Anal. Calcd for $C_{20}H_{32}Cl_2N_2O_8$: C, 48.10; H, 6.46; N, 5.61. Found: C, 48.26; H, 6.60; N, 5.66.

Di-N,N'-*cis,trans,cis*-Tricyclo[5.3.0.0^{2,6}]deca-3,8-diylidenepyrrolidinium Diperchlorate.—This material was prepared in the usual manner from 1.37 g (8.35 mmoles) of *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]decane-3,8-dione,[46] 2.86 g (16.7 mmoles) of pyrrolidine perchlorate, and 1 drop of pyrrolidine in 91% yield. Purification was effected by solution in nitromethane, treatment with Darco, followed by crystallization induced by the addition of ethanol. The colorless powder had mp >315° (the crude material *explodes* at about 315°); ν_{max}^{Nujol} 1710 cm^{-1} (C=N$^+$); nmr τ values (TFA–TMS) at 5.95, 6.30, 6.55, 6.69, 7.69.[52]

Anal. Calcd for $C_{18}H_{28}Cl_2N_2O_8$: C, 46.25; H, 5.99; N, 5.95. Found: C, 45.93; H, 6.26; N, 5.75.

Acknowledgment.—The authors wish to express their appreciation to Miss Gail Gregory for her assistance.

(52) Nmr spectral curves for the compounds reported herein are given in the Ph.D. Thesis of W. J. Musliner, University of Illinois, 1965.

The Chemistry of Carbanions. XI. Michael Reactions with 2-Methylcyclopentanone and 2-Methylcyclohexanone[1a]

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Received September 16, 1965

The reaction of 2-methylcyclopentanone with methyl acrylate and the reactions of 2-methylcyclohexanone with methyl acrylate, methyl propiolate, and the methyl *cis*- and *trans*-3-chloroacrylates have been studied. The predominant formation of 2,2-disubstituted cycloalkanones as Michael products in certain of these reactions appears to be attributable to a combination of two factors. First, the positions of the relevant enolate anion equilibria favor the 2,2 isomer. Secondly, the minor product, the 2,6 isomer **5** from 2-methylcyclohexanone, is converted to dialkylated products (or other products) more rapidly than the 2,2 isomer **2** with the result that the proportion of 2,6 isomer **5** in the monoalkylated product decreases as the reaction proceeds. The initial Michael adducts **2a** and **5a** have been shown not to be interconverted under the Michael reaction conditions.

Earlier studies[2] of the Michael addition[3] of 2-methylcyclohexanone (**1**) to methyl acrylate in the presence of potassium *t*-butoxide and *t*-butyl alcohol indicated that the only monoalkylated product formed in appreciable quantity was the 2,2 isomer **2**. In the present study, both this reaction and the corresponding addition of 2-methylcyclopentanone (**3**) to methyl acrylate have been examined. The 2,6 stereoisomers **5** were described previously[2] and the 2,5 isomer **6** (a mixture of *cis* and *trans* isomers) has been obtained by the reaction scheme indicated in Chart I. Appropriate physical measurements (see Experimental Section) on the crude reaction products demonstrated that the crude monoalkylated product from the cyclopentanone **3** was largely (*i.e.*, >90%), if not exclusively, the 2,2 isomer **4a**. The monoalkylated product from 2-methylcyclohexanone (**1**) contained the 2,2 isomer **2a** (93%) and the 2,6 isomer **5a** (7%); when this latter reaction was run with 1,2-dimethoxyethane (DME) as the solvent, the monoalkylated product was composed of 88% of **2a** and 12% of **5a**. In all of these reactions higher molecular weight products were present which are believed to be dialkylated (*e.g.*, **9** from **1**) or trialkylated materials.

In seeking an explanation for the structural specificity of these Michael reactions, it was of interest to consider the equilibrium positions and the relative rates of formation of the enolate anions **10** and **11** derived from ketones **1** and **3**. For both of these cyclic ketones, the relative rates of formation of the isomeric enolate anions (*e.g.*, **10a** and **10b** from **1**) are approximately equal.[4] Consequently, any argument based on a rate-limiting enolate anion formation does not account for the structural specificity observed. The equilibrium concentrations for these enolate anions **10** and **11** are summarized in Chart II. The values for enolate anions generated with triphenylmethyl potassium in 1,2-dimethoxyethane (DME) were described previously[4] and the corresponding values for anions **10** generated from potassium *t*-butoxide were obtained by quenching the solutions in excess acetic anhydride to form the enol acetates **12** and **13**. Because of our previously noted[4a] inability to resolve these enol acetates, **12** and **13**, by gas chromatography, it was necessary to estimate the composition of the mixture from its nmr spectrum. Of incidental interest are the yields of enol acetates **12** and **13** which were obtained. The solution prepared from equimolar amounts of the ketone **1** and potassium *t*-butoxide in *t*-butyl alcohol gave 13–15% of the enol acetate mixture; the corresponding reaction in 1,2-dimethoxyethane yielded 50–60% of the enol acetate mixture. These yield data provide an estimate of the fraction of the ketone **1** which has been converted to its enolate anions by potassium *t*-butoxide in *t*-butyl alcohol and in 1,2-dimethoxyethane. It is clear that a larger fraction of the ketone **1** is present as its enolate anions in 1,2-dimethoxyethane solution.[5]

(1) (a) This research has been supported by Grant No. AF-AFOSR-573-64 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research. (b) National Institutes of Health Postdoctoral Fellow, 1964–1965. (c) National Science Foundation Predoctoral Fellow, 1963–1965.

(2) H. O. House and M. Schellenbaum, *J. Org. Chem.*, **28**, 34 (1963), and references therein.

(3) E. D. Bergmann, D. Ginsberg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

(4) (a) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963); (b) H. O. House and B. M. Trost, *ibid.*, **30**, 1341 (1965). A typographical error resulted in interchanging the formulas for the 2-methylcyclopentanone enolate anions in Table I of this reference. For the correction, see Additions and Corrections, *ibid.*, **30**, 4395 (1965).

(5) It should be noted that, while the commercially available *alcohol-free* potassium *t*-butoxide (and also lithium *t*-butoxide) is readily soluble in 1,2-dimethoxyethane, the corresponding alkoxides (both potassium and lithium) are much less soluble when 1 equiv of *t*-butyl alcohol is added. As a result the potassium *t*-butoxide prepared by reaction of potassium with excess *t*-butyl alcohol in the usual manner followed by distillation of the solvent is not readily soluble in 1,2-dimethoxyethane. Apparently, the 1:1 complex of potassium *t*-butoxide and *t*-butyl alcohol is distinctly less soluble in 1,2-dimethoxyethane than is the pure metal alkoxide. For discussion and other examples, see ref 6 and C. W. Kamienski and D. H. Lewis, *J. Org. Chem.*, **30**, 3498 (1965).

CHART I

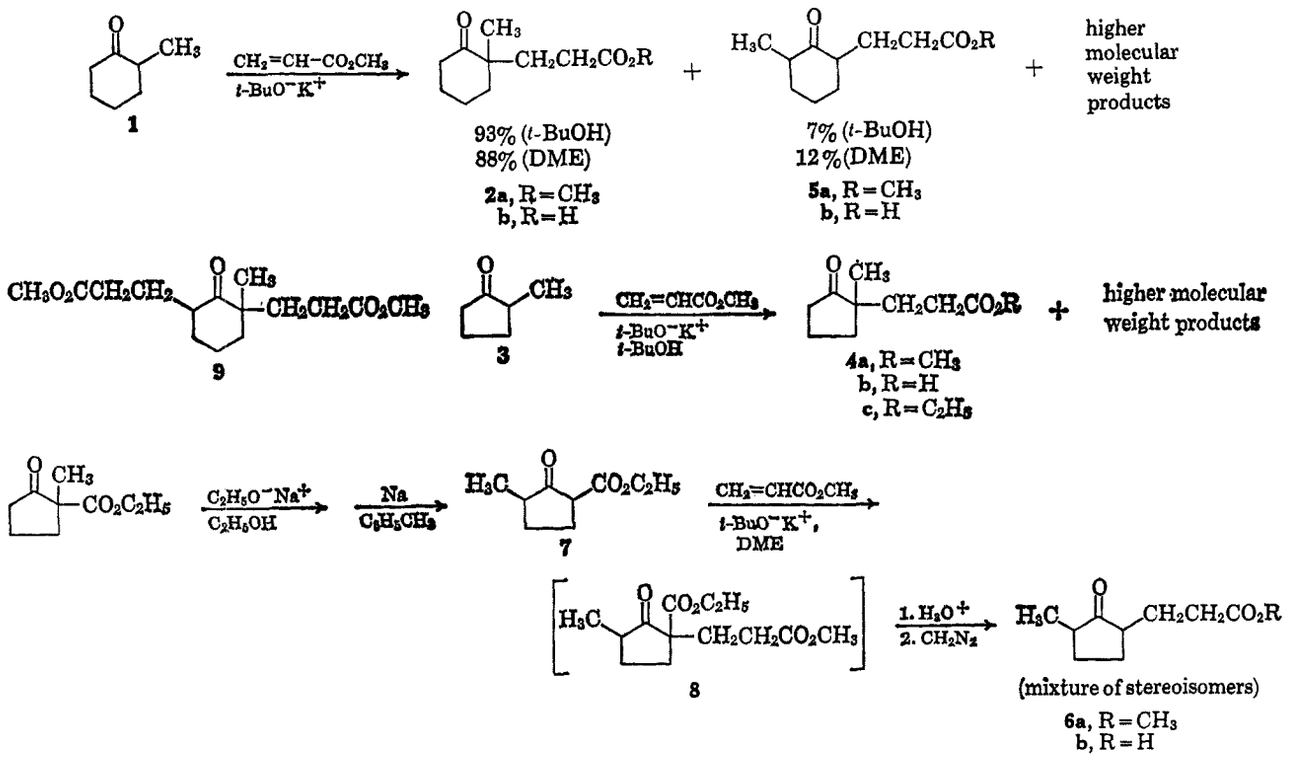
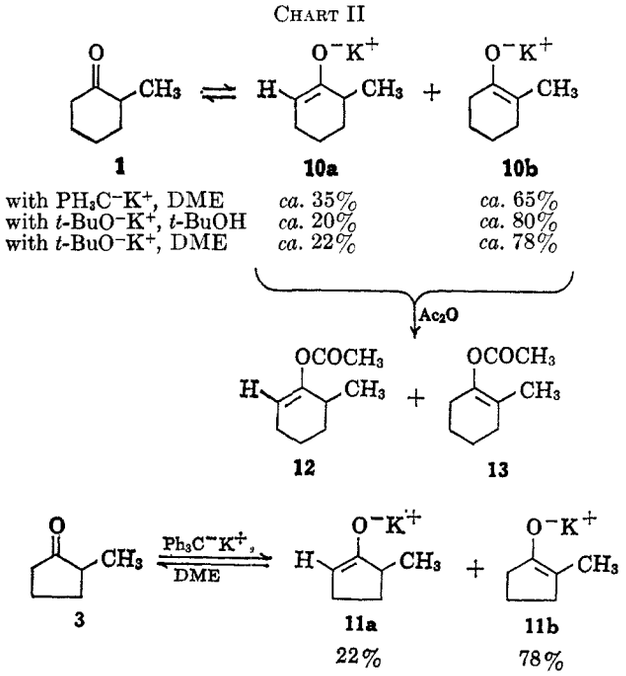
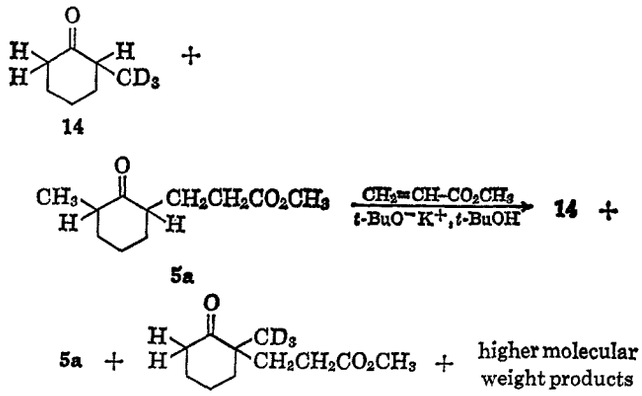


CHART II



It is apparent that, under the typical conditions of a Michael reaction, the monoalkylated products contain less of the 2,6 isomer **5a** (or the 2,5 isomer **6a**) than would be expected from the position of equilibrium for the enolate anions **10** and **11**. Since there is every reason to expect that reaction of the more hindered enolate anions **10b** and **11b** with methyl acrylate will be comparable in rate or will be slower than the corresponding reaction with the less hindered anions **10a** and **11a**,[6,7] the fact that the proportion of 2,2 isomer **2a** or **4a** in the monoalkylated product is greater than the equilibrium concentration of the more highly substituted enolate anion **10b** or **11b** is best explained in one of two ways. Either the monoalkylated products (*e.g.*, **2a** and **5a**) are interconverted under the conditions of the reaction or the symmetrically substituted isomer (*e.g.*, **5a**) is consumed in the reaction mixture more rapidly than the unsymmetrical isomer (*e.g.*, **2a**). Although a previous experiment[2] in which the 2,6 isomer **5a** was treated with potassium *t*-butoxide appeared to exclude the interconversion of the 2,6 isomer **5a** to the 2,2 isomer **2a** under the reaction conditions, we felt that further confirmation of this result was desirable. Accordingly, an equimolar mixture of the trideuterio ketone **14** and the unlabeled 2,6 isomer **5a** was allowed to react with methyl acrylate in the presence of potassium *t*-butoxide. The ketone **14** and the 2,2 isomer **15** recovered from this reaction were both labeled to the same extent as the starting ketone **14**, whereas the recovered 2,6 isomer **5a** contained a smaller percentage of d_3 species than could be detected by our analytical method (*i.e.*,

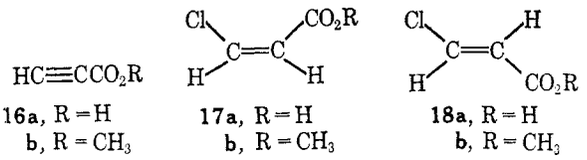


(6) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965).
(7) (a) H. Zook and W. L. Rellahan, *J. Am. Chem. Soc.*, **79**, 881 (1957); (b) J. M. Conia, *Record Chem. Prog.* (Kresge-Hooker Sci. Lib.), **24**, 43 (1963).

<5%). Consequently, we conclude that, under the conditions typical for Michael reactions, the structurally isomeric products **2a** and **5a** are not interconverted to any appreciable extent and, furthermore, that the reverse Michael reaction, **5a** → **1**, occurs to no appreciable extent.[8]

In view of these results, the most probable explanation for the observed structural specificity in the Michael reactions being studied is that the 2,6 isomer **5a** is converted to polyalkylated products (*e.g.*, **9**) or other products more rapidly than is the 2,2 isomer **2a**. Support for this idea was obtained by conducting this Michael reaction with 1 equiv of methyl acrylate and 3 equiv of the ketone **1**, reaction conditions which diminished substantially the proportion of high molecular weight products. Under these circumstances the monoalkylated product from the reaction run in *t*-butyl alcohol contained 88% of the 2,2 isomer **2a** and 12% of the 2,6 isomer **5a**; from the corresponding reaction in 1,2-dimethoxyethane, the proportions of monoalkylated products were 67% of **2a** and 33% of **5a**. The results of these experiments parallel the results obtained on methylation of the enolate anions derived from 2-methylcyclohexanone[4a] where the high proportion of 2,2-dimethylcyclohexanone in the monoalkylated product obtained in preparative experiments is, in part, attributable to the more rapid polyalkylation of the second monoalkylated product, 2,6-dimethylcyclohexanone.

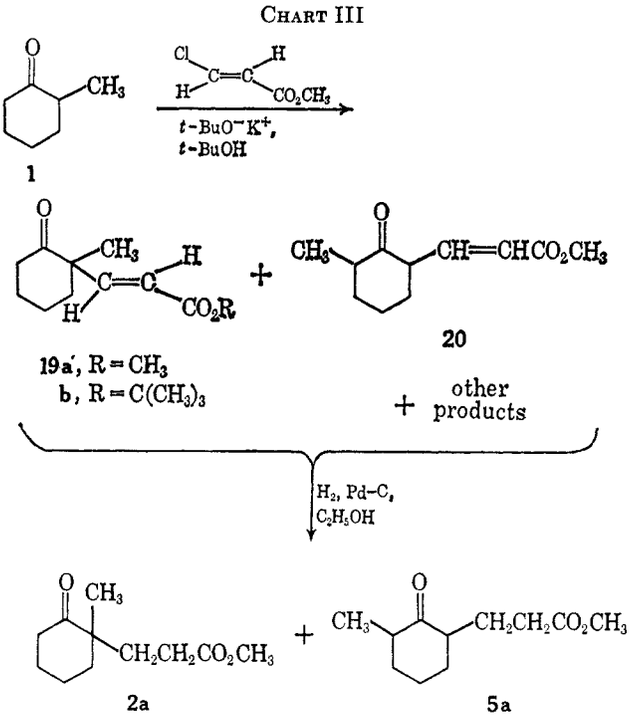
We turned our attention to a study of the reaction of the ketone **1** with the potential Michael acceptors, methyl propiolate (**16b**), methyl *cis*-3-chloroacrylate (**17b**), and methyl *trans*-3-chloroacrylate (**18b**).[9,10]



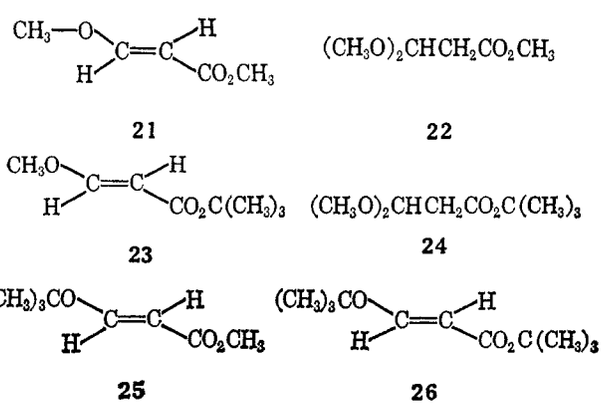
16a, R = H; **b**, R = CH_3 — **17a**, R = H; **b**, R = CH_3 — **18a**, R = H; **b**, R = CH_3

It was our thought that the initial products **19a** and **20** (formed by Michael addition and either prior or subsequent dehydrochlorination) might be capable of interconversion[11] unlike the saturated analogs **2a** and **5a**. Since the adduct **20** (a vinylogous β-keto ester) could form a very stable enolate anion, it appeared that, if the aforementioned equilibration between **19a** and **20** could be achieved, then the predominant reaction product would be the isomer **20** corresponding to the minor product **5b** in the saturated series. Apparent support for this idea was obtained in preliminary experiments involving reaction of the ketone **1** with the *trans*-β-chloro ester **18b** in the presence of 2 equiv of potassium *t*-butoxide. The crude reaction product was hydrogenated and distilled to yield a mixture in which the 2,6 isomer **5a** was the major constituent (*ca.* 80% of the mixture). However, the yields of material boiling in the range of the monoalkylated products **2a** and **5a** were very low (5–15%). (See Chart III.) For this reason a more detailed study of the reactions was made.

CHART III



The esters **16b**, **17b**, and **18b** were found to react rapidly with potassium *t*-butoxide in *t*-butyl alcohol to form a complex mixture of esters from which the products **21**–**26** were separated. It is likely that both the *cis* and *trans* isomers of the unsaturated esters were present in the initial reaction mixtures. The gas chromatograph employed for the separations was found to convert a mixture of *cis* and *trans* esters cor-



(8) Although we believe it unlikely that the reverse Michael reaction **15** (or **2a**) to **14** (or **1**) occurs to any appreciable extent, our labeling experiment provides no information on this point.

(9) For other studies of the conjugate addition of enolate anions to these and related Michael acceptors, see (a) F. Scotti and E. J. Frazza, *J. Org. Chem.*, **29**, 1800 (1964); (b) R. B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950); (c) P. R. Hills and F. J. McQuillin, *J. Chem. Soc.*, 4060 (1953); (d) G. N. Walker, *J. Am. Chem. Soc.*, **76**, 309 (1954); (e) N. K. Kochetkov, L. J. Kudryaskov, and B. P. Gottich, *Tetrahedron*, **12**, 63 (1961).

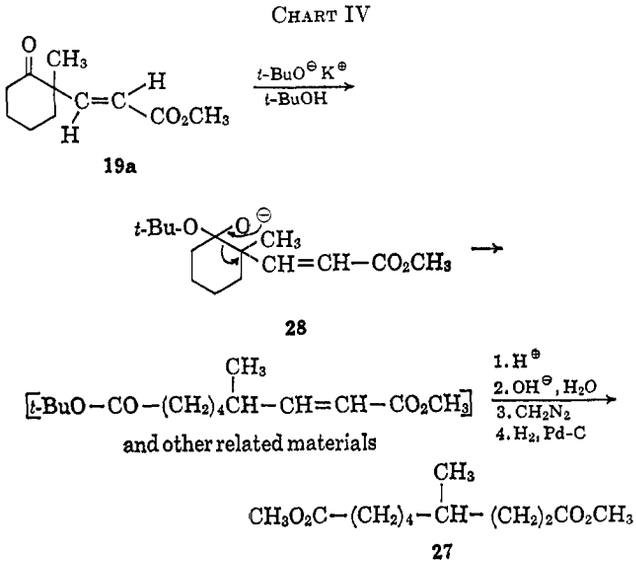
(10) For other studies of the conjugate addition of oxygen, sulfur, and nitrogen nucleophiles to these and related Michael acceptors, see ref 9a and (a) W. J. Croxall, J. O. Van Hook, and R. Luckenbaugh, *J. Am. Chem. Soc.*, **71**, 2736 (1949); (b) E. H. Ingold, *J. Chem. Soc.*, **127**, 1199 (1925); (c) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. White, *ibid.*, 2349 (1960); (d) F. Bohlmann and E. Bresinsky, *Chem. Ber.*, **97**, 2109 (1964); (e) D. E. Jones and C. A. Vernon, *Nature*, **176**, 791 (1955); (f) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964); (g) P. Bieber, *Ann. Chim.* (Paris), **9**, 674 (1954); (h) W. J. Croxall and H. J. Schneider, *J. Am. Chem. Soc.*, **71**, 1257 (1949); (i) J. Klosa, *Arch. Pharm.*, **287**, 129 (1954); (j) F. Montanari and A. Negrini, *Gazz. Chim. Ital.*, **87**, 1061 (1957); (k) F. W. Gray, H. S. Mosher, F. C. Whitmore, and T. S. Oakwood, *J. Am. Chem. Soc.*, **73**, 3577 (1951); (l) L. N. Owen and H. M. Batatunde Somade, *J. Chem. Soc.*, 1030 (1947).

(11) For example, an intramolecular Michael reaction to form a four-member ring intermediate followed by a retrograde Michael reaction could accomplish this interconversion.

responding to **26** to the *trans* ester which was isolated. We assume that other *cis* esters which might have been present would have undergone similar isomerization; consequently, only the indicated *trans* esters **21**, **23**, **25**, and **26** were isolated. Some, if not all, of these relatively low-boiling products were present as contaminants in all of the subsequently described reactions of the unsaturated esters **16b**, **17b**, and **18b** with the ketone **1**.

Reaction of the ketone **1** with the *trans*-chloro ester **18b** in the presence of 1 equiv of potassium *t*-butoxide led to a complex mixture of products including the above-mentioned low-boiling esters and high-boiling material of unknown constitution. The fraction of the product boiling in the range of monoalkylated products contained primarily the unsaturated ester **19a** accompanied by lesser amounts of materials believed to be the *t*-butyl ester **19b** and the ester **20**. Hydrogenation of this mixture yielded the saturated keto esters **2a** (major component) and **5a** (minor component). To examine the possibility of the base-catalyzed isomerization, **19a** → **20**, the unsaturated ester **19a** was treated with potassium *t*-butoxide in *t*-butyl alcohol. The crude product, a mixture of *t*-butyl esters, was converted successively to the free acid, the unsaturated methyl ester, and the saturated methyl ester, a product which proved to be the acyclic diester **27** and not the keto ester **5a**. Thus, reaction of the unsaturated ester **19a** resulted in cleavage (as in structure **28**) and not isomerization. The reaction

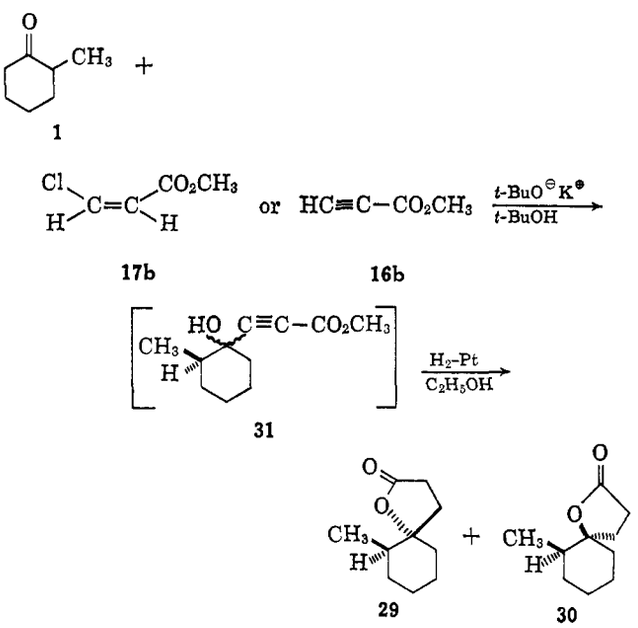
CHART IV



of the ketone **1** with the *trans*-chloro ester **18b** in the presence of 2 equiv of potassium *t*-butoxide followed by hydrogenation to give in low yield a monoalkylated product containing primarily the 2,6 isomer **5a** becomes understandable in view of these results. The majority of the initially formed 2,2 isomer **19a** is cleaved (*i.e.*, structure **28**) by the extra equivalent of base, whereas the unsaturated 2,6 isomer is apparently stable.

Reaction of the ketone **1** with either the *cis*-chloro ester **17b** or the acetylenic ester **16b** followed by hydrogenation of the crude product yielded, in addition to low-boiling and high-boiling components, a fraction corresponding in boiling point to monoalkylated products. This fraction contained neither of the keto esters **2a** or **5a** but rather the stereoisomeric γ-lactones **29** and **30**.[12] Thus, the *cis*-chloro ester **17b** was evidently dehydrochlorinated (a concerted *trans* elimination is possible with **17b** but not **18b**) more rapidly than it underwent Michael addition. Reaction of the ketone **1** with the propiolate **16b** involved addition of the acetylide anion to the ketone to form **31** rather than a Michael reaction. (See Chart V.)

CHART V



Experimental Section[13]

Reaction of 2-Methylcyclopentanone (3) with Acrylic Acid Esters. A. With Methyl Acrylate.—To a solution of 4.9 g (50 mmoles) of 2-methylcyclopentanone (**3**) and 5.2 mmoles of potassium *t*-butoxide in 50 ml of *t*-butyl alcohol was added, dropwise and with stirring at room temperature, 4.5 g (50 mmoles) of methyl acrylate. After the addition, which was accompanied by evolution of heat, was complete, the reaction mixture was stirred overnight at room temperature and then poured into dilute, aqueous sulfuric acid and extracted with ether. The organic extract was washed with aqueous sodium chloride, dried, concentrated, and distilled to separate 4.9 g (53%) of the **keto ester 4a**, bp 83–84° (0.05 mm), $n^{26.5}$D 1.4571. The product has infrared absorption[14] at 1735 cm^{-1} (C=O of ester and cyclopentanone) with nmr[14] singlets at δ 3.64 (3H, CO_2CH_3) and 0.98 (3H, >C-CH_3), as well as a complex multiplet in the region δ 1.5–2.5 (10H, aliphatic C-H). The mass spectrum of the product has a weak molecular ion peak at *m/e* 184 with abundant fragment peaks at *m/e* 128, 98, 97, 96, 74, 69, 68, 55, 41, and 39. This product was identified with a subsequently described sample by comparison of infrared spectra.

(12) (a) The same product, presumably a mixture of stereoisomers **29** and **30**, bp 148–152° (11 mm), was previously prepared by reaction of the ketone **1** with methyl propiolate (**16b**) in the presence of sodium amide followed by hydrogenation: W. E. Bachmann and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2530 (1950). (b) This same product was also prepared by R. C. Chatterjee and B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **34**, 515 (1957).

(13) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer, Model 237, infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian, Model A-60, nmr spectrometer; tetramethylsilane was the internal standard used. The mass spectra were obtained with a CEC, Model 21–130, mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

(14) Determined as a solution in carbon tetrachloride.

B. With Ethyl Acrylate.[16]—Reaction of 6.95 g (71 mmoles) of 2-methylcyclopentanone (**3**), 6.4 g (64 mmoles) of ethyl acrylate, and 4.1 mmoles of potassium *t*-butoxide in 60 ml of *t*-butyl alcohol as described above afforded 1.60 g of unchanged cyclopentanone (bp 139–140°) and 5.52 g (54% based on unrecovered cyclopentanone) of the **keto ester 4c**, bp 125–126° (6 mm), $n^{26.5}$D 1.4555 [lit.[15a] bp 130° (9 mm)]. This product has infrared absorption[14] at 1735 cm^{-1} (C=O of ester and cyclopentanone) with nmr peaks[14] at δ 4.09 (2H, quadruplet with J = 7 cps, O–CH_2–), 1.22 (3H, triplet with J = 7 cps, methyl group of –O–CH_2–CH_3), and 0.98 (3H, singlet, >C–CH_3), as well as a complex multiplet in the region δ 1.5–2.5 (10H, aliphatic C–H). The mass spectrum of the material has a weak molecular ion peak at m/e 198 with abundant fragment peaks at m/e 98, 97, 96, 69, 55, and 41.

Preparation of the Keto Acid 4b.—A solution of 4.0 g (22 moles) of the keto ester **4a** in 80 ml of 20% aqueous hydrochloric acid was refluxed overnight and then concentrated, saturated with ammonium sulfate, and extracted with ether. The ethereal solution was extracted with aqueous sodium carbonate, and the aqueous layer was separated, acidified, and extracted with ether. This final ether extract was dried, concentrated, and distilled to separate 3.2 g (87%) of the keto acid **4b** as a colorless liquid, bp 130–131° (0.05 mm), n^{28}D 1.4700. The product has broad infrared absorption[14] in the 3-μ region (carboxyl associated O–H) with peaks at 1735 (cyclopentanone C=O) and 1710 cm^{-1} (carboxyl C=O). It has nmr singlets[14] at δ 11.70 (1H, COOH) and 1.00 (3H, >C–CH_3), as well as a complex multiplet in the region δ 1.5–2.5 (10H, aliphatic C–H). The mass spectrum of the product has a weak molecular ion peak at m/e 170 with abundant fragment peaks at m/e 114, 98, 69, 55, 41, and 39.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.21; H, 8.28.

Similarly, hydrolysis of 4.5 g (23 mmoles) of the keto ester **4c** with 80 ml of refluxing 20% aqueous hydrochloric acid for 12 hr afforded 2.52 g (65%) of the keto acid **4b**, bp 130–131° (0.05 mm), n^{25}D 1.4700. This product was identified with the previous sample by comparison of infrared spectra. In addition a 1.0-g sample of the keto acid **4b** (from the ethyl ester **4c**) was esterified with excess ethereal diazomethane to yield 0.97 g (90%) of the **keto ester 4a**, bp 80–84° (0.05 mm), $n^{26.5}$D 1.4570. This sample was identified with the methyl ester from the Michael reaction as already described.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.10; H, 8.76.

Michael Reaction with 2-Carboethoxy-5-methylcyclopentanone (7).—2-Carboethoxy-2-methylcyclopentanone was cleaved with refluxing ethanolic sodium ethoxide to diethyl α-methyladipate [yield 87%, bp 140–142° (24 mm), n^{25}D 1.4262, lit.[16] bp 133–134° (18 mm)], and the diester was reclosed by reaction with sodium in toluene at 120° to form 2-carboethoxy-5-methylcyclopentanone (**7**) [yield 63%, bp 116–117° (19 mm), $n^{24.5}$D 1.4530, lit.[17] bp 123–124° (31 mm)].[18] To a cold (−5°) mixture of 1.70 g (10 mmoles) of the ester **7** and 185 mg of a potassium *t*-butoxide–*t*-butyl alcohol 1:1 complex in 20 ml of 1,2-dimethoxyethane was added, dropwise with stirring, 0.86 g (10 mmoles) of methyl acrylate. The resulting mixture was stirred for 3 hr at −5° and then poured into cold, dilute aqueous hydrochloric acid and extracted with ether. The extract was concentrated and heated overnight with 25 ml of refluxing 20% aqueous hydrochloric acid. After the solution had been concentrated under reduced pressure, it was saturated with ammonium sulfate and extracted with ether. This ethereal extract was dried and concentrated to leave 1.15 g of the crude **acid 6b** as a yellow oil with infrared absorption[14] at 3000 (broad, carboxyl-associated O–H), 1740 (cyclopentanone C=O), and 1710 cm^{-1} (carboxyl C=O). This product was esterified with excess ethereal diazomethane to yield 0.95 g (52% based on the ester **7**) of the **keto ester 6a**, a mixture of stereoisomers, as a colorless liquid, bp 77–78° (1.5 mm), $n^{24.5}$D 1.4533. The material has infrared absorption[14] at 1735 cm^{-1} (ester and cyclopentanone C=O) with an nmr peak[14] at δ 3.57 (3H, CO_2CH_3) and two overlapping doublets (J = 6 cps for each) at δ 1.02 and 1.05 (3H, methyl protons of the CH_3–CH< grouping in the *cis* and *trans* isomers), as well as a complex multiplet in the region δ 1.2–2.5 (10H, aliphatic C–H). The mass spectrum has a weak molecular ion peak at m/e 184 with abundant fragment peaks at m/e 152, 124, 111, 110, 98, 97, 82, 74, 59, 55, 42, 41, and 39.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.13; H, 8.79.

The two stereoisomers of keto ester **6a** were not resolved either on a silicone gas chromatography column[19] or on a variety of other columns; also the keto esters **6a** were eluted[19] only slightly before the structural isomer **4a** with the result that we were unable to analyze mixtures of the keto esters **4a** and **6a** by this procedure. The mass spectrum of ester **4a** has peaks at m/e 169 (M − CH_3). 156, and 140 which are either very weak or absent in the spectrum of **6a**. Also, the spectrum of the keto ester **6a** has peaks at m/e 152, 151, and 150 which are either very weak or are missing in the spectrum of ester **4a**. On this basis we conclude that neither keto ester **4a** or **6a** is significantly contaminated by the other isomer. The nmr C-methyl absorption for each keto ester **4a** or **6a** also indicates that neither isomer is contaminated with the other.

Propiolic Acid and Its Methyl Ester (16).—Following a previous procedure,[20] a solution of 400 g (2.62 moles) of the monopotassium salt of acetylenedicarboxylic acid in 1 l. of water was heated on a steam bath for 4 hr. After the solution had been saturated with ammonium sulfate, acidified with dilute aqueous hydrochloric acid, and extracted with ten portions of ether, the ethereal extract was dried, concentrated, and distilled to yield 119 g (54%) of **propiolic acid (16a)**, bp 77–90° (40 mm), n^{25}D 1.4231 [lit.[21] bp 57–58° (12 mm), $n^{20.4}$D 1.4302]. The product has broad infrared absorption[14] at 3000 cm^{-1} (carboxyl-associated O–H), with peaks at 2150 (C≡C) and 1710 cm^{-1} (carboxyl C=O).

A solution of 75 g (0.93 mole) of propiolic acid (**16a**) and 250 ml of boron trifluoride etherate[22] in 400 ml of methanol was stirred at room temperature for 24 hr and then diluted with ether and poured into water. The ether layer was separated, combined with the ethereal extract of the aqueous layer, washed with aqueous sodium bicarbonate, dried, concentrated, and distilled. The **methyl propiolate (16b)**, bp 100–104°, n^{25}D 1.4070 [lit bp 102° (742 mm),[10b] $n^{19.1}$D 1.4085[21]), amounted to 37.2 g (48%). The ester has infrared absorption[14] at 3310 (acetylenic C–H), 2135 (C≡C), and 1725 cm^{-1} (ester C=O) with nmr singlets[14] at δ 3.75 (3H, O—CH_3) and 2.88 (1H, C≡C—H).

***cis*-3-Chloroacrylic Acid and Its Methyl Ester (17).**—A sample of the *cis* acid **17a**,[23] mp 60–61° (lit. mp 63–64°,[23b] 60.8–61.4°[23c]), has infrared absorption[14] at 3000 (broad, carboxyl associated O–H), 1695 (carboxyl C=O), and 1615 cm^{-1} (conjugated C=C) with an ultraviolet maximum[24] at 213 mμ (ε 10,000) and an nmr peak[14] at δ 12.90 (1H, COOH) with doublets (J = 8.5 cps) at δ 6.40 and 7.04 (2H, vinyl C–H). The mass spectrum of the product has molecular ion peaks at m/e 106 and 108 with abundant fragment peaks at m/e 91, 89, 71, 63, 61, 45, and 44.

A solution of 5.0 g (47 mmoles) of the *cis* acid **17a** and 1.0 ml of concentrated sulfuric acid in 55 ml of methanol was refluxed overnight and then poured into ice–water and extracted with ether. After the ethereal extract had been washed with aqueous sodium carbonate, dried, and concentrated, distillation of the residue afforded 3.79 g (68%) of the ***cis* ester 17b**, bp 144–145°, $n^{26.5}$D 1.4538 [lit.[23c] bp 79–83° (78 mm), n^{20}D 1.4570]. The product was identified with an authentic sample ($n^{26.5}$D 1.4538)[23] by comparison of gas chromatographic retention times and infra-

(15) Each of the following reactions with 2-methylcyclopentanone has been reported to give the 2,2-disubstituted product: (a) with ethyl β-bromopropionate, P. C. Mukharji, *J. Indian Chem. Soc.*, **24**, 91 (1947); (b) with acrylonitrile, N. K. Chaudhuri and P. C. Mukharji, *ibid.*, **33**, 155 (1956); (c) with a Mannich base precursor of methyl vinyl ketone, E. C. du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937).

(16) R. Cornubert and C. Borrell, *Bull. Soc. Chim. France*, [4] **47**, 301 (1930).

(17) A. Haller and R. Cornubert, *ibid.*, [4] **39**, 1621 (1926).

(18) This preparative sequence has recently been discussed by (a) W. L. Meyer, A. P. Lobo, and E. T. Marquis, *J. Org. Chem.*, **30**, 181 (1965); (b) K. Sisido, K. Utimoto, and T. Isida, *ibid.*, **29**, 2781 (1964).

(19) A column packed with Silicone Fluid, No. 710, suspended on ground firebrick, was employed.

(20) K. Alder and G. Stein, *Ann.*, **525**, 209 (1936).

(21) R. Sabathy, *Z. Physik. Chem.*, **B41**, 183 (1938).

(22) The esterification procedure of J. Mitchell, Jr., D. M. Smith, and W. M. D. Bryant, *J. Am. Chem. Soc.*, **62**, 4 (1940).

(23) Obtained from Dr. A. Kurtz, Union Carbide Olefins Co., Charleston, W. Va. See (a) T. H. Vaughn, Belgian Patent 631,355 (Aug 16, 1963); *Chem. Abstr.*, **60**, 11900 (1964); (b) H. J. Backer and A. E. Beute, *Rec. Trav. Chim.*, **54**, 167 (1935); (c) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).

(24) Determined as a solution in 95% ethanol.

red spectra. A solution of 3.19 g (29 mmoles) of the *cis* acid **17a** in 25 ml of ether was also esterified with excess ethereal diazomethane to yield 3.17 g (88%) of the *cis* **ester 17b**, bp 144–144.5°, $n^{26.5}$D 1.4538, which was identified with the aforementioned product by comparison of infrared spectra and retention times. The *cis* ester **17b**, bp 146–148°, n^{25}D 1.4526, was also obtained in 69% yield by reaction of 65 g of the acid **17a** with 400 ml of methanol in the presence of 150 ml of boron trifluoride etherate.[22] The *cis* ester **17b** has infrared absorption[14] at 1730 (ester C=O) and 1615 cm^{-1} (conjugated C=C) with an ultraviolet maximum[24] at 216 mμ (ε 21,800) and nmr[14] doublets (J = 8.5 cps) at δ 6.28 and 6.86 (2H, vinyl C–H), as well as a singlet at δ 3.82 (3H, $-CO_2CH_3$). The mass spectrum has molecular ion peaks at m/e 120 and 122 with abundant fragment peaks at 91, 89, 85, 63, and 61. The retention times of the *cis* and *trans* esters on gas chromatography[19] are *trans* ester **18b**, 7.7 min, and *cis* ester **17b**, 13.9 min.

trans-**3-Chloroacrylic Acid and Its Methyl Ester (18).**—A mixture of 25 g (0.24 mole) of the crude *cis* acid **17a** and 100 ml of 6 *M* aqueous hydrochloric acid was heated on a steam bath with stirring for 2 hr and then treated with decolorizing carbon and filtered.[23] The resulting solution was refrigerated to separate the crude *trans* acid, which was collected and recrystallized from petroleum ether (bp 30–60°). The pure *trans* acid **18a**[25] separated as 13.1 g (52%) of white plates, mp 84.5–85° (lit.[23b] mp 85.5–86°), with infrared absorption[14] at 3000 (broad, carboxyl-associated O–H), 1690 (carboxyl C=O), 1605 (conjugated C=C), and 942 cm^{-1} (*trans* CH=CH), and an ultraviolet maximum[24] at 212 mμ (ε 16,000). The nmr spectrum[14] has a peak at δ 12.90 (1H, –COOH) with doublets (J = 13.5 cps) at δ 6.42 and 7.68 (2H, vinyl C–H). The mass spectrum has molecular ion peaks at m/e 108 and 106 with abundant fragment peaks at m/e 91, 89, 71, 63, 61, 45, and 44.

A 5.0-g (47 mmoles) sample of the *trans* acid **18a** was esterified with 55 ml of methanol and 1.0 ml of concentrated sulfuric acid to yield, after distillation, 3.5 g (63%) of the *trans* **ester 18b**, bp 123–124°, $n^{26.5}$D 1.4581 [lit. bp 22° (12 mm),[26] 74–75° (131 mm),[23c] n^{20}D 1.4510[23c]]. The *trans* acid (3.19 g, 29 mmoles) was also esterified with ethereal diazomethane. The crude liquid product was filtered from some crystalline solid (presumably the pyrazoline) and distilled to separate 2.24 g (62%) of the *trans* **ester 18b**, bp 123–124°, $n^{26.5}$D 1.4581. The two *trans* ester samples were identified with one another and with an authentic sample ($n^{26.5}$D 1.4581)[23] by comparison of gas chromatographic retention times and infrared spectra. The *trans* ester **18b**, bp 121–125°, n^{25}D 1.4494, was also obtained in 82% yield by reaction of 34 g (0.32 mole) of the acid **18a** with 200 ml of methanol in the presence of 91 ml of boron trifluoride etherate.[22] The *trans* ester has infrared absorption[14] at 1735 (ester C=O), 1630 (conjugated C=C), and 945 cm^{-1} (*trans* CH=CH) with an ultraviolet maximum[24] at 215 mμ (ε 16,100) and nmr[14] doublets (J = 13.5 cps) at δ 7.52 and 6.36 (2H, vinyl C–H), as well as a singlet at δ 3.80 (3H, $-CO_2CH_3$). The mass spectrum has molecular ion peaks at m/e 122 and 120 with abundant fragment peaks at m/e 91, 89, 85, 63, and 61.

Reaction of the Esters 16b, 17b, and 18b, with Potassium *t*-Butoxide in *t*-Butyl Alcohol. A. Methyl Propiolate (16b).—A solution of 2.90 g (34 mmoles) of the ester **16b** in 20 ml of *t*-butyl alcohol was added, dropwise and with stirring under a nitrogen atmosphere, to a solution of 3.8 mmoles of potassium *t*-butoxide in 20 ml of *t*-butyl alcohol. The solution, which immediately turned dark red, was stirred at room temperature for 15 min and then acidified with acetic acid, diluted with water, and extracted with ether. The ethereal solution was washed with aqueous sodium bicarbonate, dried, and concentrated to leave 8.07 g of crude liquid product. An aliquot of this crude product was mixed with a weighed sample of *m*-diisopropylbenzene (as an internal standard) and analyzed by gas chromatography.[27] the chromatograph having been calibrated with a known mixture prepared from collected samples of esters **21–26**. The crude product contained the following components (calculated per cent yield, chromatographic[27] retention time): **21** (13%, 15.2 min), **22** (3%, 17.8 min), **23** (28%, 19.8 min), **24** (2%, 24.6 min), **25** (8%, 31.2 min), and **26** (3% 51.9 min).

B. Methyl *cis*-3-Chloroacrylate (17b).—To a solution of 51 mmoles of potassium *t*-butoxide in 40 ml of *t*-butyl alcohol was added, dropwise and with stirring under a nitrogen atmosphere, 6.02 g (50 mmoles) of the ester **17b**. The resulting mixture, which immediately turned a red-brown color with the separation of a precipitate, was stirred for 15 min at room temperature and then subjected to the previously described isolation procedure. The crude liquid product (18.21 g) contained[27] **21** (13% calculated yield), **22** (1%), **23** (22%), **24** (3%), **25** (17%), and **26** (7%).

C. Methyl *trans*-3-Chloroacrylate (18b).—Following the previous procedure, reaction of 5.97 g (50 mmoles) of the ester **18b** with 51 mmoles of potassium *t*-butoxide in 40 ml of *t*-butyl alcohol afforded 20.51 g of crude liquid product which contained[27] **21** (20% calculated yield), **22** (2%), **23** (24%), **24** (1%), **25** (17%), and **26** (6%).

D. Identification of Products.—Although gas chromatographic analysis[27] as well as the subsequently described properties of the products collected from the chromatograph indicated the presence of only the *trans* isomers **21, 23, 25,** and **26** of the olefinic products, the conditions required for the gas chromatograhic separation were found to isomerize *t*-butyl *cis*-3-*t*-butoxyacrylate (and presumably the other *cis*-3-alkoxyacrylates) to the *trans* isomer **26**. Fractional distillation of the crude product from the previously described reaction of the *cis*-chloro ester **17b** afforded 1.60 g of a fraction, bp 55–63° (0.15 mm), which exhibited one major gas chromatographic[27] peak corresponding to the *t*-butyl ester, **26**. However, the nmr spectrum[14] of this distilled fraction has both a pair of doublets (J = 12 cps) centered at δ 7.14 and 4.88 (*trans* –CH=CH– of **26**) and a pair of doublets (J = 7 cps) centered at δ 6.29 and 4.39 attributable to the –CH=CH– grouping of a *cis*-3-alkoxyacrylate. The areas under these nmr peaks corresponded to an approximately equal mixture of the *cis* and *trans* isomers. After a sample had been collected from the gas chromatograph,[27] only the pair of nmr doublets attributable to the *trans* isomer **26** were present.

The crude product from reaction of 44 mmoles of the *cis* ester **17b** with 51 mmoles of potassium *t*-butoxide in 40 ml of *t*-butyl alcohol as previously described was fractionally distilled to effect partial separation of the components **21–26**. Fractions (0.609 g) boiling in the range 65–85° (10 mm) contained[27] primarily ester **21**; later fractions [1.080 g, bp 95–107° (10 mm)] contained mainly mixtures of esters **23** and **24**, and the final fractions [1.383 g, bp 66–79° (0.7 mm)] contained primarily esters **25** and **26**, Each of the samples **21** and **23–26** was collected[27] from the gas chromatograph of an appropriate distillation fraction. The quantity of the component believed to be ester **22** was inadequate for satisfactory identification; it was tentatively identified by demonstrating that it had the same retention time as a subsequently described sample of the ester **22**.

A collected[27] sample of the ester **21**, n^{31}D 1.4466 [lit.[10b] bp 56° (18 mm), n^{20}D 1.4500], has infrared absorption[14] at 1720 (conjugated ester C=O) and 1650 and 1630 cm^{-1} (conjugated C=C) with an ultraviolet maximum[25] at 227 mμ (ε 18,300). The nmr spectrum[13] has two singlets at δ 3.62 and 3.67 (6H, O–CH_3) with two pairs of doublets (J = 12.5 cps) centered at δ 7.51 and 5.10 (2H, β- and α-vinyl C—H of *trans* CH=CH). The mass spectrum of the material has a molecular ion peak at m/e 116 with a very abundant fragment peak at m/e 85 ($CH_3\overset{+}{O}$=CH—CH=C=O), as well as relatively abundant peaks at m/e 87, 59, 42, and 31.

A collected[27] sample of the ester **23**, n^{31}D 1.4363, has infrared absorption[14] at 1710 (conjugated ester C=O) and 1650 and 1630 cm^{-1} (conjugated C=C) with an ultraviolet maximum[24] at 227 mμ (ε 12,000). The nmr spectrum[14] of the ester has singlets at δ 3.63 (3H, O–CH_3) and 1.43 [9H, $(CH_3)_3$C–O] with a pair of doublets (J = 12.5 cps) centered at δ 7.41 and 5.01 (2H, *trans* –CH=CH–). The mass spectrum of the ester **23** exhibits no molecular ion peak but has relatively abundant fragment peaks at m/e 85 (CH_3O=CH—CH=C=O), 56, 41, and 39.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92, Found: C, 60.54; H, 8.90.

Attempts to collect[27] a pure sample of the ester **24** were complicated by the presence in the collected sample of small amounts of the unsaturated ester **23** which we were unable to separate. Consequently, this sample was only partially characterized by virtue of its infrared absorption[14] at 1735 cm^{-1} (ester C=O) and its nmr absorption[14] with singlets at δ 3.25 (6H, OCH_3) and

(25) E. Gryszkiewicz-Trochimowski, O. Gryszkiewicz-Trochimowski, and W. Schmidt, *Bull. Soc. Chim. France*, 593 (1948).

(26) J. Niwa and H. Kasiwagi, *Bull. Soc. Chem. Japan*, **36**, 1144 (1963).

(27) A gas chromatography column packed with LAC-728 (diethylene glycol succinate) suspended on Chromosorb P was employed for this analysis.

1.42 [9H. $(CH_3)_3C$–O] with a doublet (J = 6 cps) at δ 2.40 (2H, CH_2–CO) and a triplet (J = 6 cps) at δ 4.66 [1H, (RO_2)-CH–].

A collected[27] sample of the ester **26**, $n^{31}D$ 1.4406, has infrared absorption[14] at 1705 (conjugated ester C=O) and 1640 cm^{-1} (conjugated C=C) with an ultraviolet maxima[24] at 237 mμ (ϵ 16,500). The sample has two nmr[14] singlets at δ 1.35 and 1.42 [18H, $(CH_3)_3C$–O] with two pairs of doublets (J = 12 cps) centered at δ 7.45 and 5.10 (2H, *trans* –CH=CH–). The mass spectrum exhibits no molecular ion peak but has relatively abundant fragment peaks at m/e 144, 127 [$(CH_3)_3C{=}\overset{+}{O}{=}CH$–CH=C=O], 89, 71, 57, and 41.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.60; H, 9.98.

A collected[27] sample of the ester **25**, $n^{31}D$ 1.4482, has infrared absorption[14] at 1715 (conjugated ester C=O) and at 1660 (shoulder) and 1640 cm^{-1} (conjugated C=C) with an ultraviolet maximum[24] at 238 mμ (ϵ 17,900) and nmr singlets[14] at δ 3.63 (3H, CO_2CH_3) and 1.37 [9H, $(CH_3)_3C$–O] accompanied by two pairs of doublets (J = 12 cps) centered at δ 7.62 and 5.22 (2H, *trans* –CH=CH–). The mass spectrum has a weak molecular ion peak at m/e 158 with relatively abundant fragment peaks at 143, 127 [$(CH_3)_3C{-}\overset{+}{O}{=}CH$–CH=C=O], 103, 102, 85, 71, 57, and 41.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.79; H, 8.96.

The positions of the ultraviolet maxima (227 mμ for the β-methoxyacrylates **21** and **23** and 237–238 mμ for the β-*t*-butoxyacrylates **25** and **26**) were used to assign structures to the isomers **23** and **25**. These ultraviolet maxima are in agreement with the values previously reported[10l] for 3-*t*-butoxyacrylic acid λ_{max} 237 mμ (ϵ 15,400)] and 3-methoxyacrylic acid [λ_{max} 228 mμ (ϵ 14,100)].

Reaction of the *cis* Ester 17b with Methanolic Potassium Methoxide.—To a solution of 28 mmoles of potassium methoxide in 20 ml of methanol was added, dropwise and with stirring under a nitrogen atmosphere, 3.2 g (27 mmoles) of the ester **17b**. The colorless reaction mixture, from which a precipitate separated, was stirred for 20 hr at room temperature and then acidified with acetic acid and subjected to the previously described isolation procedure. The crude product, which exhibited only a single gas chromatographic peak[27] corresponding to the ester **22**, was distilled to separate 3.01 g (78%) of the ester **22**, bp 91–92° (30 mm), $n^{31}D$ 1.4054 [lit.[10b] bp 77° (20 mm), $n^{20}D$ 1.4095]. This product has infrared absorption[14] at 1745 cm^{-1} (ester C=O) with nmr singlets[14] at δ 3.63 (3H, CO_2CH_3) and 3.28 (6H, OCH_3), as well as a doublet (J = 6 cps) at δ 2.53 (2H, CH_2–CO) and a triplet (J = 6 cps) at δ 4.73 [1H, (RO_2)-CH–]. The mass spectrum has a very weak molecular ion peak at m/e 148 with a very abundant fragment peak at m/e 75 ($CH_3\overset{+}{O}{=}CHOCH_3$).

Anal. Calcd for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.45; H, 8.20.

2-Trideuteriomethylcyclohexanone (14).—Trideuteriomethyl iodide (5% d_2 species and 95% d_3 species) was prepared as previously described.[28] A cold (−10°) solution prepared from 83 mmoles of sodium ethoxide, 13.56 g (83 mmoles) of ethyl cyclohexanone-2-carboxylate, and 50 ml of absolute ethanol was stirred for 1 hr at −10° and under a nitrogen atmosphere and then 12.0 g (83 mmoles) of trideuteriomethyl iodide was added to the cold solution. The cooling bath was removed and the resulting mixture was stirred overnight under a nitrogen atmosphere. After the reaction mixture had been poured into water and extracted with ether, the ethereal extract was washed successively with cold (0°) 10% aqueous potassium hydroxide, with aqueous hydrochloric acid, and with aqueous sodium carbonate and then dried and concentrated. A solution of the residual oil in a mixture of 25 ml of concentrated hydrochloric acid, 50 ml of water, and 20 ml of acetic acid was refluxed overnight and then diluted with water and extracted repeatedly with ether. The ethereal extract was dried, concentrated, and distilled to separate 5.94 g (64%) of the pure[27] trideuterio ketone **14** which contained 94% d_3 species and 6% d_2 species. The nmr spectrum[14] of this product corresponded to the nmr spectrum of 2-methylcyclohexanone (**1**), except for the absence of the doublet (J = 6 cps) at δ 0.97 (CH_3). The infrared spectrum[14] of the deuterated ketone **14** had bands not present in the nondeuterated sample **1** at 2060, 2110, 2140, and 2220 cm^{-1} (C–D stretching); the spectra of the two samples differ in a number of places in the fingerprint region.

Reaction of 2-Methylcyclohexanone (1) with Methyl Acrylate. A. In *t*-Butyl Alcohol.—To a solution of 15.1 g (135 mmoles) of the ketone **1** and 13.5 mmoles of potassium *t*-butoxide in 120 ml of *t*-butyl alcohol was added, dropwise and with stirring under a nitrogen atmosphere, 13.0 g (151 mmoles) of methyl acrylate. The resulting solution was stirred at room temperature for 1.5 hr and then acidified with acetic acid, concentrated, and diluted with ether. This ethereal solution was washed with aqueous sodium carbonate, dried, concentrated, and distilled to separate 16.32 g (61%) of a fraction, bp 105–110° (0.5 mm), and 4.3 g of a higher molecular weight fraction, bp 160–175° (0.15 mm). The lower boiling fraction contained[27] 93% of the 2,2 isomer **2a** (retention time 25.6 min) and 7% of the 2,6 isomer **5a** (a mixture of stereoisomers, retention time 20.8 min). A collected[27] sample of each component was identified with previously described authentic samples[2] by comparison of infrared spectra and gas chromatographic retention times. The 2,6 product **5a** has broad nmr absorption[14] in the region δ 1.1–2.7 (12H, aliphatic C–H) with a singlet at δ 3.58 (3H, O–CH_3) and two overlapping doublets at δ 0.95 (J = 6 cps, *ca.* 80% of 3H) and 1.02 (J = 6.5 cps, *ca.* 20% of 3H). These two doublets are attributable to the previously reported[2] *cis* isomer and to the less abundant *trans* isomer of the keto ester **5a**.

The higher boiling fraction from the distillation contained[29] at least two components and had infrared absorption[14] at 1740 and 1700 cm^{-1}, suggesting the presence of ester and ketone carbonyl functions as in a keto diester derived from polyalkylation. However, our efforts to isolate a single pure substance from this mixture, either before or after hydrolysis of the ester functions, were unsuccessful.

From a comparable reaction employing excess ketone (1.9 mmoles of potassium *t*-butoxide, 19.4 mmoles of the ketone **1**, and 6.8 mmoles of methyl acrylate in 20 ml of *t*-butyl alcohol) the proportions[27] of the monoalkylated materials in the crude product were 12% of the 2,6 isomers **5a** and 88% of the 2,2 isomer **2a**. The gas chromatographs[27,29] of the total crude product exhibited peaks corresponding to the starting ketone **1** and lower boiling materials, to the keto esters **2a** and **5a**, and to a small amount (<5%) of polyalkylated material.

To demonstrate that the 2,6 isomer **5a** did, in fact, react faster with methyl acrylate than the 2,2 isomer **2a**, a solution of 375 mg (3.3 mmoles) of potassium *t*-butoxide, 1.418 g (7.1 mmoles) of a mixture of keto esters **2a** (64% of mixture) and **5a** (36% of mixture), and 562 mg (6.6 mmoles) of methyl acrylate in 15 ml of *t*-butyl alcohol was stirred, at room temperature and under a nitrogen atmosphere for 1 hr. The resulting mixture was diluted with aqueous hydrochloric acid and extracted with ether, The crude product recovered from the ethanol extract contained the monoalkylated products in the proportions 82% of the 2,2 isomer **2a** and 18% of the 2,6 isomer **5a**.

B. In 1,2-Dimethoxyethane.—To a solution of 16.70 g (150 mmoles) of the ketone **1** and 1.84 g (16 mmoles) of potassium *t*-butoxide[30] in 130 ml of 1,2-dimethoxyethane was added, dropwise and with stirring under a nitrogen atmosphere, 13.98 g (160 mmoles) of methyl acrylate. After the resulting solution had been stirred for 3 hr at room temperature, it was diluted with dilute, aqueous hydrochloric acid and subjected to the previously described isolation procedure. The fraction with bp 95–105° (0.2 mm), yield 11.75 g (40%), contained[27] the 2,2 isomer **2a** (88%) and the mixture of stereoisomeric 2,6 compounds **5a** (12%).[31] Samples of each of the products **2a** and **5a** were collected[13] and identified with authentic samples[2] by comparison of retention times and infrared spectra. The higher boiling fraction [5.24 g, bp 120–155° (0.2 mm)] from the reaction corresponded in retention time[29] to one of the peaks in the chromatogram of the high-boiling by-product from the reaction run in *t*-butyl alcohol. A redistilled sample [bp 140–142° (0.1 mm), $n^{29}D$ 1.4770] has infrared absorption[14] at 1745 and 1710 cm^{-1}

(28) (a) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959); (b) for a number of modifications in the original procedure, see H. O. House and C. G. Pitt, *J. Org. Chem.*, in press.

(29) A gas chromatography column packed with Silicone Gum, No. SE-30, suspended on Chromosorb P was employed for this analysis.

(30) Commercially available from the MSA Research Corp., Callery, Pa.

(31) Fractions of the monoalkylated product from comparable reactions contained (ref 27) 9–23% of the ketone **5a** and 77–91% of the ketone **2a**.

(ester and ketone C=O) with nmr singlets[14] at δ 3.66 (*ca.* 6H, O–CH_3) and 0.97 (*ca.* 3H, CH_3–C–), as well as complex absorption in the region δ 0.9–2.7. These data suggest that this crude product is one or both of the stereoisomers of the keto diester **9**.

From a comparable reaction in which excess ketone (3.5 mmoles of potassium *t*-butoxide, 36 mmoles of the ketone **1**, and 10 mmoles of methyl acrylate in 30 ml of 1,2-dimethoxyethane) was added to diminish dialkylation, the proportions[27] of monoalkylated products were 33% of the 2,6 isomer **5a** and 67% of the 2,2 isomer **2a**. The gas chromatographs[27,29] of the total crude products exhibited peaks corresponding to the ketone **1** and lower boiling materials, to the keto esters **2a** and **5a**, and to a small amount (<5%) of polyalkylated material.

Reaction of 2-Trideuteriomethylcyclohexanone (14) with Methyl Acrylate.—To a cold solution of 2.075 g (18 mmoles) of the ketone **14** and 1.8 mmoles of potassium *t*-butoxide in 20 ml of *t*-butyl alcohol was added, dropwise and with stirring under a nitrogen atmosphere, 3.60 g (18.3 mmoles) of the 2,6-keto ester **5a** followed by 1.55 g (18 mmoles) of methyl acrylate. After the resulting solution had been stirred for 20 min at 0° and then for 2 hr at room temperature, it was diluted with 2 *N* aqueous hydrochloric acid and subjected to the usual isolation procedure. The fractions from distillation were mixed with weighed quantities of internal standards (*m*-diisopropylbenzene or acenaphthene) and analyzed by gas chromatography employing a column[27] previously calibrated with known mixtures. Fraction I (3.412 g, bp 70–105°) contained the unchanged starting ketone **14** (calculated weight, 1.32 g or 64% recovery) and lower boiling materials. A collected[27] sample of this ketone **14**, identified with the starting material by comparison of retention times and infrared spectra, contained 94% of d_3 species and 6% of d_2 species. Fraction II [2.92 g, bp 92–98° (0.15 mm)] contained[27] the 2,2 isomer **15** (calculated weight, 0.53 g or 41% yield based on unrecovered ketone **14**) and the 2,6 isomer **5a** (calculated weight, 2.02 g or 69% recovery). A collected sample of the 2,2 isomer **15**, which corresponded in retention time to an authentic sample of the ketone **2a**, had infrared absorption[14] at 1745 and 1710 cm^{-1} (ester and ketone C=O), as well as peaks at 2060, 2120, 2150 (shoulder), and 2225 cm^{-1} (C–D stretching), and contained 94% d_3 species and 6% d_2 species. A collected[27] sample of the 2,6 isomer **5a** was identified with an authentic sample by comparison of retention times, infrared spectra, and mass spectra and contained less than 5% (if any) trideuterated species. Fraction III from the distillation [0.721 g, bp 130–145° (0.15 mm)] had infrared absorption (1740 and 1710 cm^{-1}) and a gas chromatographic[29] behavior suggesting that it was one or more of the polyalkylated isomers (*e.g.*, **9**).

Reaction of 2-Methylcyclohexanone (1) with Methyl *cis*-3-Chloroacrylate (17b).—To a solution of 2.83 g (25 mmoles) of the ketone **1** and 51 mmoles of potassium *t*-butoxide in 90 ml of *t*-butyl alcohol was added, dropwise and with stirring under a nitrogen atmosphere, 6.24 g (52 mmoles) of the chloro ester **17b**. The reaction mixture, which rapidly turned dark and heated to boiling, was stirred for 1 min after the addition was complete and then poured into cold 2 *N* aqueous hydrochloric acid and extracted with ether. The ethereal extract was concentrated and a solution of the residue in 50 ml of ethanol was hydrogenated at room temperature and atmospheric pressure over the catalyst from 0.4 g of platinum oxide. After the hydrogen uptake (1380 cc or 61 mmoles) ceased, the reaction mixture was filtered and concentrated under reduced pressure. An ether solution of the residue was washed with aqueous sodium bicarbonate, dried, concentrated, and distilled to separate 1.81 g of material, bp 85–100° (0.1 mm), and 0.41 g of a fraction, bp 100–140° (0.1 mm), which was not characterized further. Only 0.1 g of crude acidic material was recovered from the aqueous sodium bicarbonate washings. The lower boiling fraction[19,27] contained the two stereoisomeric lactones, **29** and **30**, and lower boiling components, but not the keto esters **2a** and **5a**.[32] After adding a weighed sample of acenaphthene (internal standard) to an aliquot of this fraction, the yield of the two lactones, **29** and **30**, was calculated to be 1.62 g (37%), composed of isomer A (22% of the lactone mixture, retention time 23.2 min) and isomer B (78% of the lactone mixture, retention time 32.0 min). A collected[27] sample of lactone isomer A[12] has infrared absorption[14] at 1775 cm^{-1} (γ-lactone C=O) with weak ultraviolet absorption[24] (ε 267 at 227 mμ) and complex nmr absorption[14] in the regions δ 1.1–2.6 (13H, aliphatic C–H) and 0.7–1.1 (3H, CH_3–C). The mass spectrum has a molecular ion peak at *m/e* 168 with abundant fragment peaks at *m/e* 125, 111, 98, 68, 55, and 41.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.24; H, 9.70.

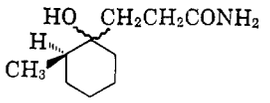
A collected[27] sample of lactone isomer B has infrared absorption[14] at 1775 cm^{-1} (γ-lactone C=O) with weak ultraviolet absorption[24] (ε 127 at 210 mμ) and complex absorption[14] in the region δ 1.1–2.6 (13H, aliphatic C–H) with a doublet (J = 6 cps) at δ 0.87 (3H, CH_3–C). The mass spectrum has a molecular ion peak at *m/e* 168 with abundant fragment peaks at *m/e* 125, 111, 98, 68, 55, and 41.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.80.

From two comparable reactions of the chloro ester **17b** with the ketone **1**, one run without external cooling and one run with ice-bath cooling, the proportions of lactone isomers were 17–18% of isomer A and 82–83% of isomer B.

Reaction with aqueous acid served to interconvert the lactones **29** and **30**. After a solution of 10 mg of lactone isomer A in 5 ml of 50% aqueous sulfuric acid and 2 ml of tetrahydrofuran had been allowed to stand overnight at room temperature, it was diluted with water, neutralized with sodium bicarbonate, and extracted with ether. The crude product recovered from the ether contained[27] 48% of isomer A and 52% of isomer B. Similar treatment of 18.3 mg of lactone isomer B afforded a mixture containing[27] 38% of isomer A and 62% of isomer B. Collected[27] samples from this latter reaction were identified with the previously described samples by comparison of retention times and infrared spectra.

A mixture of 7.7 mg of lactone isomer B and 0.5 ml of concentrated aqueous ammonium hydroxide was allowed to stand at room temperature for 1 week with occasional shaking. The precipitate of the **hydroxyamide 32** was collected as 0.7 mg of white crystals, mp 173–173.5° (lit.[12a] mp 174–176°). This material has broad infrared absorption[33] in the 3600–3400-cm^{-1} region (O–H and N–H) with a band at 1675 cm^{-1} (amide C=O).



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Reaction of 2-Methylcyclohexanone (1) with Methyl Propiolate (16b).—Methyl propiolate (3.75 g, 45 mmoles) in 10 ml of *t*-butyl alcohol was added, dropwise under a nitrogen atmosphere with stirring and external cooling, to a solution of 51 mmoles of potassium *t*-butoxide and 4.85 g (43 mmoles) of ketone **1** in 40 ml of *t*-butyl alcohol. After the addition was complete (10 min), the dark reaction mixture was removed from the ice bath, stirred for an additional 3 min, and then poured into cold 2 *N* aqueous hydrochloric acid. After the ether extract of the resulting mixture had been concentrated, the residue was subjected to the previously described hydrogenation (hydrogen uptake 1250 cc or 56 mmoles) and isolation procedures. Distillation of the crude neutral product afforded 2.01 g of a fraction, bp 85–110° (0.15 mm), and 0.721 g of a higher boiling fraction, bp 110–145° (0.15 mm), which was not characterized further. A weighed sample of acenaphthene (internal standard) was added to an aliquot of the lower boiling fraction; gas chromatographic analysis[27] indicated that the yield of the mixture of lactones **29** and **30** was 12%. The proportions of lactone isomers were 19% of isomer A and 81% of isomer B. No gas chromatographic peaks were observed corresponding to the keto methyl esters **3a** and **5a**.[32] Samples of each of the isomeric lactones were collected[27] and identified with the previously described samples by comparison of retention times and mass spectra.

Reaction of 2-Methylcyclohexanone (1) with Methyl *trans*-3-Chloroacrylate (18b). A. Hydrogenation of the Initial Products.—The chloro ester **18b** (3.66 g, 31 mmoles) was added in the usual way with external cooling to a solution of 2.85 g (26 mmoles) of the ketone **1** and 54 mmoles of potassium *t*-butoxide in 40 ml of *t*-butyl alcohol. The resulting orange mixture was stirred at room temperature for 1 hr and then poured into dilute, aqueous hydrochloric acid. The ether extract of the resulting mixture was washed with aqueous sodium bicarbonate

(32) Since *t*-butyl esters were decomposed and not eluted from the chromatography columns employed, it is possible that *t*-butyl esters corresponding to **2a** and **5a** may have been present.

(33) Determined as a solution in chloroform.

and concentrated. Hydrogenation of a solution of the residue in 50 ml of ethanol at room temperature and atmospheric pressure over 0.2 g of a 5% palladium-on-carbon catalyst[34] resulted in the uptake of 130 ml (28 mmoles) of hydrogen overnight. The resulting mixture was filtered, concentrated, mixed with a weighed amount of internal standard (acenaphthene), and analyzed.[27] The product consisted of 82% of the 2,6 isomer **5a** (calculated yield, 0.70 g, 13%) and 18% of a component believed to be either the 2,2 isomer **2a** or the diester **27** or both. The composition of any *t*-butyl esters (probably present but not eluted from the chromatography column[27]) present in the reaction mixture was not examined. The lactones **29** and **30** were present in the reaction mixture in very small amounts if at all. A collected[27] sample of the 2,6 isomer was identified with an authentic sample by comparison of retention times and infrared spectra. The infrared and mass spectra of a collected[27] sample of the second peak suggested that it was a mixture of the keto ester **2a** and the diester **27**.

B. With 1 Equiv of Base.—A solution of 14.30 g (128 mmoles) of the ketone **1** and 128 mmoles of potassium *t*-butoxide in 100 ml of *t*-butyl alcohol was treated with 15.28 g (127 mmoles) of the *trans*-chloro ester **18b** in the usual way. After the resulting red mixture had been stirred for 5 min, it was subjected to the previously described isolation procedure. An acidic fraction (1.07 g of yellow liquid) was isolated from the aqueous sodium bicarbonate washings and 20.04 g of crude, neutral product was separated from the ether extract. Distillation of the neutral material separated the following liquid fractions: (1) 0.90 g, bp 30–40° (*ca.* 0.1 mm); (2) 4.24 g, bp 90–95° (0.1 mm); (3) 0.54 g, bp 105–115° (0.1 mm); and (4) 7.10 g of dark, high-boiling residue. The first fraction contained[27] primarily the starting ketone **1** (calculated recovery, 5%) accompanied by lesser amounts of the methoxyacrylate ester **21** (calculated yield, 1%) and minor peaks corresponding in retention times to **22** and **23**. The gas chromatogram[27] of fractions 2 an 3 exhibited two peaks. The major peak corresponded to the unsaturated ester **19a** (95% of the peak area, retention time 11.9 min) while the minor peak (5% of the peak area, retention time 19.2 min) is believed to be one or more of the stereoisomers or double bond isomers of the unsaturated ester **20**. A collected[27] sample of the minor peak has broad infrared absorption[13] centered at 1730 cm^{-1} (ester and lactone C=O) with a peak at 1645 cm^{-1} (C=C). A collected[27] sample of the ester **19a** has a broad infrared[14] peak centered at 1725 cm^{-1} (conjugated ester and ketone C=O) with a peak at 1640 cm^{-1} (conjugated C=C) and an ultraviolet maximum[35] at 202 mμ (ε 11,500). The nmr spectrum[14] of the material has two singlets at δ 3.68 (3H, O-CH_3) and 1.18 (3H, C-CH_3) with a pair of doublets (J = 16 cps) at δ 7.02 and 5.66 (2H, *trans* -CH=CH-) and complex absorption in the region δ 1.3–2.5 (8H, aliphatic C-H). The mass spectrum has a molecular ion peak at m/e 196 with abundant fragment peaks at m/e 125, 95, 93, 82, 81, 67, 55, and 41.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.34; H, 8.34.

The infrared spectra[14] of the aforementioned distillation fractions 2 and 3 differed from the spectrum of the collected[27] sample of ester **19a** in having additional bands at 1365 and 1385 cm^{-1}. The nmr spectra[14] of these fractions have an additional singlet at δ 1.45 [$(CH_3)_3C$-O] and an additional pair of doublets (J = 16 cps) at δ 5.55 and 6.92 (*trans* -CH=CH-). These observations indicated that the distilled fractions 2 and 3 contained an unsaturated *t*-butyl ester which was not eluted from the gas chromatograph.[27] To learn the nature of this *t*-butyl ester, a solution of 3.97 g of fraction 2 and 200 mg of anhydrous *p*-toluenesulfonic acid in 50 ml of benzene was refluxed for 4 hr and then diluted with ether and extracted with aqueous sodium bicarbonate. The remaining ethereal layer was dried, concentrated, and distilled to separate 3.13 g of liquid, bp 93–100° (10.1 mm), which had a gas chromatogram comparable with the original fraction but lacked the aforementioned infrared and nmr absorption indicative of a *t*-butyl ester impurity. The acidic fraction (0.44 g of viscous liquid) recovered from the sodium bicarbonate extract has broad infrared absorption[14] in the 3-μ region (associated O-H) with an nmr[14] singlet at δ 1.25 (3H, C-CH_3), a pair of doublets (J = 16.5 cps) at δ 7.25 and 5.73 (2H, *trans* -CH=CH-), a peak at δ 9.07 (1H, -CO_2H), and complex absorption in the region δ 1.4–2.8 (8H, aliphatic C-H). A 169-mg sample of this crude acid was esterified with excess ethereal diazomethane to yield 168 mg of crude neutral product which contained[27] the keto ester **19a** (a collected sample was identified by comparison of retention times and infrared spectra) and a minor unidentified component which was eluted more slowly. Application of this same procedure to 385 mg of distillation fraction 3 afforded 295 mg of a neutral fraction free from the *t*-butyl ester impurity and 119 mg of an acidic fraction which was identified with the acidic fraction of the previous experiment by comparison of infrared spectra. Thus, the *t*-butyl ester impurity is primarily the ester **19b**.

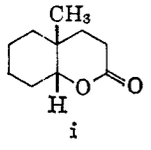
A 280-mg sample of distillation fraction 2 (containing ester **19a** and a minor component thought to be **20** or an isomer, but free of *t*-butyl ester contaminants) in 15 ml of ethanol was hydrogeated at room temperature and atmospheric pressure over 70 mg of a 5% palladium-on-carbon catalyst. After the hydrogen uptake ceased, the reaction solution was filtered, concentrated, mixed with a weighed sample of acenaphthene (internal standard), and analyzed.[27] The crude product contained a mixture (calculated yield 93%) of the 2,2 isomer **2a** (97% of the mixture) and the 2,6 isomers **5a** (3% of the mixture). Collected[27] samples of the esters **2a** and **5a** were identified with authentic samples by comparison of retention times and infrared spectra.

The 1.07-g fraction of the acidic material isolated from the original Michael reaction was extracted with boiling petroleum ether (bp 30–60°) to extract 0.11 g of crude *trans*-3-chloroacrylic acid, and then the residual acid was esterified with excess ethereal diazomethane. The crude neutral product (0.58 g of yellow liquid) exhibited two partially resolved gas chromatographic[27] peaks, the first of which corresponded to the unsaturated ester **19a**. After an ethanol solution of this crude material had been hydrogenated over a 5% palladium-on-carbon catalyst at room temperature and 1 atm pressure, the crude neutral product was isolated in the usual way. This reduced product exhibited two partially resolved gas chromatographic[27] peaks corresponding in retention times to the keto ester **2a** (eluted second) and the diester **27** (eluted first). The gas chromatographic[27] retention times for the diester and two isomeric keto esters follow: 2,6 isomer **5a**, 21.2 min; diester **27**, 25.0 min; and 2,2 isomer **2a**, 26.0 min.

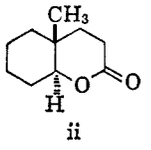
C. With 2 Equiv of Base.—The *trans* ester **18b** (8.72 g, 73 mmoles) was added in the usual way to a solution of 7.14 g (64 mmoles) of the ketone **1** and 130 mmoles of potassium *t*-butoxide in 115 ml of *t*-butyl alcohol. After the orange reaction mixture had been stirred at room temperature for 30 min, it was subjected to the usual isolation procedure to separate 0.51 g of acidic material and neutral products collected as the following distillation fractions: (1) 0.64 g, bp 35–40° (0.1 mm); (2) 3.34 g, bp 100–105° (0.1 mm); (3) 3.79 g, bp 140–165° (0.1 mm); and (4) 1.98 g of residual liquid. After a weighed amount of internal standard (*m*-diisopropylbenzene) had been added to an aliquot of fraction 1, analysis[27] indicated the presence of the following components (calculated yield): ester **21** (0.5%); ester **22** (0.2%); ester **23** (1.2%); a component believed to be ester **24** (0.4%); ester **25** (2.4%); and ester **26** (0.1%). The gas chromatogram[27] of fraction 2 exhibited the following four peaks (retention time): peak A (27.4 min); peak B (29.9 min, only partially resolved from peak A); peak C (36.6 min, the largest peak in the chromatogram); and peak D (44.5 min). Peak A corresponded in retention time to the unsaturated ester **19a**. The infrared and nmr spectra of this fraction and various components collected from it suggested that the material was a complex mixture of methyl and *t*-butyl esters. Consequently, the constituents of this fraction were subjected to the subsequently described chemical transformations before an attempt was made to characterize the components of the mixture.

A solution of 857 mg of distillation fraction 2 in 25 ml of ethanol was hydrogenated (hydrogen uptake 89 ml, 4.0 mmoles) over 0.2 g, of 5% palladium-on-carbon catalyst in the usual way. The crude product recovered from this reaction exhibited gas chromatographic[27] peaks corresponding to the 2,6 isomer **5a**

(34) Attempts to reduce this crude product (containing keto ester **19a**, among other products) over a platinum catalyst resulted in partial reduction of the saturated keto ester **2a** to the corresponding hydroxy esters, which were eluted from gas chromatography as the previously described[2] *cis* and *trans* lactones i and ii.



i



ii

(35) Determined as a solution in *n*-heptane.

(81% of the peak area) and to either the 2,2 isomer **2a** or the diester **27** (19% of the peak area). A collected[27] sample of the major component, the 2,6 isomer **5a**, was identified with an authentic sample by comparison of retention times and infrared spectra. The mass spectrum of a collected[27] sample of the minor component indicated that it was predominantly the diester **27**, accompanied by a small amount of a second component.

A 927-mg sample of distillation fraction 2 was heated with 200 mg of *p*-toluenesulfonic acid in 50 ml of boiling benzene for 4 hr, and then the neutral component (514 mg of yellow oil) and acidic component (270 mg of liquid) were separated as in previous experiments. After the neutral product had been hydrogenated (hydrogen uptake 68 ml, 3.0 mmoles) over a 5% palladium-on-carbon catalyst in the usual way, the crude product contained[27] at least four components. The first two chromatographic peaks were the major components. A collected[27] sample of the first component was identified as the keto ester **5a** by comparison of infrared spectra and retention times. The second peak has a retention time[27] corresponding to the diester **27**; however, this peak could contain both the diester **27** and the keto ester **2a** since these two materials were only partially resolved by the chromatographic column employed.

A portion of the above acidic fraction (260 mg) in ethanol solution was hydrogenated over 0.1 g of a 5% palladium-on-carbon catalyst in the usual manner, and the crude reduction product (150 mg) was esterified with excess ethereal diazomethane. The resulting neutral product exhibited two gas chromatographic[27] peaks corresponding in retention time to the diester **27** (minor component eluted first) and the 2,2 isomer **2a** (major component eluted second). A collected[27] sample of the major component was identified as the keto ester **2a** by comparison of retention times and infrared spectra.

Reaction of the Unsaturated Ester 19a with Potassium *t*-Butoxide.—A solution of 2.07 g (10 mmoles) of the ester **19a** and 20 mmoles of potassium *t*-butoxide in 25 ml of *t*-butyl alcohol was stirred at room temperature and under a nitrogen atmosphere for 1.5 hr. The resulting dark red solution was poured into dilute, aqueous hydrochloric acid and extracted with ether. After the ethereal extract had been dried and concentrated, distillation of the residue (2.81 g of yellow oil) afforded 1.62 g of liquid, bp 115–121° (0.8 mm). Since the infrared[14] (ester C=O at 1730 cm^{-1}) and nmr[14] absorption (intense singlets at δ 1.47) of this crude product suggested that it contained *t*-butyl ester functions, a 1.24-g sample of the distillate was heated with 100 mg of *p*-toluenesulfonic acid in boiling benzene for 4 hr. After the usual isolation procedure the neutral (0.19 g of liquid) and acidic (0.65 g of viscous liquid) fractions were seprated. The neutral fraction, with infrared absorption[14] at 1775 and 1740 cm^{-1}, appeared to be a mixture of lactones and esters and was not investigated further. The initial acid fraction had infrared absorption[14] at 1775 and 1740 cm^{-1} suggesting the presence of lactone and ester functions as well as carboxyl functions (absorption at 1710 cm^{-1}). Consequently, the crude acid fraction was treated with refluxing 25% aqueous sodium hydroxide for 30 min and then acidified with cold, aqueous hydrochloric acid and extracted with ether. The acid recovered from the ethereal extract was a viscous liquid with infrared absorption at 2950 (broad, associated O–H) and 1710 cm^{-1} (carboxyl C=O). A 201-mg sample of this acid was esterified with excess ethereal diazomethane to give the crude neutral product as a yellow liquid [infrared absorption[14] at 1740 (ester C=O) and 1650 cm^{-1} (C=C)] which exhibits three peaks (retention times 26, 32, and 36 min) on gas chromatography.[27] A solution of this crude product in 10 ml of ethanol was hydrogenated at room temperature and 1-atm pressure over 50 mg of 5% palladium-on-carbon catalyst. After 18 hr the hydrogen uptake (40 ml, 1.8 mmoles) ceased, and the crude product (260 mg of liquid) was isolated in the usual way. This material exhibits a single peak on gas chromatography[27] corresponding to the diester **27**. A collected[27] sample of the diester **27** has infrared absorption[14] at 1740 cm^{-1} (ester C=O) with an nmr[14] singlet at δ 3.58 (6H, O–CH_3), a triplet (J = 7 cps) at δ 2.20 (4H, CH_2–CO–), a doublet (J = *ca.* 4 cps with further partially resolved splitting possibly from virtual coupling[36]) at δ 0.88 (3H, C–CH_3), and a complex multiplet in the region δ 1.0–2.0 (9H, aliphatic C–H).[37] The mass spectrum of the diester exhibits no molecular ion peak but has abundant fragment peaks at *m/e* 125, 83, 74, 59, 55, 43, and 41. The highest mass peak in the spectrum was at *m/e* 199 ($M^+ - OCH_3$).

Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.50; H, 9.51.

Enolate Anions from 2-Methylcyclohexanone (1) and Potassium *t*-Butoxide. A. In *t*-Butyl Alcohol.—A solution of 5.65 g (50 mmoles) of the ketone 1 and 51 mmoles of potassium *t*-butoxide in 40 ml of *t*-butyl alcohol was stirred, at room temperature and under a nitrogen atmosphere, for 30 min and then added, dropwise and with stirring, to 50 ml of acetic anhydride. After the reaction mixture had been stirred for 30 min, it was mixed with pentane and cold (5°) aqueous sodium bicarbonate and the resulting mixture was stirred at 5° for 2 hr.[4] The pentane layer was separated, combined with the pentane extract of the aqueous layer, dried, concentrated, and combined with a weighed sample of *m*-diisopropylbenzene (internal standard). The crude product contained[27] the recovered ketone 1 (calculated yield 3.63 g, 64%) and the unresolved mixture of enol acetates **12** and **13** (calculated yield 1.04 g, 13%). A sample of the enol acetate mixture was collected[27] and its composition was estimated from its nmr spectrum[4a] to be *ca.* 78% of **13** and *ca.* 22% of **12**. From a duplicate run, the calculated yields were 64% of ketone 1 and 15% of the enol acetate mixture; the estimated composition of the enol acetate mixture was *ca.* 81% of **13** and *ca.* 19% of **12**.

B. In 1,2-Dimethoxyethane.—A solution of 1.127 g (10 mmoles) of potassium *t*-butoxide[30] and 1.11 g (10 mmoles) of the ketone 1 in 10 ml of 1,2-dimethoxyethane was stirred, at room temperature and under a nitrogen atmosphere, for 30 min and then added, dropwise and with stirring, to 15 ml of acetic anhydride. The resulting mixture was stirred for 30 min and then subjected to the previously described isolation and analysis procedures. The crude product contained[27] the ketone 1 (calculated yield, 325 mg, 29%) and the mixture of enol acetates **12** and **13** (calculated yield, 943 mg, 60%). The composition of the enol acetate mixture was *ca.* 77% of **13** and *ca.* 23% of **12**. In a duplicate experiment where the calculated yields were 29% of ketone 1 and 50% of the enol acetates, the enol acetate mixture contained *ca.* 78% of **13** and *ca.* 22% of **12**.

(36) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

(37) The diester **27** has been reported to boil at 158° (16 mm): H. Stetter and M. Coener, *Chem. Ber.*, **87**, 90 (1954).