

Reactions Proceeding by Bicyclic Mechanisms in Acyclic Systems¹

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Pyrolysis of derivatives of 4-benzoylbutanoic acid (1), 4-benzoyl-4,4-dimethylbutanoic acid (2), 4-benzoyl-3,3-dimethylbutanoic acid (3), 4-benzoyl-2,2-dimethylbutanoic acid (4), and 4-hexahydrobenzoylbutanoic acid (1c) have been studied. The mixed anhydrides with methylcarbonic acid (1_{MA}–4_{MA}) yielded pseudo methyl esters (1_{PE}–4_{PE}) and unsaturated lactones (1_{UL}, 3_{UL}, 4_{UL}) on pyrolysis. The 1-ethoxyvinyl esters (1_{VE}–4_{VE}, 1_{OVE}) yielded mainly unsaturated lactones. Since 2_{VE}, 3_{VE}, and 4_{VE} required higher temperatures for pyrolysis than did 1_{VE}, the *gem*-dimethyl effect is retarding on the [4.2.2] bicyclic mechanism proposed to account for the formation of the unsaturated lactones. Treatment of 1_{VE} in methylene chloride with boron fluoride etherate afforded a small yield of δ -(carboethoxymethyl)- δ -phenyl- δ -valerolactone (1_{LE}). All of the δ -keto acids yielded only normal methyl esters on acid-catalyzed esterification.

Certain reactions may occur by intramolecular bicyclic mechanisms involving [3.2.1],^{2–5} [3.3.1],^{6,7} and [4.2.2]⁷ paths. Since the examples studied in the cases of the [3.3.1] and [4.2.2] paths involved ortho-substituted aromatic compounds, the present study was undertaken not only to see if compounds in which the functions involved were in an acyclic chain would undergo similar reactions, but also to provide additional examples of new reactions of the above types.

The acids studied were 4-benzoylbutanoic acid (1), 4-benzoyl-4,4-dimethylbutanoic acid (2), 4-benzoyl-3,3-dimethylbutanoic acid (3), and 4-benzoyl-2,2-dimethylbutanoic acid (4). The *gem*-dimethyl acids were chosen because we wished to see if the *gem*-dimethyl effect, which usually facilitates ring closures involving the formation of five- and six-membered rings, would exert a similar effect in reactions involving bicyclic paths.

The reactions chosen for study were: pyrolysis of the mixed anhydrides of each of these acids with methyl carbonic acid (CH₃COOH); and pyrolysis of the 1-ethoxyvinyl esters. These reactions were picked because of previous studies in the cases of *o*-(α,α -dimethylphenacyl)benzoic and *o*-benzoyl- α,α -dimethylphenylacetic acids.^{6,7} Of additional interest was the question as to whether normal or pseudo methyl esters would be formed on acid-catalyzed esterifications of the keto acids.^{8,9}

Acids 1 and 3 were prepared by Friedel–Crafts condensation of glutaric and β,β -dimethylglutaric anhydrides with benzene. Acids 2 and 4 were prepared as shown in Scheme I. The mixed anhydrides of the acids with methylcarbonic acid were prepared in high yields as described,³ as were the ethoxyvinyl esters.¹⁰

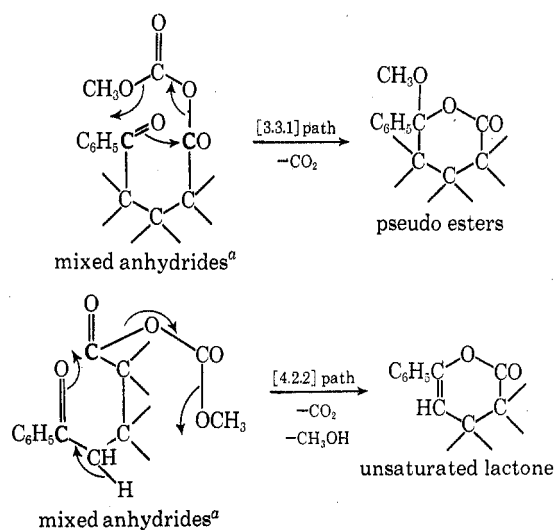
On pyrolysis at 150°, the mixed anhydrides of the acids (1_{MA}, 2_{MA}, 3_{MA}, and 4_{MA}) gave mixtures of the pseudo esters (1_{PE}, 2_{PE}, 3_{PE}, and 4_{PE}) and the unsaturated lactones (1_{UL}, 3_{UL}, and 4_{UL}) in the amounts listed in Table I, except that 2_{MA} gave only 2_{PE} as the un-

TABLE I
PYROLYSIS^a OF MIXED ANHYDRIDES

Compd	Substituents ^b			PE ^c [3.3.1]	UL ^d [4.2.2]
	γ	β	α		
1 _{MA} ^e	H	H	H	91	5
2 _{MA}	CH ₃	H	H	98	
3 _{MA}	H	CH ₃	H	62	28
4 _{MA}	H	H	CH ₃	71	20

^a All pyrolyses were carried out in glass flasks which had been carefully washed and then steamed for 15–20 min before drying. The yields indicated in the table are isolated yields (see Experimental Section). ^b Two groups as indicated are present at each position. ^c PE represents pseudo ester. ^d UL represents unsaturated lactone. ^e MA represents the mixed anhydride of the acid involved with methyl carbonic acid.

saturated lactone of 2 cannot exist. As in previous cases^{3,5–7} formation of the pseudo esters may be explained by postulating a [3.3.1] bicyclic path and the unsaturated lactones by a [4.2.2] path as shown below.¹¹



^a In all formulas depicting bicyclic paths, the bridgehead carbons are those which have thicker lines. The 2, 3, and 4 carbons are substituted with CH₃ or H as required. The arrows pointing from the π bond of the ketonic carbonyl does not mean necessarily that only the electrons in the π cloud are involved. The unshared electrons on the carbonyl oxygen may be involved.

In the present cases pseudo esters were produced simultaneously with loss of carbon dioxide both at low

(11) A bicyclic mechanism is defined as a cyclic mechanism in which the atoms involved in bonding change are not continuously joined.

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(1) This research was supported by Grant 6262-C from the U. S. Army Research Office, Durham, N. C.

(2) M. S. Newman and C. Courduvelis, *J. Amer. Chem. Soc.*, **86**, 2042 (1964).

(3) M. S. Newman and C. Courduvelis, *ibid.*, **88**, 781 (1966).

(4) M. S. Newman, N. Gill, and B. Darre, *J. Org. Chem.*, **31**, 2713 (1966).

(5) M. S. Newman and L. K. Lala, *ibid.*, **32**, 3225 (1967).

(6) M. S. Newman and S. Mladenovic, *J. Amer. Chem. Soc.*, **88**, 4523 (1966).

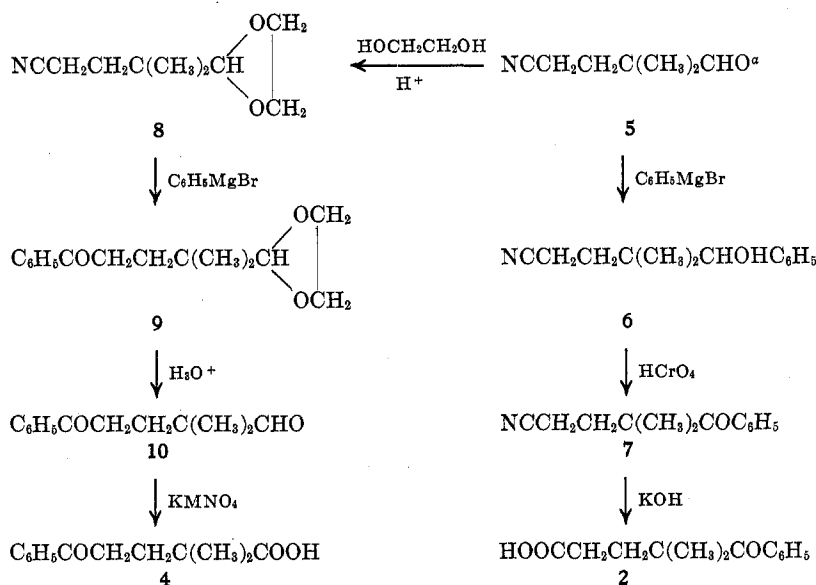
(7) M. S. Newman, S. Mladenovic, and L. K. Lala, *ibid.*, **90**, 747 (1968).

(8) M. S. Newman and C. W. Muth, *ibid.*, **73**, 4627 (1951), and references therein.

(9) M. S. Newman and C. Courduvelis, *J. Org. Chem.*, **30**, 1795 (1965).

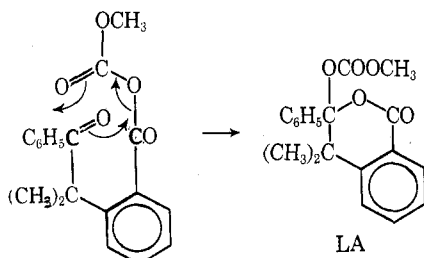
(10) H. H. Wasserman and P. S. Wharton, *J. Amer. Chem. Soc.*, **82**, 1411 (1960).

SCHEME I



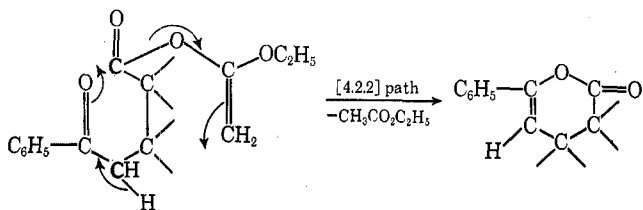
^a We thank the Eastman Kodak Co. for a generous gift of Ibanitrile, 4-cyano-2,2-dimethylbutanal (5).

(ca. 100°) and high (ca. 150–200°) temperatures. These results contrast with those in previous studies^{3,7} in which reaction by two competing bicyclic paths occurred. At low temperatures (50–100°) rearrangement of the acyclic mixed anhydride to lactonic anhydrides (e.g., LA) took place, whereas at higher temperatures the acyclic mixed anhydrides rearranged to pseudo esters directly with loss of carbon dioxide. Although we



ran no kinetic studies on the presently reported reactions, qualitative experiments showed no great difference in the rates of reaction of the parent mixed anhydride as compared to the *gem*-dimethyl ones. Thus, the *gem*-dimethyl effect to facilitate cyclization reactions does not appear of importance in these reactions.

On pyrolysis of the 1-ethoxyvinyl esters **1_{VE}**, **2_{VE}**, **3_{VE}**, and **4_{VE}** no lactone esters were obtained; rather, the unsaturated lactones **1_{UL}**, **3_{UL}**, and **4_{UL}**, were formed in the amounts listed in Table II. The formation of unsaturated lactone on pyrolysis undoubtedly proceeds by the [4.2.2]bicyclic path shown.



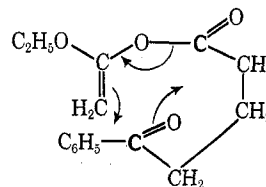
On allowing solutions of the esters, **1_{VE}**–**4_{VE}**, in methylene chloride containing boron fluoride etherate to stand at room temperature for 18 hr, cyclization to un-

TABLE II
PYROLYSIS^a OF 1-ETHOXYVINYL ESTERS^b AND
ACID-CATALYZED REARRANGEMENT^c

Compd	Substituents			UL ^d	NPA ^e	LE ^f
	γ	β	α			
1_{VE} ^g	H	H	H	38 ^g (60)	61	(28)
2_{VE}	CH ₃	H	H		88 (95) ^h	
3_{VE}	H	CH ₃	H	65 ⁱ (93)		
4_{VE}	H	H	CH ₃	85 (86)		
1_{CVE}	H	H	H	81 (94)		

^{a, b} Same as *a*, *b* in Table I. ^c All experiments were run in methylene chloride for 18 hr with a small amount of boron fluoride etherate as catalyst. The numbers in parentheses represent the yields of product obtained in the acid-catalyzed runs. ^d UL represents per cent of unsaturated lactone isolated. ^e NPA represents per cent of normal pseudo anhydride isolated. ^f LE represents per cent of lactone ester isolated. ^g Estimated from the amount of **1** obtained on acidification of a sodium carbonate extract of reaction mixture. ^h Normal normal anhydride as determined by the uv absorption (ethanol) at 238 mμ (log ε 4.18), 273 (3.17), whereas the normal methyl ester absorbs at 238 mμ (log ε 3.80), 273 (2.77). ⁱ In addition, 34% of **3** was isolated.

saturated lactones occurred (see Table II). A 28% yield of **1_{LE}** was obtained from **1_{VE}**. These experiments were carried out because 1-ethoxyvinyl levulinate has been converted to *γ*-carbethoxymethyl-*γ*-valerolactone in this way.¹² This reaction probably involves a [3.3.1]bicyclic mechanism as shown.



When the reaction of **1_{VE}** with boron fluoride was allowed to proceed in ether a 90% yield of **1_{UL}** was obtained and no **1_{LE}**. Thus, the effect of solvent on the

rearrangement of 1-ethoxyvinyl ethers may be of interest.

Heating the esters at 150° for 1 hr showed that 1_{VE} was more reactive than 2_{VE} and 4_{EV} as the latter two were from 40 to 60% unchanged, whereas the former had disappeared completely. Hence the *gem*-dimethyl group exerts a retarding effect on these cyclization reactions. Molecular models indicate that a steric effect is responsible. However, discussion of this factor should await the results of kinetic measurements. The results are listed in Table II.

For the pyrolytic conversion of mixed anhydrides and ethoxyvinyl esters into the unsaturated lactones a route involving (a) enolization of the ketonic function, (b) addition of the enolic hydroxyl across the carbonyl group of the carbonyl derived from the acid function (either in the vinyl ester or the mixed anhydride), and (c) elimination of ethyl acetate (or CO₂ and CH₃OH) by a six-atom cyclic mechanism to form the unsaturated lactone is possible. Since pyrolysis of the normal methyl esters of acids 1 and 4 at 150° for 4 hr yielded only the starting ester, we do not believe that the enolization path is followed. Similarly, the normal methyl ester of 1 was recovered unchanged after standing for 18 hr at room temperature in methylene chloride containing boron fluoride etherate.

1-Ethoxyvinyl γ -cyclohexyl- γ -oxobutanoate (1_{CVE}) was heated at 200° for 30 min to give only the unsaturated lactone 1_{CUL} in 81% yield. Thus the cyclohexyl group, as compared to the phenyl group, favors the reaction which proceeds by the [4.2.2] path (see results for 1_{VE} and 1_{CVE} in Table II).

Only normal methyl esters were obtained when the acids, 1, 2, 3, and 4, were refluxed with methanol and hydrogen chloride for 4 hr. Nmr and ir examination of the entire reaction product showed that within the spectroscopic limits of the instruments no pseudo methyl esters were present. The purest pseudo methyl esters were formed by pyrolysis of the mixed anhydrides above mentioned. When the acid chlorides of 1, 2, 3, and 4 were treated with methanol saturated with urea,¹³ mixtures of about 10–20% normal and 80–90% pseudo methyl esters were obtained.

Experimental Section¹⁴

4-Benzoylbutanoic acid (1), mp 125–126°, was prepared in 75% yield as described.¹⁵

4-Benzoyl-3,3-dimethylbutanoic acid (3), mp 58.0–59.5°, was prepared in 95% yield as described¹⁶ except that the acid was isolated by crystallization from benzene–hexane and was not distilled.

4-Benzoyl-4,4-dimethylbutanoic Acid (2).—To the cooled (0–10°) Grignard reagent prepared from 126 g of bromobenzene,

(13) M. S. Newman and L. K. Lala, *Tetrahedron Lett.*, 3267 (1967). See an earlier missed reference to the use of urea as a base: C. Bodenco, R. K. Allison, and P. H. Dirstine, *Ind. Eng. Chem.*, **43**, 1196 (1951).

(14) All melting points are uncorrected and were taken with standardized thermometers. Analyses by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Infracord. Identity of known compounds was always established by spectral comparisons and mixture melting point determinations. The phrase "worked up as usual" means that an ether–benzene solution of the products was washed with aqueous acid and/or alkali and saturated sodium chloride solution, and was filtered through anhydrous magnesium sulfate. The solvents then were removed on a rotary evaporator and the residue was treated as described. All experiments were repeated at least one time. All key compounds reported gave ir and nmr spectra consistent with the assigned structures.

(15) L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 81.

(16) A. T. Blomquist and F. Jaffe, *J. Amer. Chem. Soc.*, **80**, 3405 (1958).

18.6 g of ethylene dibromide,¹⁷ and 24 g of magnesium in 800 ml of ether was added a solution of 100 g of Ibanitrile (Eastman Kodak Co.) (5) in 400 ml of ether. A solid separated immediately. The mixture was then heated at reflux for 2 hr, cooled, and treated with dilute hydrochloric acid. After the usual work-up there was obtained 170 g of a yellow oil, bp ca. 170° (3.5 mm). On trituration with ether the oil partly solidified. The solid was recrystallized from ethanol to yield 25 g (12%) of a compound, mp 100–102°, undoubtedly 2,2-dimethyl-1,5-diphenyl-1,2-dihydropyran as judged by the nmr spectrum and elemental analysis. No further work was done with this compound. The analytical sample, mp 102.0–102.5°, was obtained by recrystallization from ethanol.

Anal. Calcd for C₁₃H₂₀O: C, 86.4; H, 7.6. Found: C, 86.6; H, 7.8.

The remaining product was distilled to yield 140 g (86%) of 4,4-dimethyl-5-hydroxy-5-phenylpentanonitrile (6), bp ca. 130° (0.05 mm).

Anal. Calcd for C₁₃H₁₇NO: C, 76.8; H, 8.4; N, 6.9. Found: C, 76.7; H, 8.4; N, 6.8.

A mixture of 30.0 g of 6, 30 g of potassium dichromate, and 300 ml of 10% sulfuric acid was held at reflux for 2 hr. After the usual work-up there was obtained 27.0 g (91%) of 4-benzoyl-4,4-dimethylbutanonitrile (7) as a pale yellow oil, bp ca. 140° (0.7 mm).

Anal. Calcd for C₁₃H₁₅NO: C, 77.6; H, 7.5; N, 7.0. Found: C, 77.6; H, 7.5; N, 6.9.

A solution of 30 g of 7 in 300 ml of 6% aqueous–ethanolic potassium hydroxide was refluxed for 4 hr. The solvent was then removed on a rotary evaporator. An aqueous solution of the residue was extracted with ether and acidified. After dissolving the acid in ether–benzene, the usual work-up afforded 26.5 g (81%) of crude 2. On vacuum distillation there was obtained 25.0 g (76%) of 2 as a colorless viscous oil, bp ca. 145° (0.1 mm).

Anal. Calcd for C₁₃H₁₆O₃: C, 70.9; H, 7.3. Found: C, 71.2; H, 7.5.

4-Benzoyl-2,2-dimethylbutanoic Acid (4).—A solution of 125 g of 5 (Eastman Kodak Co.) and 62 g of ethylene glycol in 100 ml of toluene containing 2 g of toluenesulfonic acid was refluxed into a small column topped by a phase-separating head. After 3 hr, 19 ml of water layer had separated and the usual work-up afforded an oil which on distillation yielded 163 g (96%) of the acetal 8, bp ca. 87° (1.2 mm).

Anal. Calcd for C₉H₁₆NO₂: C, 63.9; H, 8.5. Found: C, 63.7; H, 8.5.

To the Grignard reagent prepared from 63 g of bromobenzene and 9 g of ethylene dibromide in 500 ml of ether was added at 15–20° a solution of 42.3 g of 8 in 250 ml of ether. After stirring at 25° for 3 hr the mixture was treated with dilute hydrochloric acid and worked up as usual. Distillation afforded an oil, bp 140–145° (0.6 mm), which solidified. Recrystallization from hexane yielded 50.5 g (82%) of 9 as colorless plates, mp 47–48°.

Anal. Calcd for C₁₅H₂₀O₃: C, 72.6; H, 8.1. Found: C, 72.5; H, 8.1.

A solution of 49.6 g of 9 in 50 ml of dioxane, 50 ml of water, and 50 ml of concentrated HCl was refluxed for 2 hr. After the usual work-up distillation yielded 35.4 g (85%) of 10 as a pale yellow oil, bp ca. 112° (0.2 mm). The analysis indicated a hemihydrate but the ir spectrum had bands at 6.05 and 5.85 μ (benzoyl and aldehyde, respectively, and at 3.75 aldehyde CH). The analytical sample may have become exposed to moisture.

Anal. Calcd for C₁₃H₁₆O₂· $\frac{1}{2}$ H₂O: C, 73.2; H, 8.0. Found: C, 73.1; H, 7.9.

To 30.0 g of 10 cooled in an ice bath was added 120 ml of saturated KMnO₄ solution during 1 hr. The mixture was stirred overnight and acidified with sulfuric acid. The manganese dioxide was destroyed by slow addition of sodium bisulfite. The usual work-up yielded 24.2 g (75%) of 4 which on recrystallization from benzene–hexane yielded 22.0 g (68%) of pure 4 as colorless needles, mp 119–120°, not depressed by mixing with a sample of 4 prepared as described¹⁸ in 21% yield by the condensation of benzene with α,α -dimethylglutaric anhydride.

4-Hexahydrobenzoylbutanoic acid (1c), mp 57–58°, was prepared essentially as described.¹⁹ In one attempt to react

(17) D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

(18) E. Rothstein and W. G. Schofield, *J. Chem. Soc.*, 4566 (1965).

(19) J. English, Jr., and J. E. Dayan, *J. Amer. Chem. Soc.*, **72**, 4187 (1950).

cyclohexylmagnesium chloride in ether with glutaric anhydride, no 1c was obtained.

Preparation of Mixed Anhydrides with Methylcarbonic Acid.—These anhydrides were prepared essentially as described^{8,7} from the acids and methyl chlorocarbonate and Dabco²⁰ except that methylene chloride was used in place of ether as solvent. All were obtained as oils in essentially quantitative yields. The nmr spectra were in complete agreement with theory and the oils were used in the pyrolytic experiments directly. By low temperature crystallization from benzene-hexane, 1_{MA} was obtained in one case as colorless crystals, mp 35–36°. Because of instability during drying analytical results were not satisfactory.

Preparation of Ethoxyvinyl Esters.—Esters 1_{VE}, 2_{VE}, 3_{VE}, 4_{VE}, and 1_{CV} were made essentially as described³ using ethoxyacetylene²¹ in methylene chloride and were obtained in almost quantitative yield. All of the vinyl esters were obtained as oils except 1_{VE}, mp 39–40°, which was obtained in 95% yield on low temperature crystallization from chloroform-hexane.

Anal. Calcd for C₁₅H₁₈O₄: C, 68.7; H, 6.9. Found: C, 68.7; H, 6.8.

The oily vinyl esters gave nmr and ir spectra in complete agreement with theory but analyses were off except in the case of 4_{VE}. These esters could not be distilled under reduced pressure without decomposition.

Anal. Calcd for C₁₇H₂₂O₄: C, 70.3; H, 7.6. Found: C, 70.4; H, 7.3.

Pyrolytic Experiments.—All pyrolyses were carried out in small weighed flasks which had been well washed and then steamed for 20 min before drying. In many larger scale experiments the loss in weight on pyrolysis agreed well with that predicted from the amount of unsaturated lactone as determined by nmr analysis of the products. For the vinyl esters the =CH₂ band at about δ 3.8 was present in the quartet at about δ 3.7–4.1 due to the methylene group in the OCH₂CH₃ group. When unsaturated lactone was formed a triplet at about δ 5.7 appeared because of the vinylic hydrogen present. For the mixed methylcarbonic anhydrides the OCH₃ singlet at about δ 3.75 was used to estimate the amount of starting mixed anhydride present. For the pseudo methyl esters formed the OCH₃ singlet was in the δ 3.5–3.6 range. The amount of unsaturated lactone was again estimated by the triplet at about δ 5.7. Any methanol which formed was removed by applying a vacuum until no further loss in weight occurred.

The above facts were used in preliminary experiments to estimate the rates at which reaction was occurring. The information thus gained was used to determine the conditions for the larger scale runs, the results of which are reported in Tables I and II. Small scale pyrolyses under similar conditions were run at least twice for each compound and the nmr spectra of the mixtures produced used to determine the per cent of the compounds formed. These agreed well with the per cent isolated in the larger runs.

Pyrolysis of Mixed Anhydrides.—After heating 12.30 g of 1_{MA} at 150° for 1 hr the mixture was taken into ether-benzene and extracted with sodium carbonate solution. On acidification 0.50 g (5%) of 1, mp and mmp 125–126°, was obtained. This represents the amount of 1_{UL} present in the pyrolysate. From the neutral portion was obtained 9.3 g (91%) of 1_{PE}, mp 125–126°, having satisfactory ir and nmr spectra (OCH₃, s, δ 3.55).

Anal. Calcd for C₁₂H₁₄O₃: C, 69.9; H, 6.8. Found: C, 69.8; H, 6.6.

On heating 2.75 g of 2_{MA} at 150° for 1 hr there was obtained 2.30 g (98%) of 2_{PE}, bp ca. 120° (0.3 mm) (OCH₃, s, δ 3.60). After heating 11.10 g of 3_{MA} at 150° for 1 hr the mixture was taken into ether-benzene and extracted with sodium carbonate solution. After acidification of the alkaline extract there was obtained 2.50 g (28%) of 3, melting point not depressed by mixing with an authentic sample. Distillation of the neutral fraction yielded 5.86 g (62%) of 3_{PE}, as a colorless oil, bp ca. 110° (0.3 mm) (OCH₃, s, δ 3.50). After heating 5.60 g of 4_{MA} at 150° for 1 hr, there were obtained (as above) 0.88 g (20%) of 4, melting point not depressed with an authentic sample, and 3.30 g (71%) of 4_{PE} as a colorless oil, bp ca. 108° (0.3 mm). Recrystallization of this distillate (which solidified) from hexane afforded 4_{PE} as colorless needles, mp 47–48°, OCH₃ singlet at δ 3.60.

Anal. Calcd for C₁₄H₁₈O₃: C, 71.8; H, 7.7. Found: (2_{PE}) C, 71.9; H, 7.4; (3_{PE}) C, 72.2; H, 7.8; (4_{PE}) C, 71.5; H, 7.6.

Pyrolysis of Ethoxyvinyl Esters.—The products of pyrolysis in the case of 1_{VE} (12.6 g) were separated by a sodium carbonate extraction of an ether-benzene solution of the reaction mixture. From the neutral fraction was obtained 5.4 g (61%) of 1_{NPA} as colorless prisms, mp 103–104°.

Anal. Calcd for C₂₂H₂₂O₅: C, 72.1; H, 6.0. Found: C, 72.1; H, 5.9.

This anhydride absorbed at 242 mμ (log ε 3.87) and at 280 (2.81) in ethanol. Since normal ethyl 4-benzoylbutanoate absorbs at 242 mμ (log ε 4.10) and 278 (3.03) and pseudo ethyl 4-benzoylbutanoate absorbs at 245 mμ (log ε 3.24), we assign the *n*, *ψ*-anhydride structure to 1_{NPA}.

Acidification of the carbonate extract yielded 3.5 g (38%) of 1, mp 125–126°, undepressed on mixing with an authentic sample. The amount of acid 1 is equivalent to the amount of unsaturated lactone as the latter is converted quantitatively to the corresponding ketoacid on treatment with sodium carbonate solution.

On heating 5.0 g of 2_{VE} at 200° for 1 hr, bulb-to-bulb distillation [130–135° (0.002 mm)] afforded 3.2 g (88%) of a colorless liquid which analyzed correctly for an anhydride of 2.

Anal. Calcd for C₂₆H₃₀O₅: C, 73.9; H, 7.1. Found: C, 74.0; H, 7.2.

After pyrolysis of 3.2 g of 3_{VE} at 220° for 1.5 hr careful distillation yielded 1.5 g (65%) of 3_{UL}, bp 115–120° (0.5 mm), and 0.8 g (34%) of 3, bp 150–160° (0.5 mm). A sample of 3_{UL} was converted into 3 by treatment with sodium carbonate solution.

Anal. Calcd for C₁₃H₁₄O₂: C, 77.2; H, 6.9. Found: C, 77.1; H, 6.9.

On pyrolysis of 5.2 g of 4_{VE} at 200° for 1 hr only 4_{UL}, bp ca. 134° (0.3 mm), was obtained (85%) as a colorless oil: ir 5.62, 5.9 μ; nmr (in CCl₄ with TMS as internal standard at δ 0.0) δ 1.28 (s, 6 H, (CH₃)₂C), 2.37 (d, 2 H, CH₂CH=), 5.75 (t, 1 H, CH=C), 7.5 (m, 5 H, ArH), which solidified on standing. Recrystallization from hexane yielded 4_{UL}, mp 73–74°.

Because of great sensitivity to moisture, an elemental analysis within 0.3% of the theoretical values for C and H was not obtained. However, on treatment with water quantitative conversion to 4 resulted.

The pyrolysis of ethoxyvinyl 4-hexahydrobenzoylbutanoate (1_{CV}) required somewhat higher temperatures than did that of 1_{VE}. After pyrolysis of 9.75 g of 1_{CV} at 200° for 30 min, there was obtained 8.0 g (81%) of 1_{CVL}, bp ca. 91° (0.3 mm), as a colorless oil.

Anal. Calcd for C₁₁H₁₀O₂: C, 73.3; H, 8.9. Found: C, 73.3; H, 9.2.

On hydrolysis, 1c was obtained in essentially quantitative yield.

Acid-Catalyzed Esterification.—On refluxing in excess methanol containing HCl for 3 hr all of the acids, 1, 2, 3, and 4, were converted into their normal methyl esters in over 95% yield. The properties were as follows: 1_{NE},^{22,23} bp ca. 133° (1.5 mm),²³ OCH₃ singlet, δ 3.65; 2_{NE}, bp ca. 126° (0.5 mm), OCH₃ singlet, δ 3.60; 3_{NE},¹⁶ bp ca. 135° (1.0 mm), OCH₃ singlet, δ 3.65; 4_{NE}, bp ca. 130° (1.1 mm), OCH₃ singlet, δ 3.75.

Anal. Calcd for C₁₄H₁₈O₃: C, 71.8; H, 7.7. Found: (2_{NE}) C, 72.0; H, 7.4; (4_{NE}) C, 71.7; H, 7.6.

Boron Fluoride Etherate Catalyzed Reactions.—Samples of the 1-ethoxyvinyl esters of 1, 2, 3, 4, and 1c were dissolved in 5 ml/g of freshly distilled dry methylene chloride and a few drops of boron fluoride etherate added. After standing at room temperature for 18 hr the solvent was distilled and the residue carefully fractionated in a small Claisen flask under reduced pressure. The amounts of unsaturated lactones produced were obtained as low boiling component and are recorded in Table II. Under similar conditions methyl γ -benzoylbutanoate was recovered unchanged. The anhydride, 2_{NPA}, and lactone-ester, 1_{LE}, were higher boiling.

δ -(Carboethoxymethyl)- δ -phenyl- δ -valerolactone (1_{LE}).—A redistilled sample of 1_{LE}, bp 130–133° (0.001 mm), was analyzed.

Anal. Calcd for C₁₅H₁₈O₄: C, 68.7; H, 6.9. Found: C, 68.7; H, 6.9.

After refluxing 1_{LE} in ethanol containing HCl the crude hydroxy diester formed lost water on attempted distillation. The unsaturated ester formed was reduced catalytically over palladium

(20) We thank the Houdry Process Co., Marcus Hook, Pa., for a generous sample of Dabco, 1,4-diazabicyclo[2.2.2]octane.

(21) The ethoxyacetylene was used as obtained from the Farchan Research Laboratories, Willoughby, Ohio 44094.

(22) 1_{NE}, etc., means normal methyl ester.

(23) R. Levine and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1768 (1944).

on carbon to yield diethyl 3-phenylpimelate, bp 145–150° (0.5 mm), in high yield. The same ester was synthesized by a Reformatsky condensation of ethyl bromoacetate with ethyl 4-benzoylbutanoate to the expected hydroxy diester (86% yield). This ester was dehydrated and reduced as above to yield diethyl 3-phenylpimelate, identical by ir and nmr analysis with that of the product obtained from 1_{LE}.

Anal. Calcd for C₁₇H₂₄O₄: C, 69.9; H, 8.2. Found: C, 70.2, 70.3; H, 8.4, 8.4.

3-Phenylpimelic Acid.—Alkaline hydrolysis of the above ester followed by acidification afforded 3-phenylpimelic acid, bp 180–183° (0.004 mm) (bath temperature), in high yield.

Anal. Calcd for C₁₃H₁₆O₄: C, 66.1; H, 6.8. Found: C, 66.2; H, 7.1.

The above acid on treatment with thionyl chloride gave the diacid chloride. Upon reaction of the crude diacid chloride in tetrahydrofuran with liquid ammonia the diamide, mp 152–153°,

ir bands at 3.0, 6.08 μ (broad), was obtained in high yield after recrystallization from alcohol-benzene.

Anal. Calcd for C₁₃H₁₈N₂O₂: N, 12.0. Found: N, 11.8.

Registry No.—1_{MA}, 20633-23-2; 1_{VE}, 20633-26-5; 1_{PE}, 20633-25-4; 1_{NPA}, 26366-16-5; 1_{CUL}, 4055-00-9; 1_{LE}, 20678-81-3; 2, 2938-68-3; 2_{NE}, 20633-40-3; 3_{UL}, 26366-19-8; 3_{PE}, 20633-29-8; 4_{UL}, 26366-21-2; 4_{NE}, 20633-63-0; 4_{VE}, 26366-23-4; 4_{PE}, 20633-31-2; 6, 20633-33-4; 7, 4412-28-6; 8, 20633-35-6; 9, 20633-36-7; 10, 13544-27-9; 2,2-dimethyl-1,5-diphenyl-1,2-dihydropyran, 26372-49-6; diethyl 3-phenylpimelate, 26372-50-9; 3-phenylpimelic acid, 26372-51-0; 3-phenylpimelic acid diamide, 26372-52-1.

Preparation and Reactions of Siloxanylpropanals

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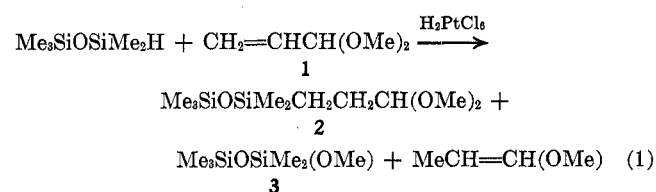
Received May 18, 1970

1,1,3,3-Tetramethyldisiloxane or pentamethyldisiloxane with 3,3-dimethoxypropene in the presence of chloroplatinic acid formed mostly the 3,3-dimethoxypropyl along with the corresponding 2,2-dimethoxy-1-methylethyl adducts. Hydrolysis of the former afforded the corresponding siloxanylpropanals. Hydrolysis of the latter caused cleavage of the Si-C bond to form siloxanes and propionaldehyde.

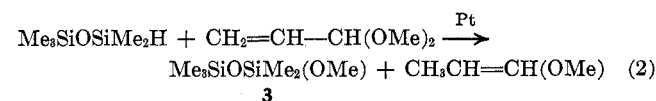
Silanes of the formula R¹R²R³SiH add to acetals of acrolein with platinum catalysts to form R¹R²R³SiCH₂CH₂CH(OR)₂.^{1,2} However, no aldehydes have been prepared from these acetals and characterized except for 3-triethylsilylpropanal² and 3-diethylmethylsilylpropanal.³ We wished to prepare compounds having siloxane structures substituted with propanal groups and to study the chemistry of the aldehyde group in such molecules.

Results and Discussion

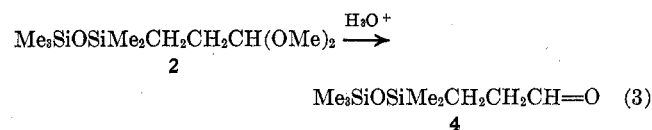
Pentamethyldisiloxane and acrolein dimethylacetal (1) gave (3,3-dimethoxypropyl)pentamethyldisiloxane (2) along with methoxypentamethyldisiloxane (3) and 1-methoxypropene (eq 1).



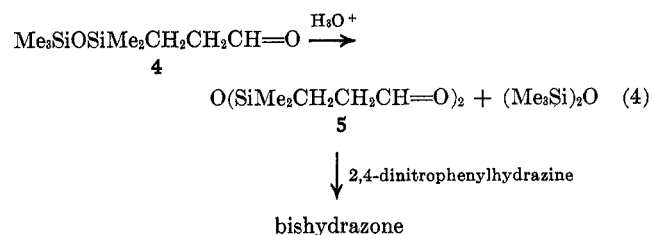
The formation of 1-methoxypropene and 3 probably occurred by a route shown by eq 2 analogous to that reported for the formation of propene and silicon tetrachloride from allyl chloride and trichlorosilane.⁴



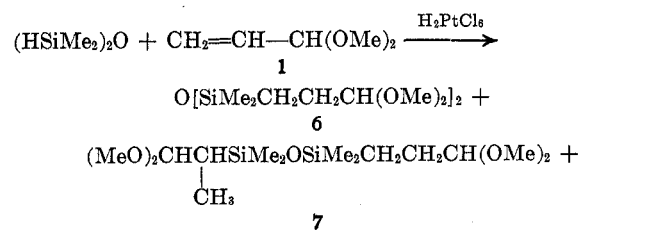
Hydrolysis of 2 gave 3-pentamethyldisiloxanylpropanal (4) (eq 3).



Treatment of 4 with acidic aqueous ethanolic 2,4-dinitrophenylhydrazine gave the bis-2,4-dinitrophenylhydrazone of *sym*-tetramethyldisiloxanedipropional (5) (eq 4).



sym-Tetramethyldisiloxane and 1 gave *sym*-bis(3,3-dimethoxypropyl)tetramethyldisiloxane (6) and six other compounds by glc analysis (eq 5). One of these



compounds was 1-methoxy-3-(3',3'-dimethoxypropyl)-tetramethyldisiloxane which was obtained in 10.5% yield. The formation of this compound was expected in light of the formation of 3 during the addition of pentamethyldisiloxane. The five other minor compo-

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