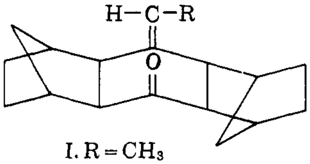
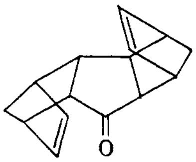
In spite of the numerous assumptions which have had to be made during the execution of the present analysis (the applicability of equation II, the constancy of f_d and the very questionable validity of equations for predicting ν_d and ν_{ct}), it is concluded that Tables IV and V suggest very concretely that there is value in this correlation method. Highly gratifying is the easy accommodation of data for three γ,δ-unsaturated ketones. This observation should help dispel any lingering preference for a hyperconjugation mechanism of interaction. Harmonious also is the data for the highly strained ketone, norbornenone, which, while having a relative small value of S_0, has a large value of ϵ.

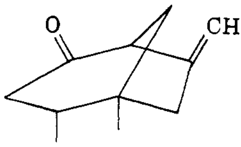
There are instances of difficulty, however. In Table IV the value of $K_{n-\pi}$ for bicyclo[3.2.0]hept-6-en-2-one is low and this is confirmed by the data of the analogous compound in Table V. This discrepancy is probably related, not only to the impossibility of adequate model representation of four-membered rings, but also to a similar failure for five-membered rings. The latter system, seen in models as rigid, is known to be flexible and groups depicted as largely axial are often largely equatorial.[21] Analysis of such substances by observation of bond angles is obviously severely inaccurate.



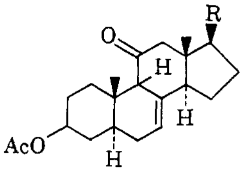
I. R = CH_3
II. R = H



III



IV. Napellonine, partial formula



V. R = C_9H_{17}
VI. R = OAc
VII. R = C_8H_{17}

The only serious problem is found in Table V, substance V. 3-β-Acetoxy-9-β-ergosta-7,22-dien-11-one,[22] represented by Dreiding models as completely rigid, exhibited an absorption band at 295 mμ, (120),[22] values well substantiated by other workers.[23] However, it was also shown by this latter group that the values for compound VII were similar but those for VI were noticeably different (298 mμ, 95.5). Reported also was the high residual absorption of Δ^{22}-3-β-acetoxy-7,8-oxido-11-keto-9-β-ergostene (295 mμ, 42). For construction of Table V, a problem of selection was involved; it was decided that the most unfavorable case should be included. Had there been selected instead substance VI, with the assumption of a background absorption of 42,[24] the calculations would have appeared as follows: VI, *185; 214;* 298 (95.5)—43.5 142.5° 240° 180.7 55.24—0.79. In these substances, V–VII, the size of R may be a factor which influences the relative dispositions of the ketone and olefin groups.

Attention is called to the fact that, unfortunately, all of the compounds discussed in this report have bond angles falling in the region ψ = 90–270° and θ = 60–142°. The treatment therefore makes no comment concerning the validity of I at larger values of S_0. Nor does the favorable report concerning the validity of II carry great weight, since the variations in S_c in the restricted region are comparatively minor.

Acknowledgment.—We wish to thank Professor R.C. Cookson for the many courtesies of his department at Southampton during 1960–1961 and the Research Corporation for financial support during that period. We are also grateful to Professor H. A. Bender for assistance with the most complex program, to S.F. Marsocci for proofreading programs, and to the University of Rhode Island for a summer grant.

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(21) Some earlier literature on this point is given in ref. 10.

(22) P. Bladon, *et al.*, *J. Chem. Soc.*, 2921 (1953).

(23) K. Heusler and A. Wettstein, *Helv. Chim. Acta*, **36**, 398 (1953).

(24) A similar correction would be necessary for a completely successful treatment of compounds I and II.

Potentially Cyclic Difunctional Compounds Containing Substituent Methyl Groups

JAMES CASON AND FRANCIS J. SCHMITZ[1]

Chemical Laboratories, University of California, Berkeley 4, California

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A β,β-dimethyl-δ-keto acid behaves similarly to the unsubstituted compound, in that the acid chloride exists as the cyclic structure, but the pseudo ester could not be obtained. Unsubstituted ε-keto acids gave only the open-chain acid chloride. 2,3-Dimethyl-4-oxo acids, in contrast with the unsubstituted γ-keto acids, exist partly in the cyclic (lactol) form in solution. The cyclic acid chloride may be converted to the pseudo ester, but the pseudo ester is converted to the normal ester with acid catalysis, as in the case of the unsubstituted compounds. Both the acid chloride and pseudo ester crack readily to yield the α,β-unsaturated butenolide (double bond migration), and this butenolide is also obtained readily by treatment of the normal keto ester with methoxide.

In previous publications,[2,3] it has been reported that, although succinyl and glutaryl dichlorides exist as normal open-chain structures, unsubstituted γ- and δ-keto acid chlorides exist only as cyclic structures (chloro lactones), even at 0°. In view of the well recognized tendency of substitution, especially *gem*-disubstitution (the "*gem*-dimethyl effect"), to promote cyclization,[4,5] it is somewhat surprising that the infrared

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[1] Recipient of a National Science Foundation Summer Fellowship, 1960; a U. S. Rubber Co. predoctoral Fellowship, 1959–1960; a Procter and Gamble Co. predoctoral Fellowship, 1960–1961.

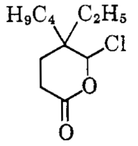
[2] J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1492 (1958).

[3] J. Cason and E. J. Reist, *ibid.*, **23**, 1675 (1958).

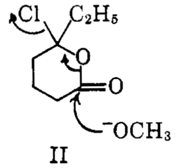
[4] R. F. Brown and N. M. van Gulick, *ibid.*, **21**, 1046 (1956).

[5] N. L. Allinger and V. Zalkow, *ibid.*, **25**, 701 (1960).

spectrum of γ-ethyl-γ-formylcaprylic acid chloride gives a rather clear indication[2] that this compound at room temperature is partly open-chain and partly cyclic (I). The unsubstituted γ- and δ-keto acids, as well as the δ-keto esters were observed only in the open-chain form. The γ-keto esters could be obtained in both normal and cyclic (pseudo) structures, but the pseudo ester was unstable with respect to the normal one. The present investigation is directed primarily towards examining the structures of methyl-substituted compounds, although certain unsubstituted keto acid derivatives are included.



I



II

Further efforts to obtain the pseudo ester of an unsubstituted δ-keto acid, 5-oxoheptanoic acid, have failed; not even traces could be detected by gas chromatography.[6] The pseudo acid chloride (II) no doubt reacts at the carbonyl group to yield the normal ester directly, in contrast with behavior observed[2] in the five-membered ring. This is consistent with the combined observations that attack at the carbonyl group[7] is some twenty to forty times faster in the cyclohexane series than in the cyclopentane series, whereas displacement reactions[8] at a saturated carbon proceed about one hundred times faster in the cyclopentane series.

The effect of *gem*-disubstitution in the δ-keto acid series has been explored by examination of 3,3-dimethyl-5-oxohendecanoic acid, synthesized by an organocadmium reaction with the appropriate ester acid chloride. This acid appears to be entirely in the open-chain form (single carbonyl band in the infrared at 5.86 μ, keto and carboxyl unresolved); however, the acid chloride is entirely in the cyclic form. The latter derivative has a strong carbonyl band at 5.63 μ, whereas γ-carbomethoxy-β,β-dimethylbutyryl chloride absorbs at 5.55 μ (acid chloride) and 5.75 μ (ester). As was the case with the unsubstituted keto acid chloride (II), the *gem*-dimethyl compound was contaminated with some of the enol lactone (infrared absorption at 5.93 μ) resulting from loss of hydrogen chloride from the cyclic acid chloride. Efforts to convert the acid chloride to the pseudo ester resulted in a very sluggish reaction to yield only normal ester. Thus, for the three derivatives examined, the more stable structures are the same for the *gem*-disubstituted and unsubstituted compounds.

Since an ester acid chloride of a dibasic acid will give rearrangements *via* a seven-membered cyclic oxonium ion,[9] two ϵ-keto acid chlorides have been examined. 6-Oxoöctanoyl chloride and 6-oxodecanoyl chloride show absorptions of similar intensity at 5.56 and 5.83 μ, with no absorption in the region (5.70 μ) where the cyclic acid chloride would be expected to absorb.[10]

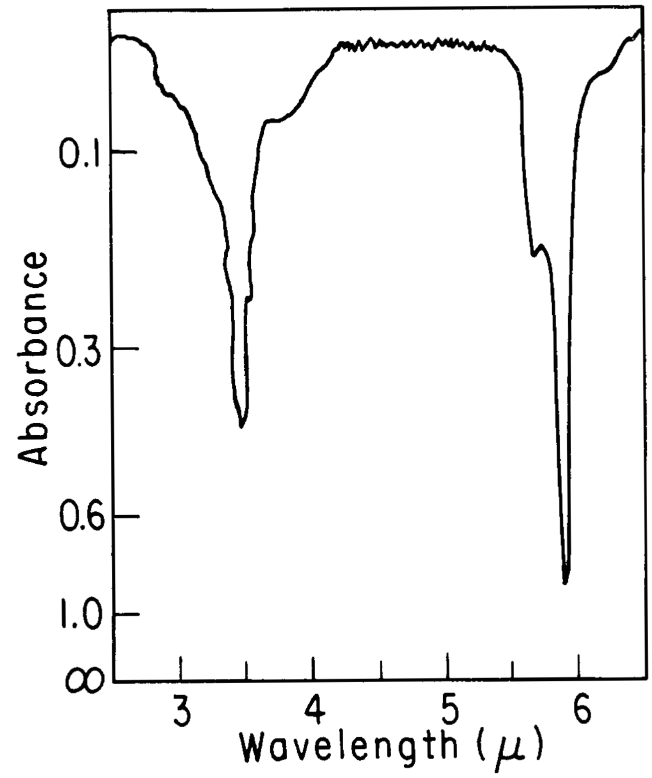


Fig. 1.—Infrared spectrum, in chloroform, of 2,3-dimethyl-4-oxodecanoic acid. Spectra of the stereoisomers[11] were essentially identical. In carbon tetrachloride solution, the band at 5.68 μ becomes a barely detectable shoulder.

The diastereoisomers of a 2,3-dimethyl-4-oxo acid might be expected to show different tendencies towards formation of cyclic structures; however, the isomers appear not to show significant differences[11] in equilibrium ratios of cyclic products. The calculations of Allinger and Zalkow[5] predict that both stereoisomers would be more prone to cyclization than the unsubstituted structure. Methyl 2,3-dimethyl-4-oxodecanoate (mixture of *threo* and *erythro* isomers) was prepared by reaction of dihexylcadmium reagent with the ester acid chloride of *s*-dimethylsuccinic acid, and the keto acid was obtained by hydrolysis of the ester. In contrast with the unsubstituted γ-keto acids, this acid has an infrared spectrum (Fig. 1) which indicates equilibration with a small amount of the pseudo acid (lactol). The absorption at about 5.68 μ, which compares with absorption of the pseudo ester at 5.60 μ, has a lower intensity in carbon tetrachloride than in chloroform. The *threo* and *erythro* isomers of 2,3-dimethyl-4-oxopentanoic and 2,3-dimethyl-4-oxo-hexanoic acids[11] also showed absorption near 5.68 μ.

The 2,3-dimethyl-4-oxodecanoic acid (stereoisomeric mixture) gave a cyclic acid chloride, which, in turn, yielded a pseudo ester, and the latter was converted to the normal ester under acid catalysis. This behavior is similar to that reported[2] for an unsubstituted γ-keto

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(6) The pseudo and normal esters may be separated with ease by gas chromatography. On a 5-ft. DEGS column (diethylene glycol succinate), retention times at 150° for the normal and pseudo esters of levulinic acid were, respectively, 5.5 and 9.0 min. On a 5-ft. silicone grease column at 105°, times for the respective esters of γ-ketocaproic acid were 11.7 and 16.5 min.

(7) H. C. Brown, A. H. Wheeler, and K. Ichihaua, *Tetrahedron*, **1**, 214 (1957).

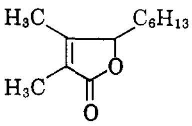
(8) For a summary of pertinent data, *cf.* A. Streitwieser, *Chem. Rev.*, **56**, 667 (1956).

(9) J. Cason and R. D. Smith, *J. Org. Chem.*, **18**, 1201 (1953).

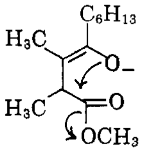
(10) H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6428 (1958), have reported absorption of ϵ-valerolactone at 5.79 μ, in contrast with δ-valerolactone at 5.74 μ; hence, a cyclic ϵ-keto acid chloride would be expected to absorb at about 0.05 μ longer wave length than the δ-keto acid chloride.

(11) The preparation, separation, reactions, and equilibration of the diastereoisomers are the subject of the following paper in this journal.

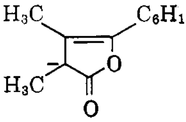
acid; however, presence of the substituents causes facile loss of hydrogen chloride from the acid chloride or methanol from the pseudo ester. The product of this elimination is not the enol lactone, but the Δ^2-butenolide (III) resulting from double bond migration. The structure of the butenolide is assigned on the basis of the infrared absorption at 5.67 μ, the ultraviolet absorption (λ_{max} 213 mμ, ϵ 12,000) which requires α,β-unsaturation,[12] and the n.m.r. spectrum (*cf.* Experimental) which agrees with the assigned structure. It is of interest that the butenolide (III) is also formed readily by treatment of the normal ester of 2,3-dimethyl-4-oxodecanoic acid with sodium methoxide. Although the butenolide might arise *via* the pseudo ester, it seems much more probable that the enol anion (IV) displaces methoxide. Shift of the double bond to the α,β-position would result *via* the resonance stabilized anion, V.



III



IV



V

Experimental[13]

Methyl 3,3-Dimethyl-5-oxohendecanoate.—A Grignard reagent was prepared in an atmosphere of nitrogen from 25.25 g. (0.15 mole) of *n*-hexyl bromide and an equivalent amount of magnesium turnings, with a total of 95 ml. of ether as solvent. As the solution of Grignard reagent was cooled in an ice bath, 0.08 mole of dry, powdered cadmium chloride was added during about 2 min., then the cooling bath was removed and stirring was continued without heating for 5 min., followed by 30 min. under reflux (negative Gilman test for Grignard reagent). Ether was rapidly distilled from this mixture until only a thick paste remained in the flask and distillation had become slow, then 110 ml. of dry benzene was added without delay. After mixing had been effected by vigorous stirring during rapid heating to boiling, the resultant cadmium reagent was cooled to 10° (thermometer in mixture), and there was added during about 2 min. a solution of 0.075 mole of γ-carbomethoxy-β,β-dimethylbutyryl chloride[14] in 25 ml. of dry benzene. When the cooling bath was lowered after completion of addition, the mixture warmed spontaneously and was allowed to rise to a temperature of about 35°, at which point cooling was applied to maintain this temperature. When the reaction was no longer exothermic, the temperature was maintained at 45° for 1 hr., then the mixture was heated under reflux for an additional hour. The reaction mixture was decomposed by addition of ice and 6 *N* sulfuric acid, and the product was extracted with ether. The extracts were washed with water, 0.5 *M* sodium carbonate solution, water, and saturated sodium chloride solution. Keto ester recovered from the dried solution amounted to 14.11 g. (78%), b.p. 113–114.5°/2 mm., n^{25}D 1.4394. The ester was characterized by conversion to the 2,4-dinitrophenylhydrazone of the keto acid (see below).

3,3-Dimethyl-5-oxohendecanoic Acid.—Saponification of the ester yielded the acid as a colorless oil. The 2,4-dinitrophenylhydrazone, crystallized once from aqueous ethanol, had m.p. 126.3–127.2°, unchanged by further crystallization (lit.,[15] m.p. 122°).

Anal. Calcd. for $C_{19}H_{28}O_6N_4$: C, 55.9; H, 6.9; N, 13.7. Found: C, 56.1; H, 6.9; N, 13.9.

3,3-Dimethyl-5-oxohendecanoyl chloride was prepared from 35.5 mmoles of keto acid and 43.1 mmoles of purified thionyl chloride. After the mixture had stood overnight and been warmed at 40° for 3 hr., the thionyl chloride was removed at reduced pressure to leave a viscous residue which exhibited a strong carbonyl band at 5.63 μ, and a weak band at 5.94 μ. Evaporative distillation at 75°/0.3 mm. gave a sample with similar infrared absorption, except that a weak band appeared at 5.85 μ. This latter band is not regarded as resulting from a component of open-chain acid chloride, for no absorption could be detected at 5.55 μ. Presence of enol lactone is indicated by the band at 5.94 μ and chlorine content of only 8.8% (theory for $C_{13}H_{23}O_2Cl$, 14.4%).

Attempted preparation of the pseudo ester of this acid chloride was carried out as previously described for making pseudo esters[16] from keto acid chlorides and methanol in presence of sodium carbonate, except that the very viscous acid chloride was diluted with a small amount of benzene and reaction was continued for 3.5 hr. instead of 0.5 hr. After this extended reaction period, infrared absorption in the carbonyl region showed remaining acid chloride (5.62 μ), as well as normal ester (5.75, 5.83 μ). In a similar run carried out for 5 hr. and using potassium carbonate, the sole product detected by gas phase chromatography was normal keto ester (comparison with synthetic sample previously described).

6-Oxoöctanoic Acid.—Ethyl 6-oxoöctanoate, prepared by the procedure described above from ethyl bromide and ω-carbethoxyvaleryl chloride, was obtained in 54% yield, b.p. 111–112°/5 mm., n^{25}D 1.4319, infrared 5.80, 5.86 μ (carbon tetrachloride); lit.,[17] b.p. 125–127°/12 mm. Saponification yielded the keto acid, which, after recrystallization, had m.p. 51.5–52.0°, infrared 5.88 μ (chloroform); lit.,[17] m.p. 52°.

The acid chloride, prepared with thionyl chloride, had infrared absorption at 5.55, 5.83 μ (carbon tetrachloride), with the bands of about equal intensity or with the band at 5.55 μ somewhat stronger. A sample evaporatively distilled at 86°/1 mm. showed an unchanged infrared spectrum.

6-Oxodecanoic Acid.—Ethyl 6-oxodecanoate, obtained in 79% yield, had b.p. 115–116°/2 mm., n^{21}D 1.4372; lit.,[18] b.p. 125–130°/6 mm. The keto acid, after recrystallization, had m.p. 45–45.5°; lit.,[18,19] 42°, 45–46°.

The acid chloride, prepared as described above, showed infrared absorption at 5.57, 5.87 μ (chloroform), with the longer wave length band of slightly higher density.

Methyl 2,3-dimethyl-4-oxodecanoate was prepared according to the procedure described above from hexyl bromide and the ester acid chloride of *s*-dimethylsuccinic acid,[14] in 62–74% yields, b.p. 114–116°/3 mm., n^{25}D 1.4367–1.4372, infrared 5.77, 5.84 μ (thin film).

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.4; H, 10.5. Found: C, 68.25; H, 10.5.

The keto acid, obtained as an oil by either acid or alkaline hydrolysis of the ester, exhibited the infrared spectrum shown in Fig. 1.

Reaction of 2,3-Dimethyl-4-oxodecanoyl Chloride with Methanol. A. Butenolide III.—The acid chloride was prepared by adding 1.18 ml. (16.4 mmoles) of purified thionyl chloride dropwise during 0.5 hr. to 1.75 g. (9.1 mmoles) of keto acid, then allowing the mixture to stand at room temperature for 4.5 hr. Removal of excess thionyl chloride at reduced pressure left an oil consisting of about equal amounts of the pseudo acid chloride and butenolide III, as shown by the infrared absorption, a split band of about equal intensities at 5.53 and 5.68 μ. This crude product was added dropwise during 0.5 hr. to a rapidly stirred mixture of 1.28 g. (12 mmoles) of sodium carbonate in 5 ml. of methanol. Stirring was continued for an additional 2.5 hr. After addition of 15 ml. of ether and filtration, solvent was removed at reduced pressure to leave 1.5 g. of a product whose carbonyl absorption indicated about equal amounts of pseudo

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(12) D. E. Ames, R. E. Bowman, and T. F. Grey, *J. Chem. Soc.*, 375 (1954), reported for 2,3-dimethyl-Δ^2-butenolide: infrared absorption 5.67 μ; ultraviolet absorption, λ_{max} 213 mμ, ϵ 13,400.

(13) Infrared spectra were determined on an Infracord spectrometer or on a Baird instrument, in 0.1-mm. cells, with chloroform or carbon tetrachloride as solvent. Microanalyses were by the Microanalytical Division, Department of Chemistry, University of California. Unless otherwise specified, all distillations were through a 2-ft. Podbielniak type column with partial reflux head.

(14) J. Cason, G. Sumrell, and R. S. Mitchell, *J. Org. Chem.*, **15**, 856 (1950).

(15) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 494 (1942).

(16) D. P. Langlois and H. Wolff, *J. Am. Chem. Soc.*, **70**, 2624 (1948).

(17) F. Fichter and S. Lurie, *Helv. Chim. Acta*, **16**, 885 (1933).

(18) T. Yoshioka, *J. Pharm. Soc. Japan*, **75**, 606 (1955).

(19) H. E. Holmquist, H. S. Rothrock, C. W. Theobald, and B. E. Englund, *J. Am. Chem. Soc.*, **78**, 5339 (1956).

ester and butenolide (split band of equal intensities at 5.60 and 5.66 μ). Gas phase chromatography under a standard set of reference conditions[20] also showed a 1:1 mixture of butenolide and pseudo ester.

When the equimolar mixture of butenolide and pseudo ester, from above, was distilled through a 2-ft. Podbielniak type column, there was a forerun of 0.136 g., then there was collected 0.745 g. of butenolide, b.p. 119°/1 mm.; infrared absorption at 5.67 μ (very weak absorption at 5.93 μ); in the ultraviolet, $\lambda_{\max}$ 213 mμ, ε 12,000. Combustion analysis of several samples gave persistently low values for carbon; highest values were obtained by slow burning at relatively high furnace temperature.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.5; H, 10.2. Found: C, 72.6, 71.1, 72.6; H, 9.9, 9.5, 10.1.

The n.m.r. spectrum, recorded on a Varian instrument, yielded the following bands:

τ	Relative area	Assignment
9.02 (split)	1	$-CH_3$ (terminal)
8.58 (broad)	3.2	$-CH_2-$
8.12	1	$-CH_3$ (β)
7.93	1	$-CH_3$ (α)
5.64 (split)	0.3	$\underset{\vert}{-CH}-O$

Assignment of the higher field band to the β-methyl is based on the reported investigation[21] of tiglic and related acids.

B. Pseudo Ester.—The acid chloride was prepared as described in method A, except that stirring at room temperature was continued for only 25 min., and the product was stored at 0° until it was added to methanol and sodium carbonate. After reaction had continued for only 0.5 hr. with methanol, the mixture was diluted with ether and worked up as before (without distillation) to give a 55% yield of an oil with an infrared band at 5.60 μ. Gas chromatographic analysis[20] showed the material to be about 75% pseudo ester, about 2% normal ester, and about 15% butenolide. There was a small band at about 35.5 min. which has not been identified.

Rearrangement of the pseudo ester was carried out by heating a 58-mg. sample of material prepared as above at 40° for 4 hr. with 1.5 ml. of a 10% solution of sulfuric acid in methanol. The reaction mixture was diluted with ether, washed with water, and dried. Removal of solvent left an oil (55 mg.) which showed carbonyl absorption at 5.76, 5.83 μ, with a shoulder at 5.67 μ. Gas chromatographic analysis[20] showed only two bands, one at 27 min. (normal ester) containing about 90% of the area, and a small band at 41 min. (butenolide III).

Butenolide III from Normal Ester.—A solution of 100 mg. of methyl 2,3-dimethyl-4-oxodecanoate was prepared in carefully dried methanol which was approximately 1 *N* in sodium methoxide. After this mixture had been heated at 45° for 3 hr. in a nitrogen atmosphere, it was cooled in an ice bath and the pH was reduced to about 5.5 with dry methanol which was about 2 *N* with anhydrous hydrogen chloride. The mixture was then diluted with about 25 ml. of dry ether, sodium chloride was removed by filtration, and solvent was removed at reduced pressure to leave 82 mg. of an oil, which was shown by gas chromatography[20] to consist of about equal amounts of starting material (normal ester) and butenolide III. No other bands were observed. This mixture was easily separated by gas chromatography at 200° on a 15-mm. i.d. × 3-m. column containing 30% high vacuum silicone grease dispersed on Chromosorb P. Fractions collected were 33 mg. of starting material (infrared spectrum and gas chromatography) and 34 mg. of butenolide III (infrared and ultraviolet spectra, gas chromatography).

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[20] For analysis of the mixtures encountered in these reactions, chromatography was carried out at 130° on a 1/4 in. × 5 ft. column of 10% high vacuum silicone grease dispersed on 40–60 mesh Chromosorb P, with helium flow rate of 70 ml./min. Under these conditions, retention times were as follows: normal ester, 27 min.; pseudo ester, 33 min.; butenolide, 41 min. On some occasions, material in bands was collected and identity checked by use of the infrared spectrum.

[21] R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

Epimerization of s-Dimethylsuccinic Acids and Derivatives. Cadmium Reactions on the Ester Acid Chlorides

JAMES CASON AND FRANCIS J. SCHMITZ[1]

Chemical Laboratories, University of California, Berkeley 4, California

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Convenient methods are described for securing *meso* and *racemic* s-dimethylsuccinic anhydrides, whose purity may be verified by gas phase chromatography. The isomeric anhydrides may be converted to isomerically pure half esters and diesters. Epimerization does not occur at a significant rate under acidic conditions. The half esters may be converted to ester acid chlorides, with 10–15% epimerization, as determined by conversion of the ester acid chlorides to diesters, whose composition may be determined by gas chromatography. The ester acid chlorides are slowly epimerized on standing at room temperature, to yield an equilibrium mixture of the diastereo isomers containing slightly more than half of the *threo* isomer. Equilibration of the s-dimethylsuccinic acids by heating with hydrochloric acid also gives equilibration slightly in favor of the *racemic* form (same geometry as *threo* form). Reaction of either isomeric ester acid chloride with dihexylcadmium reagent yields a keto ester of the same geometry as was the ester acid chloride, with little or no epimerization. Separation of isomeric keto esters by gas chromatography was possible only in the case of the methyl ketones; however, structure could be determined by Baeyer–Villiger oxidation of the keto esters and transesterification to the dimethyl s-dimethylsuccinates. Ratio of secondary to primary alkyl migration, in oxidation with perfluoroperacetic acid, was only 2:1. Catalytic or chemical reduction of the isomeric keto esters yielded mixtures of four lactones, separable into three bands in gas chromatography. Structures were assigned to the two lactones appearing as single components of two of the chromatography bands, on the basis of origins of the lactones, relative rate of formation from the hydroxy acids, and isomers related by epimerization.

In view of the considerable enolization noted in reaction of α-chloro acid chlorides with organocadmium reagents,[2] it has been presumed that epimerization at the α-position is likely to occur in ketone syntheses utilizing the cadmium reagents. For example, in the preparation of optically active α-phenylethyl methyl ketone,[3] it was suggested that the highly variable amount of racemization observed (0–90%) occurred during reaction of hydrotropyl chloride with dimethylcadmium reagent. It was not determined, however, whether racemization might be occurring during preparation and/or storage of the acid chloride. Such equili-

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[1] Recipient of a National Science Foundation Summer Fellowship, 1960; a U. S. Rubber Co. predoctoral Fellowship, 1959–1960; a Procter and Gamble Co. predoctoral Fellowship, 1960–1961.

[2] J. Cason, *J. Am. Chem. Soc.*, **68**, 2078 (1946).

[3] K. Mislow and J. Brenner, *ibid.*, **75**, 2318 (1953).