The Course of the Michael–Aldol Synthesis. II. The Formation of Cyclohexenones[1]

DAVID J. GOLDSMITH AND JOHN A. HARTMAN[2]

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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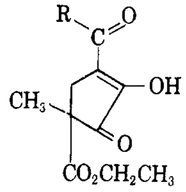
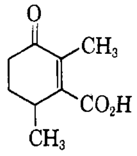
The reaction of ethyl α-ethoxalylpropionate with methyl or ethyl vinyl ketones in the presence of triethylamine leads in high yield to simple Michael adducts. These may be cyclized to cyclohexenones by acid catalysis. These results, in marked contrast to those obtained when sodium ethoxide is employed, are interpreted in terms of the rate of protonation of the initially formed adducts.

In the accompanying paper[3] we showed that the reaction of methyl vinyl ketone with the sodium salt of ethyl α-ethoxalylpropionate leads in good yield to the cyclopentanedione **1a**. The same compound, mistakenly characterized as a 1,3-cyclohexanedione was obtained by Martin and Robinson[4] in unspecified yield from the oxalyl ester and the methiodide of N,N-diethylaminobutan-3-one. In contrast with these results Büchi and Warnhoff[5] isolated a cyclohexenone carboxylic acid from the interaction of ethyl α-ethoxalylbutyrate and the methiodide of N,N-diethylaminopentan-3-one. Although the experimental conditions employed by these sets of workers differ slightly[3] it will be clear from our results that in each case both types of product are undoubtedly formed. We have found, moreover, that it is possible to control the course of this Michael–aldol sequence to give predominantly either structural type. As previously shown, the use of unsaturated carbonyl compounds and a sodium enolate yields cyclopentanediones. We shall discuss here first the experimental results of our attempts to synthesize the cyclohexenones **2** and **3** and then the mechanistic implications of these results.



1a, R = CH_3
b, R = CH_3CH_2



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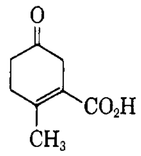

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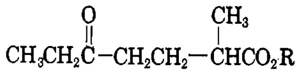
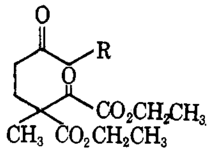
Preparation of the Michael Adducts 5a and 5b.—Application of the usual Robinson–Mannich[6] conditions to the reaction of ethyl α-ethoxalylpropionate and the freshly prepared Mannich base methiodide of diethylaminopentan-2-one led to the formation of an oily substance which was separated into a neutral and an acidic fraction. The latter was shown to be **1b** on the basis of its ultraviolet spectrum. Only one identifiable compound could be isolated from the neutral material. Distillation of this fraction provided a 12% yield of ethyl 2-methyl-5-oxoheptanoate (**4a**). The remainder was an intractable oil and attempted cyclizations of its presumed content of the Michael product **5** were delayed until this compound could be prepared as a single individual. We were able, however, to effect the desired condensation by employing triethylamine to catalyze the reacton of the oxalyl ester and ethyl vinyl ketone. Distillation of the crude product in this instance gave a 90% yield of a light oil containing approximately 10% of the cyclopentanedione **1b**. The latter could be essentially removed by either redistillation or extraction with base. From its spectral characteristics and elemental analysis, the neutral product is a 1:1 adduct of ethyl vinyl ketone and the oxalyl ester and it is assigned structure **5a**. Employment of the same conditions with methyl vinyl ketone gave **5b** in 79% yield.



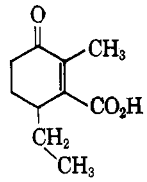
$CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{CH_3}{\overset{|}{C}}HCO_2R$

4a, R = CH_3CH_2
b, R = H



5a, R = CH_3
b, R = H

Base-Catalyzed Aldol Cyclization.—Turning to the cyclization of these materials we attempted to reproduce the conditions employed by Büchi and Warnhoff. These workers treated their crude Michael condensation product with potassium hydroxide in methanol and were able to isolate in low yield the acid **6**. In the case of **5a**, however, hydroxide ion treatment resulted after chromatography on silica gel in the isolation of about 50% of the acyclic keto acid **4b**, a product resulting from cleavage of the β-keto ester system of the starting material. Although the crude product showed ultraviolet absorption at 245 mμ amounting to about 15% of the desired cyclohexenone **2**, it was not possible to isolate the pure acid. Other base catalysis cyclization conditions were also tried. Neither sodium methoxide in methanol or potassium *t*-butoxide effected the desired change. The courses of these attempted cyclizations were followed spectroscopically. In the former case after 15 min. at room temperature approximately 13% of the enolate of **1b** could be detected. Surprisingly, the intensity of the band due to this compound remained



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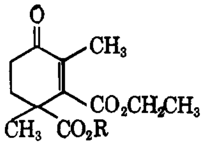

7a, R = CH_2CH_3
b, R = H

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(1) The authors gratefully acknowledge the support of this research by the National Institutes of Health, Grant No. GM 10509-01.

(2) Taken in part from the Ph.D. Thesis of J. A. Hartman, Wayne State University, 1963.

(3) D. J. Goldsmith and J. A. Hartman, *J. Org. Chem.*, **29**, 3520 (1964).

(4) R. H. Martin and R. Robinson, *J. Chem. Soc.*, 1866 (1949).

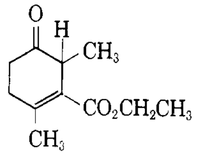
(5) G. Büchi and E. W. Warnhoff, *J. Am. Chem. Soc.*, **81**, 4433 (1959).

(6) The method used here consists of adding an alcoholic solution of freshly prepared Mannich base methiodide to a chilled solution of the sodium salt of a ketone in benzene ethanol. Both sets of previous workers employed this procedure.[4,5]

relatively constant. After standing overnight, however, the maximum at 245 mμ indicative of cyclohexenone formation was apparent. When treatment was further prolonged at steam-bath temperature, there could be isolated 25% of an acidic fraction which corresponded spectrally to the trione **1b** and a neutral portion which again on the basis of ultraviolet measurements appeared to contain approximately 25% of the diester **7a**. The remainder of the neutral material is presumably **4a**. The butoxide treatment was even less promising since the cyclohexenone chromophore could not be detected in the ultraviolet spectrum of the product mixture.

Acid-Catalyzed Cyclization.—Since base treatment apparently results for the most part in the cleavage of **5a**, we turned to acid-catalyzed cyclization. Treatment of the Michael adduct with concentrated hydrochloric acid at room temperature produced a 1.4:1 mixture of neutral and acidic materials. The neutral fraction which could be purified by short-path distillation in 38% yield proved to be the desired cyclohexenone dicarboxylic ester **7a**. Aside from the correct elemental analysis the compound exhibits an ultraviolet absorption maximum at 244 mμ (ε 10,100) and two carbonyl infrared stretching frequencies at 1730 and 1681 cm.$^{-1}$. The n.m.r. spectrum, moreover, shows the presence of two ethyl ester groups in slightly different chemical environments and the following two types of methyl groups: $\mathrm{CH_3{-}C{-}CO_2Et}$, τ 8.59, and $\mathrm{CH_3{-}C{=}C{-}CO_2Et}$, τ 8.21.

The acidic portion of the cyclization mixture could not be crystallized and it was subjected to short-path distillation. These conditions, however, suffered the material to decompose and the resulting distillate was again a neutral material. The latter and its crystalline semicarbazone gave analytical values compatible with a $C_{11}H_{16}O_3$ formulation indicating that the over-all change from **5a** was cyclization followed by the loss of one carbomethoxyl group. The structure of this compound was demonstrated to be **8** by spectral evidence.



8

In the ultraviolet, a maximum is observed at 220 mμ[7] in contrast with the 244-mμ peak of both the diester **7a** and the precursor of **8** presumed to be the monocarboxylic acid **7b**.[8] The n.m.r. spectrum of **8** shows in addition to a single ethyl ester, a doublet methyl at τ 8.9 (J = 7 c.p.s.), another doublet methyl at 8.05 ($J \simeq 0.6$ c.p.s.), a four-proton multiplet at 7.59 ($J < 1$ c.p.s.) corresponding to the two ring methylene groups of **8**, and a one-proton quartet centered at 6.91 (J = 7 c.p.s.). This latter resonance contains fine structure which was not resolved under the conditions of the measurement, but the pattern must arise from the coupling of a methinyl proton to two methyl groups, one attached to the same carbon atom and the other vinylogously related as in **8**.

Modification of the above hydrolytic procedure led to the successful preparation of the desired keto acid **2**. After treatment of the acyclic keto diester **5a** with concentrated hydrochloric acid as described, dilution of the acid medium and heating at reflux produced **2** as a crystalline solid, m.p. 126–128°. The spectral properties of the material are in accord with the suggested formulation. For example, the ultraviolet maximum [244 mμ (ε 10,100)] indicates a α,β-disubstituted cyclohexenone and the n.m.r. spectrum shows *inter alia* two methyl doublets [(τ 8.8 (J = 7 c.p.s.) and 8.12 ($J < 1$ c.p.s.), respectively].

Application of the acid cyclization and hydrolysis conditions to the methyl vinyl ketone adduct **5b** produced the unsaturated keto acid **3**, m.p. 112–114°. The position of the double bond in this compound was indicated by its ultraviolet absorption maximum at 222 mμ (ε 7600). The n.m.r. spectrum moreover shows no vinyl hydrogens but instead a vinylic methyl triplet at τ 7.8 ($J \simeq 1$ c.p.s.), a four-proton multiplet at 7.55 and a methylene quartet at 6.4 ($J \simeq 1$ c.p.s.). Since the yield of this compound is low it is not possible to determine if it is the more stable of the two possible double bond isomers.

The Course of the Michael–Aldol Sequence.—It has been generally assumed that the Michael addition of a carbonyl compound to an unsaturated ketone is equivalent to using the corresponding Mannich base alkiodide for the latter component.[9] Since in many cases the products are identical, the equating of these methods has seemed reasonable.[10] In the examples cited here and in the accompanying publication this assumption is clearly contradicted. To summarize our results (Scheme I) the addition of a sodium enolate to a vinyl ketone leads mainly to a cyclopentanedione, the addition of the enolate to a Mannich base methiodide leads to a mixture of materials, and finally addition of the carbonyl component corresponding to the above enolate to an unsaturated ketone in the presence of triethylamine leads initially to a simple Michael adduct and thence *via* acid catalysis to a cyclohexenone. The explanation for these differences in behavior appear to lie, not in the nature of the acceptor species, but rather in the type of base catalysis employed.

In the first sequence the initially formed adduct anion cyclizes (path a, below) at a far greater rate than it protonates, the only acid available being ethanol. In contrast, when triethylamine is employed, the adduct

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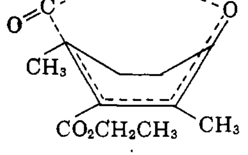
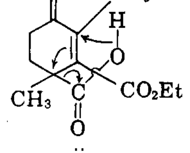
[7] The literature indicates a fairly wide range of frequencies for the absorption of unsaturated acids and esters. For example 2-methylcyclohex-1-ene-1-carboxylic acid has $\lambda_{\max}^{\mathrm{EtOH}}$ 217 mμ (log ε 3.95) [H. E. Ungnade and I. Ortega, *J. Am. Chem. Soc.*, **73**, 564 (1951)], while 2,4,4-trimethylcyclohex-1-ene-1-carboxylic acid has $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ (log ε 3.95) [W. Kuhn and H. Schinz, *Helv. Chim. Acta*, **35**, 2008 (1952)].

[8] The pyrolytic decarboxylation of **7b** to yield **8** probably does not involve the ketone carbonyl. The transition state i is too strained to allow



i



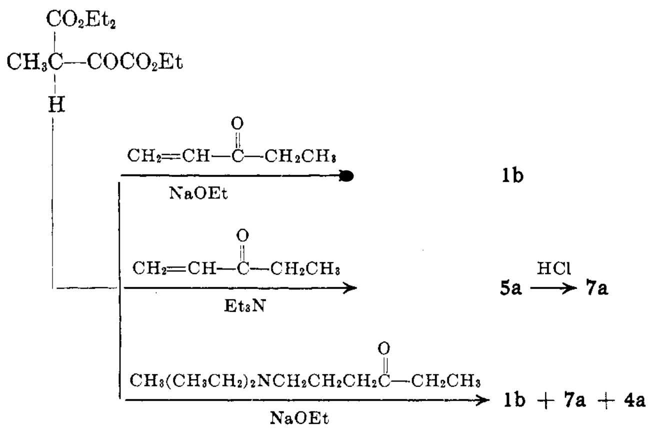
ii

transfer of the carboxyl proton to the ketone oxygen and the ease of decarboxylation can be ascribed to a reaction path such as ii, the decomposition of a β,γ-unsaturated acid [R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 4359 (1950)].

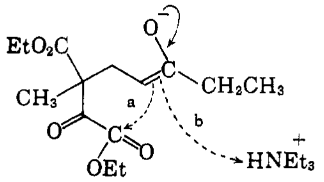
[9] T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *ibid.*, **85**, 3785 (1963), and references therein.

[10] D. Ginsburg and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

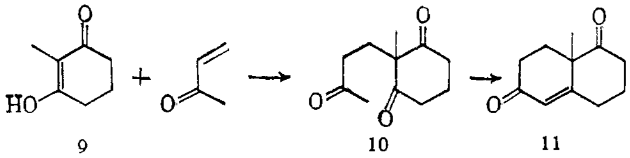
SCHEME I



is formed in the presence of a moderately strong acid (Et_3NH^+) which accompanies the adduct as the associated ion-pair cation. Here protonation is very rapid and only the acyclic product **5a** is formed (path b). That the former reaction actually involves trapping of the anion rather than the sequence, protonation ⇄ enolization → cyclization can be seen from the fact that treatment of **5a** with base does not result in the formation of more than a minor amount of the cyclopentanedione system. The products obtained from the use of the Mannich base methiodide seem to be the result of a mixture of the above pathways. This will be true if the elimination of trialkylamine from the methiodide is reasonably slow. The latter process will then lead to a reaction mixture containing the sodium enolate of the donor species, the corresponding unenolized carbonyl compound, trialkylamine, and a small concentration of vinyl ketone. It would seem, therefore, that control of the course of the Michael step is least possible when a methiodide salt is employed. In cases where several reaction pathways are open to the anion adduct, as in the examples discussed here with vinyl ketones, choice of the appropriate base (and therefore its conjugate acid) is paramount in terms of product control.



With regard to the second step of the reaction sequence, aldol cyclization, our results, though cursory, tend to support the conclusions of Spencer, *et al.*[9,11] These authors suggest that the ease of cyclization of 1,5-diketones *via* dialkylamine catalysis is the result of enamine formation. If so, then trialkylamine catalysis of the Michael–aldol sequence would be expected to stop at the Michael stage as we have found. This conclusion is also supported by the methods used to convert 2-methylcyclohexane-1,3-dione (**9**) and methyl vinyl ketone to the octalone **11**. Whereas the cyclization of **10** is best effected by the use of a secondary amine (pyrrolidine),[12] the preferred method for obtaining high yields of the triketone **10** is the use of triethylamine[13] for catalyzing the Michael addition.



9 10 11

Experimental[14]

Ethyl 2,6-Diketo-3-carbethoxy-3-methyloctanoate (5a).—Freshly distilled ethyl vinyl ketone (18 ml., 0.15 mole) and ethyl α-ethoxalylpropionate (20.1 g., 0.1 mole) were dissolved in a 1:1 mixture of absolute alcohol and dry benzene. Ten drops of triethylamine were added and the solution was heated at reflux overnight. Removal of the solvent *in vacuo* left 32.0 g. of a light brown oil. Distillation of 17 g. of crude product using an oil-jacketed flask afforded 14.3 g. (90%) of a light yellow oil, b.p. 119–129° (0.03 mm.). For analysis the material was redistilled using a short-path bulb apparatus.

Anal. Calcd. for $C_{14}H_{23}O_6$: C, 58.52; H, 8.07. Found: C, 58.38; H, 7.89.

Ethyl 2,6-Diketo-3-carbethoxy-3-methylheptanoate (5b).—Substitution of methyl vinyl ketone (same molar quantity) in the above procedure led to the isolation of 21.5 g. (79%) of the methyl ketone **5b**, b.p. 110–120° (0.05 mm.).

Anal. Calcd. for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.51; H, 7.39.

Base-Catalyzed Cyclizations of Michael Adduct (5a). A. Potassium Hydroxide in Methanol-Water.[15]—Potassium hydroxide (30 g.) dissolved in 30 g. of water was added to a solution of 29.1 g. of the Michael adduct **5a** in 300 ml. of methanol. The solution was maintained under a nitrogen atmosphere and heated at reflux for 60 min. The ultraviolet spectrum of the reaction mixture at this stage showed, after appropriate dilution, $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε 1500), 345 mμ. The solution was concentrated to remove methanol, diluted with cold water, and extracted with ether. Only traces of neutral material were obtained from the ether extracts. The aqueous solution was then acidified and extracted with methylene chloride. The usual work-up yielded 15.1 g. of a red brown oil, $\lambda_{\max}$ 245 mμ (ε 1150) (10% **2**). Chromatography of a 2-g. portion of the above oil gave 0.91 g. of 2-methyl-5-ketoheptanoic acid (**4b**) as an oil which could be crystallized from ether–petroleum ether at Dry Ice temperature as fine needles. The semicarbazone was crystallized from aqueous alcohol, m.p. 146.5–147° (lit.[16] m.p. 145–146°).

Anal. Calcd. for $C_9H_{17}N_3O_3$: C, 50.22; H, 7.96; N, 19.52. Found: C, 50.16; H, 8.10; N, 19.75.

B. Sodium Methoxide in Methanol.—The adduct **5a** (0.686 g.) was dissolved in 5 ml. of anhydrous methanol under nitrogen and treated with 0.15 g. of sodium methoxide. After 15 min. at room temperature a sample of the mixture displayed $\lambda_{\max}^{\mathrm{EtOH}}$ 359 mμ (ε 1508) equal to 13% of the enolate of **1b**. After 20 hr. at room temperature no significant change in the intensity of the above peak occurred. A maximum at 245 mμ was observable. The mixture was then warmed on the steam bath for 48 hr. and finally acidified. Extraction with methylene chloride and removal of the solvent gave 0.425 g. of amber oil, $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε 2500) (25% **7a**), 290 mμ (ε 2900) (25% **1b**). The oil was separated into a neutral fraction (0.3 g.) which contained from the ultraviolet spectrum about 36% of **7a** and an acidic fraction (0.1 g.) which spectrally was identical with **1b**.[1]

C.—In an experiment similar to the above using potassium *t*-butoxide in *t*-butyl alcohol, no maximum at 245 mμ was observed.

Acid-Catalyzed Cyclization of Michael Adducts (5a and 5b). A. 3,4-Dicarbethoxy-2,4-dimethyl-2-cyclohexen-1-one (7a).—To 100 ml. of concentrated hydrochloric acid at room temperature was added 5.72 g. of the Michael adduct **5a**. After 30 min., slight evolution of gas was observed and the straw-colored solution

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[11] T. A. Spencer and K. K. Schmeigel, *Chem. Ind.* (London), 1765 (1963).

[12] S. Ramachandran and M. S. Newman, *Org. Syn.*, **41**, 38 (1961).

[13] M. S. Newman and A. B. Meekler, *J. Am. Chem. Soc.*, **82**, 4039 (1960).

[14] See ref. 3 for details of instrumentation and measurement.

[15] This procedure is that used by Büchi and Warnhoff. We thank Professor Warnhoff for supplying us with the experimental details.

[16] I. Kawasaki, T. Okamoto, and T. Kaneko, *Nippon Kagaku Zasshi*, **81**, 1621 (1960); *Chem. Abstr.*, **56**, 2323*h* (1962).

was stirred overnight. Ice–water was then added; the solution partially was neutralized with 40% sodium hydroxide and extracted with methylene chloride. The latter solution was extracted with sodium bicarbonate to remove acidic products, and the solvent was dried over sodium sulfate and removed to yield 2.3 g. of an amber oil. Distillation of the latter afforded the diester **7a**, as a colorless oil: b.p. 109–111° (0.3 mm.); 1.4 g. (38%); λ_{max}^{EtOH} 244 mμ (ε 10,100); $\nu_{max}^{CHCl_3}$ 1681, 1730 cm.$^{-1}$; n.m.r., 8.81 (triplet, J = 7 c.p.s.), 8.75 (triplet, J = 7 c.p.s.), 6.01 (quartet, J = 7 c.p.s.), 5.91 (quartet J = 7 c.p.s.), 8.59 (singlet), 8.21 (singlet).

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.55; H, 7.61.

The semicarbazone of **7a** was crystallized from aqueous ethanol to give thin plates, m.p. 135–136°.

Anal. Calcd. for $C_{15}H_{24}N_3O_5$: C, 55.37; H, 7.12; N, 12.92. Found: C, 55.53; H, 7.19; N, 12.72.

B. **3-Carbethoxy-2,4-dimethylcyclohex-3-en-1-one** (**8**).—The bicarbonate layer from A above was acidified and yielded after extraction with methylene chloride 1.64 g. of oily material. This was combined with material from a duplicate experiment and 2.94 g. of crude acid was distilled. At a bath temperature of 140° (0.7 mm.) gas evolution occurred. The distillate **8**, b.p. 99.5–105° (1.5 mm.), was collected as a colorless oil: λ_{max}^{EtOH} 220 mμ (ε 9300) (with weak base or acid it was not possible to effect isomerization of **8** to the corresponding α,β-unsaturated ketone); $\nu_{max}^{CHCl_3}$ 1639, 1709 cm.$^{-1}$; n.m.r., 8.9 (doublet, J = 7 c.p.s.) $CH_3—\overset{|}{\underset{|}{C}}—H$, 8.78, 5.89 (triplet, quartet, J = 7 c.p.s.) $CH_3CH_2—O—\overset{|}{C}{=}O$, 8.05 (doublet, $J \simeq$ 0.6 c.p.s.) $CH_3—\overset{|}{C}{=}\overset{|}{C}—\overset{|}{\underset{|}{C}}—H$, 7.59 (multiplet), 6.91 (quartet, J = 7 c.p.s.) $H—\overset{|}{\underset{|}{C}}—CH_3$.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.10; H, 8.28.

The semicarbazone crystallized from ethanol as small plates, m.p. 149.5–150°.

Anal. Calcd. for $C_{12}H_{19}N_3O_3$: C, 56.90; H, 7.6; N, 16.59. Found: C, 56.79; H, 7.69; N, 16.89.

The residue from the distillation when triturated with petroleum ether (b.p. 30–60°) gave 0.4 g. of a tan solid. Crystallization from ether–petroleum ether yielded 0.1 g. of yellow crystals, m.p. 108–135°. From the ultraviolet spectrum, λ_{max}^{EtOH} 241 mμ (ε 8700), the material is probably mainly **2** (below).

C. **2,4-Dimethyl-3-carboxycyclohex-2-en-1-one** (**2**).—Treatment of 11.5 g. of **5a** with 100 ml. of concentrated hydrochloric acid overnight at room temperature was followed by dilution of the mixture with 100 ml. of water and heating at reflux for 20 hr. The solution was cooled, made alkaline, and extracted with ether. The aqueous solution was then acidified and extracted with methylene chloride. The acid product was crystallized from methylene chloride–petroleum ether to give 2.2 g., m.p. 124–126°. The mother liquor, 2.7 g., yielded an additional 1.0 g. of crystalline material. Recrystallization from the above solvent gave colorless prisms: m.p. 126–128°; λ_{max}^{EtOH} 245 mμ (ε 10,100); $\nu_{max}^{CH_2Cl_2}$ 1675, 1700 cm.$^{-1}$; n.m.r., 8.8 (doublet, J = 7 c.p.s.) $CH_3—\overset{|}{\underset{|}{C}}—H$, 8.12 (doublet, J = 2 c.p.s.) $CH_3—\overset{|}{C}{=}\overset{|}{C}—H$.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.40; H, 7.10. Found: C, 64.22; H, 7.32.

D. **4-Methyl-3-carboxycyclohex-3-en-7-one** (**3**).—The Michael adduct **5b** (10 g.) was dissolved in 75 ml. of cold concentrated hydrochloric acid and the resulting dark purple solution stood for 48 hr. at 0°. It was then diluted to 150 ml. and refluxed for 2 hr. The aqueous solution was extracted with ethyl acetate and removal of the solvent gave 6.4 g. of a dark oil. Short-path distillation at 180° (bath temperature) afforded material which could be crystallized from ether–petroleum ether to give 0.754 g. of prisms: m.p. 112–114°; λ_{max}^{EtOH} 222 mμ (ε 7600); $\nu_{max}^{CHCl_3}$ 1630, 1680, 1715 cm.$^{-1}$; n.m.r., 7.88 (triplet, J = 2 c.p.s.) $CH_3—\overset{|}{C}{=}\overset{|}{C}—CH_2—$, 7.55 (multiplet, four protons), 6.4 (quartet, J = 2 c.p.s.) $CH_2—\overset{|}{C}{=}\overset{|}{C}—CH_3$.

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.35; H, 6.60.

The Ultraviolet Absorption Spectra of Some Conjugated Dienes

W. F. FORBES, R. SHILTON, AND A. BALASUBRAMANIAN

Chemistry Department, University of Waterloo, Ontario, Canada, and Chemistry Department, University of Wisconsin, Green Bay Center, Green Bay, Wisconsin

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Deviations from the relationships known as Woodward rules, which empirically relate the ultraviolet spectra of conjugated dienes, are explained in terms of steric interactions and in terms of some special interactions occurring in the *cis* conformation. This special interaction also rationalizes some of the relations which form the basis of the Woodward rules. Further, a preliminary discussion is presented concerning solvent changes occurring in such systems and concerning the vibrational fine structure observed in the main absorption bands.

The ultraviolet spectra of conjugated dienes have been studied by many authors, notably by Booker, Evans, and Gillam[1] and by Woodward,[2] who have derived extremely useful empirical rules relating wave length of maximal absorption to substitution of the diene chromophore. These relations have since then been widely employed.[3] However, recent accurate spectroscopic data are not available for some of the simpler substituted butadienes. We have therefore redetermined the spectra of a number of such substituted dienes, using carefully purified dienes whenever possible, in an attempt to relate minor spectral changes to structural changes. We were prompted to do this by some preliminary work[4] which suggested that more careful investigation of the butadiene spectra might reveal additional empirical relationships, and also by some recent work[5] which indicates that in certain butadienes the *cis* isomer can be more stable than the *trans* form.

Experimental

The ultraviolet absorption spectra were determined by standard methods in 1-cm. or 5- or 2-mm. cells using a Unicam SP 500, a Beckman Model DU, or a Cary Model 14 spectrophotometer. These instruments were calibrated against standard solutions of potassium chromate and/or potassium nitrate. For each compound at least two independent sets of observations were made. The λ_{max} values obtained on the different instruments were found to be within 1 mμ of each other. The precision of λ_{max} values is estimated to be 1 mμ and the precision of ϵ_{max} values, 5% or better. Absorptivity values for most compounds were

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