: $\lambda_{\max}^{\text{film}}$ 5.85 (CO), 8.58, 8.86, 10.01, 11.58 μ.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.55. Found: C, 73.2; H, 10.3.

Numerous attempts to prepare dione **2c** by hydrolysis of chlorocrotyl ketone **1c** in sulfuric acid or various mixtures of sulfuric acid and water at temperatures ranging from 0 to −30° were unsuccessful; in all cases either recovered starting material, bridged unsaturated ketone **4c**, or mixtures of these two materials resulted.

10-Methyl-1(9)-octal-2-one (3a).—A solution of 96 mg. of dione **2a** and 0.3 ml. of 3 *M* ethanolic potassium hydroxide in 8 ml. of ethanol was allowed to stand at room temperature for 2 hr.[9c] The solution was poured into water and the product was isolated with ether.[9b] The resulting material was identified as octalone **3a** by comparison of its infrared spectrum with that of an authentic sample.[1]

***trans*-8-Methyl-1(9)-octal-2-one (3b)**.—A solution of 0.54 g. of dione **2b** and 1.5 ml. of 3 *M* ethanolic potassium hydroxide was allowed to stand at room temperature for 2.5 hr.[9c] The solution was poured into saturated brine and the product was isolated with ether.[9c] Distillation gave 0.34 g. (77%) of octalone **3b**, identified by the 2,4-dinitrophenylhydrazone derivative: m.p. 165–167°[15]; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.77 (H-1, width at half-height = 3.5 c.p.s.), 1.12 p.p.m. (C-8 CH_3, doublet, *J* = 6.5 c.p.s.).

***trans*-8,10-Dimethyl-1(9)-octal-2-one (3c)**.—A solution containing 22.5 g. of dione **2c** and sodium ethoxide (from 3.0 g. of sodium) in 500 ml. of ethanol was heated at 45–50° for 1 hr.[9c] The cooled solution was poured into water and the product was isolated with ether.[9b] Distillation afforded 18.3 g. (89%) of colorless liquid, b.p. 90–99° (0.3 mm.). The infrared spectrum of this material was identical with that of an authentic specimen prepared from 2,6-dimethylcyclohexanone *via* the procedure of Howe and McQuillin[16]: $\lambda_{\max}^{\text{film}}$ 5.99 (CO), 6.20 (C=C), 9.86, 10.12, 10.21, 10.43, 10.68, 11.22, 11.44, 11.70, 14.31, 14.75 μ; $\lambda_{\max}^{\text{EtOH}}$ 240 mμ (ϵ 15,600); $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.70 (H-1, doublet, *J* = 2 c.p.s.), 1.28 (angular CH_3), 1.05 p.p.m. (C-8 CH_3, doublet, *J* = 6.5 c.p.s.).

Octalone **3c** crystallized when cooled to −10°. The analytical sample, m.p. 28–29°, was obtained after three recrystallizations from pentane at −25°.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.20. Found: C, 80.9; H, 10.1.

Cyclization was incomplete under the conditions described above for the monomethyl analogs as judged by the infrared spectrum of the crude product.

10-Methyl-1(9),7-hexal-2-one (7a).—A solution containing 2.15 g. of dione **6a** and 6 ml. of 3 *M* ethanolic potassium hydroxide was allowed to stand at room temperature for 4 hr.[9c] The solution was poured into saturated brine, and the product was isolated with ether[9b] and distilled, affording 1.90 g. (98%) of liquid containing 70% of the desired dienone **7a**.[13] This material yielded a semicarbazone derivative, m.p. 201–203° (lit.[8] m.p. 201–203°). Admixture with the semicarbazone derivative of dienone **7a** prepared according to Yanagita and Tahara[8] gave no melting point depression.

The principal contaminant of dienone **7a** appears to be a saturated ketone ($\lambda_{\max}$ 5.85 μ) of undetermined structure. This contaminant had a slightly longer gas chromatograhic retention time[13] than dienone **7a**. The gas chromatogram indicated the complete absence of starting dione **6a**.

8,10-Dimethyl-1(9),7-hexal-2-one (7b).—A mixture consisting of 26.3 g. of dione **6b**, 7.7 g. of *p*-toluenesulfonic acid hydrate, and 550 ml. of toluene was stirred at reflux[9c] for 3 hr. with azeotropic distillation of water by means of a Dean–Stark trap. The cooled mixture was poured into 250 ml. of saturated aqueous sodium bicarbonate and the product was isolated with ether.[9b] Distillation furnished 22.4 g. (93%) of material, b.p. 70–101° (0.1 mm.). The dienone **7b** could be obtained by crystallization of the oily distillate from hexane at −25°. In this manner 9.0 g., m.p. 28–29°, was obtained: $\lambda_{\max}^{\text{CCl}_4}$ 6.00 (CO), 6.12, 6.28 (conjugated C=C), 7.56, 7.80, 7.96, 8.21, 9.26, 11.35 μ; $\lambda_{\max}^{\text{EtOH}}$ 287 mμ (ϵ 23,900); $\delta_{\max}^{\text{CCl}_4}$ = 6.09 (H-7, triplet of quartets, $J_{7,8}$ = 4 c.p.s., $J_{7,12}$ = 2 c.p.s.), 5.77 (H-1, singlet), 1.87 (vinyl CH_3, doublet, *J* = 2 c.p.s.), 1.16 p.p.m. (angular CH_3). The analytical sample, m.p. 29°, was secured after two additional recrystallizations.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.9; H, 9.2.

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(14) The procedure of G. Green and A. Long [*J. Chem. Soc.*, 2532 (1961)] as modified by Niels H. Andersen of our laboratory is described.

(15) R. Robinson, E. C. duFeu, and F. J. McQuillin, *ibid.*, 53 (1937).

(16) R. Howe and F. J. McQuillin, *ibid.*, 2423 (1955). The experiment which afforded our comparison sample was performed by Noal Cohen.