[Contribution from the Chemical Laboratories of the University of California]

Reactions of Glutaryl Dichloride with Organometallic Reagents[1]

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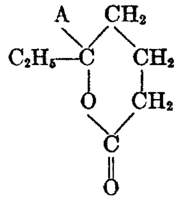
The infrared spectrum of glutaryl dichloride indicates that the substance is largely or entirely in a normal open-chain form. Reactions of glutaryl dichloride with diethylcadmium or with ethylmagnesium bromide yield products consistent with the view that this di-acid dichloride is of open-chain structure, but δ-ketoenanthyl chloride is of a cyclic structure (δ-chloro-δ-enantholactone). Formation of small amounts of 3,7-nonanedione in the cadmium reaction (in contrast with no yield of diketone in the cadmium reaction with succinyl dichloride) indicates the lesser stability of the six-atom ring with exocyclic double bond; also, δ-ethyl-δ-enantholactone was found to equilibrate readily with the isomeric γ- or δ-unsaturated acid. The striking preference of keto acid chlorides for the cyclic structure, however, is illustrated by the fact that the principal product of the Grignard reaction at 0° was found to be the cyclic δ-ketoenanthyl chloride, a result analogous to that obtained with succinyl dichloride. Grignard reactions, either with or without ferric chloride, could not be carried out satisfactorily below about −20° on account of precipitation of complexes; however, results at −20° indicated operation of the same factors observed in reactions of succinyl dichloride at −40°.

Investigation[2] of the reactions of succinyl dichloride has shown that the products may be formulated on the basis of the view[3] that this diacid dichloride is a normal open-chain structure but γ-keto acid chlorides rapidly form a cyclic structure (γ-chloro-γ-lactone), even at temperatures as low as 0°. The present report is concerned with the structure and reactions of glutaryl dichloride, wherein the cyclic structures would have six-membered rings, a form less favored[4] than the five-membered ring in instances where there is an exocyclic double bond.

The infrared spectrum of glutaryl dichloride was found to exhibit a single carbonyl band at 5.60 μ, the normal location for a low molecular weight acid chloride and that observed[3] for succinyl dichloride. There was no indication of a second carbonyl band which might be ascribed to a cyclic form of the acid chloride. Quantitative determination of carbonyl absorption by glutaryl dichloride, calculated per mole of carbonyl present in the open-chain form, gave values in excellent agreement with those[3] for caprylyl chloride and pimelyl dichloride; however, the quantitative values are of little direct utility in supporting the open-chain structure of glutaryl dichloride, on account of the high absorption of a cyclic acid chloride with a six-membered ring. Whereas an open-chain acid chloride, such as caprylyl chloride, exhibits an ϵ_{max} of about 370, the cyclic δ-ketoenanthyl chloride (I) has λ_{max} at 5.65 μ, with ϵ_{max} of about 900. In view of this strong absorption at 5.65 μ in structure I, however, it does follow that absence of a second absorption band in glutaryl dichloride indicates little, if any, of the cyclic structure.



I, A = Cl
II, A = OC_2H_5 (not isolated)
III, A = C_2H_5

Reaction with diethylcadmium. Examination of the products obtained in the cadmium reaction with glutaryl dichloride, as summarized in Table I, reveals two differences from the results with succinyl dichloride.[2] Succinyl dichloride yielded none of the open-chain dione, and the principal product was keto ester, partly the cyclic pseudo ester (five-membered ring analogous to formula II). These differences are consistent with the greater ease of formation of cyclic products with the five-atom ring. Failure of the ester to result in significant amounts may be ascribed to involvement of the cyclic transition state previously suggested,[2] for the ends of a five-atom chain are in position to cyclize with greater frequency than are the ends of a six-atom chain. For example,[5] δ-chlorosulfides and δ-chloroamines cyclize to the heterocycles at a rate seventy to seventy-five times faster than do the corresponding ε-chlorosulfides and ε-chloroamines. In addition, cyclic compounds involved in the present instance would contain the carbonyl group, and correlations developed in connection with the concept of I-strain[4] have shown the exocyclic double bond to be less favored in the case of six-atom rings. By the same token, if there is involved in the cadmium reaction with δ-ketoenanthyl chloride the previously proposed[2] cyclic transition state shown in two resonance forms in IV, reaction to give the open-chain 3,7-nonanedione would be more favored when the cyclic product (lactone III) has the six-membered ring. Although the yield of dione from glutaryl dichloride is low, no

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[1] This investigation was supported in part by a research grant (E-86) from the National Institutes of Health, U. S. Public Health Service.

[2] J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1668 (1958).

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

[4] H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

[5] G. M. Bennett, F. Heathcoat, and A. N. Mosses, *J. Chem. Soc.*, 1929, 2567; H. Freundlich and A. Krestovnikov, *Z. Physik. Chem.*, **76**, 79 (1911).

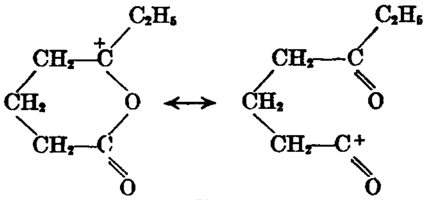
dione could be isolated in the cadmium reaction with succinyl dichloride.[2]

TABLE I

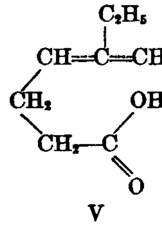
YIELDS[a] IN REACTIONS OF GLUTARYL DICHLORIDE WITH ORGANOMETALLIC REAGENTS

Compounds Isolated	Yield[b] from Diethyl-cadmium	Yield from Ethyl-magnesium Bromide		
		0°	−20°	−20°, $FeCl_3$
δ-Ethyl-δ-enantholactone[c] (III)	15–20%	11%	14%	17%
δ-Ketoenanthyl chloride[d] (I)	30–40	50	24	17
3,7-Nonanedione[e]	6–10	*ca.* 6	*ca.* 14	*ca.* 18
3-Ethylnonan-3-ol-7-one[a]	—	*ca.* 5	*ca.* 8	*ca.* 7

[a] Yield figures are approximate in all instances, for they were determined from isolation, and in some instances the isolations were troublesome. Yields preceded by *ca.* are subject to an additional uncertainty, in that mixtures of dione and hydroxy ketone were analyzed by infrared spectroscopy. Identity of the hydroxy ketone was not established with certainty. [b] Range of yields in the cadmium reaction is that observed in different runs. No yield of ethyl δ-ketoenanthate is indicated, although minor amounts of this ester were probably obtained (*cf.* Experimental). Considerable quantities of cyclic acid chloride were recovered in the cadmium reaction because the reaction was continued for only 2.5 hr. at 40°, with no additional heating under reflux as was done in reactions of succinyl dichloride reported separately.[2] This procedure was adopted in order to demonstrate the presence of the cyclic acid chloride as an intermediate. [c] Isolated in part as the isomeric unsaturated acid. [d] Isolated as δ-ketoenanthic acid, after hydrolysis. [e] Isolated in part as the cyclic aldol product, 2-methyl-3-ethyl-2-cyclohexenone.



IV

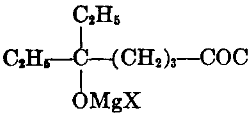


V

The persistence of the cyclic acid chloride (I), even when the six-atom ring is involved, attests the remarkable preference of the keto acid chlorides for the cyclic structure. In the instance of the 5-atom rings,[2] where the cyclic structure for the keto acid chloride was the only form encountered, the cyclic pseudo ester (analogous to II) was unstable with respect to the normal ester, in presence of acid. When the methods used for preparation of the pseudo esters of γ-keto acids were applied to δ-ketoenanthyl chloride (I), no pseudo ester could be isolated; the product exhibited the infrared spectrum of the normal ester. This result was not entirely unexpected on account of the failure to isolate ester from the cadmium reaction.

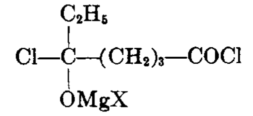
The lesser stability of six-atom rings caused some difficulty in isolation and characterization of δ-ethyl-δ-enantholactone (III), in both cadmium and Grignard reactions. Equilibration occurs between the lactone and the isomeric γ- or δ-unsaturated acid (V) in presence of mineral acid or during long heating in fractional distillation. By extraction with sodium carbonate, acid and lactone could be separated. Careful washing of the two components and rapid distillation yielded pure samples of acid showing a single carbonyl band at 5.87 μ and of lactone showing a single carbonyl band at 5.79 μ. The reported[6] region for carbonyl absorption in δ-lactones is about 5.75 μ.

Reactions with ethylmagnesium bromide. In the Grignard reaction at 0° with succinyl dichloride, the dominant formation (only product in yield greater than about 5%) of the cyclic form of γ-ketocaproyl chloride was attributed to the very rapid cyclization of the open-chain form of this acid chloride. With glutaryl dichloride, the cyclic keto acid chloride (I) remained the principal product; however, the yield of other products became about twice that observed with succinyl dichloride. This indicates occurrence of the predicted lower rate of cyclization of the open-chain form of δ-ketoenanthyl chloride. Reaction of the open-chain keto acid chloride at the acid chloride grouping would lead initially to 3,7-nonanedione, while reaction at the keto group (more reactive than the acid chloride) would give structure VI as the initial product. Direct cyclization of this intermediate would lead to lactone III, while further reaction of the acid chloride grouping would lead to the hydroxy ketone, which was present in small amount.



$$C_2H_5-\underset{OMgX}{\overset{C_2H_5}{C}}-(CH_2)_3-COCl$$

VI



$$Cl-\underset{OMgX}{\overset{C_2H_5}{C}}-(CH_2)_3-COCl$$

VII

In the Grignard reaction with succinyl dichloride, a dramatic drop in yield of cyclic acid chloride was observed when the reaction temperature was lowered to −40°. Mechanical difficulties (precipitation of unstirrable sludges) prevented lowering the temperature below about −20° in the case of glutaryl dichloride; so the change in products was less pronounced; however, even at −20°, there is observed a significant decrease in yield of cyclic acid chloride, and a proportional increase in products resulting from reaction of either the initial reaction intermediate, VII, or the open-chain keto

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(6) E. E. van Tamelen and M. Shamma, *J. Am. Chem. Soc.*, 76, 2315 (1954).

acid chloride. Thus, stabilization of the intermediate VII is indicated (for discussion of this point refer to ref. 2).

Failure to secure a significant increase in the yield of 3,7-nonanedione in presence of anhydrous ferric chloride is ascribed to the inability to secure a sufficiently low reaction temperature (−70° has been previously recommended[7]); however, a small increase in yield of dione was observed.

As was the case in the reactions of succinyl dichloride, the only procedure of preparative significance is the Grignard reaction at 0°. This probably constitutes the most convenient preparation of γ- and δ-keto acids, respectively.

EXPERIMENTAL[8]

Glutaryl dichloride. Although it has been reported[9] that glutaryl dichloride may be prepared in 80% yield by treatment of glutaric acid with a fivefold excess of thionyl chloride, our maximum yield was about 68% and large amounts of glutaric anhydride were obtained. The use of catalytic amounts of pyridine, found essential in the preparation of succinyl dichloride,[3] gave excellent results.

(*A*) *Without pyridine.* A mixture of 100 g. (0.76 mole) of glutaric acid and 300 ml. (3.8 moles) of thionyl chloride was heated under reflux for 2.5 hr. After the excess thionyl chloride had been removed under reduced pressure the product was fractionated at 7 mm. pressure to yield 61 g. (47%) of glutaryl dichloride, b.p. 89°, and 40 g. (46%) of glutaric anhydride, b.p. 138°, m.p. 52°, no depression in melting point on admixture with an authentic sample of glutaric anhydride.

(*B*) *With pyridine catalyst.* A mixture of 40 g. (0.3 mole) of glutaric acid, 0.5 ml. of pyridine, and 120 ml. (1.5 moles) of thionyl chloride was heated under reflux for 3 hr. Distillation yielded 43 g. (84%) of glutaryl dichloride, b.p. 92–93°/10 mm.

Reaction of diethylcadmium with glutaryl dichloride. According to the procedure described[2] for reaction of diethyl cadmium with succinyl dichloride, a cadmium reagent was prepared *via* the Grignard reagent from 100 g. (0.84 mole) of distilled ethyl bromide and allowed to react with 40 g. (0.24 mole) of glutaryl dichloride. Reaction time was 2.5 hr. at 40°.

After decomposition of the reaction mixture by addition of ice and extraction of the aqueous phase with three portions of ether, the combined organic phases were washed first with water, then stirred overnight[10] with 450 ml. of saturated aqueous sodium carbonate solution. The sodium carbonate extract was acidified and extracted with four portions of ether. Removal of ether left a yellow solid which was recrystallized from ether–petroleum ether to yield 10 g. (29%) of white δ-ketoenanthic acid, m.p. 48.0–48.5°, no depression in melting point on admixture with an authentic sample[3] of δ-ketoenanthic acid.

The neutral material remaining after carbonate extraction was fractionated to yield the following fractions.

Fraction	Weight, g.	B.P. (10 mm.)
1	2.03	75–115°
2	1.79	115–125°
3	6.68	125–130°
4	2.15	(column stripped)

Ethyl δ-ketoenanthate would boil near 110° at this pressure, but no significant constant-boiling fraction was noted during distillation of Fraction 1.

Fraction 2, which solidified on standing, was recrystallized from hexane to yield white 3,7-nonanedione, m.p. 53.0–53.5° (literature,[11] m.p. 53°).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.13; H, 10.33. Found: C, 69.32; H, 10.44.

The infrared spectrum exhibited a narrow intense carbonyl band at 5.84 μ.

The *bisdinitrophenylhydrazone* of the diketone was prepared by a common method.[12] This derivative was so insoluble that it was purified by heating under reflux for 1 hr. in 95% ethanol, then filtering the product from the hot solution and washing with hot ethanol, m.p. 183–184°.

Anal. Calcd. for $C_{21}H_{24}N_8O_8$: C, 49.03; H, 4.68; N, 21.69. Found: C, 48.96; H, 4.90; N, 22.24.

Fractions 3 and 4 did not yield any pure components, even after refractionation; so they were combined and heated under reflux for 3 hr. with 50 ml. of 10% aqueous sodium hydroxide. Neutral material was extracted from the cooled alkaline solution with three portions of ether, and the ether extracts were washed with water. Evaporation of ether left 0.37 g. of residue whose infrared spectrum exhibited bands at 5.88 and 6.03 μ and was identical with the spectrum of the aldol product obtained by treating 3,7-nonanedione with alkali.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.29. Found: C, 78.83; H, 10.62.

The ultraviolet spectrum had λ_{max} at 244.5 mμ, ε 10,450. For 2-methyl-2-cyclohexenone (one less substituent on the double bond), there has been reported[13] λ_{max} 234 mμ, ε 9,660.

The semicarbazone, prepared by a usual procedure,[12] had m.p. 213.5–214° (dec.).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.30; H, 9.20; N, 21.38.

The alkaline solution, from which the cyclic ketone was extracted, was acidified and heated briefly, to yield a mixture of lactone III and the isomeric unsaturated acid. From this mixture a pure sample of lactone was obtained, while a pure sample of unsaturated acid was obtained in the Grignard reaction at 0° (see below).

The mixture of lactone and acid was extracted with ether, and the acid was re-extracted into aqueous sodium carbonate solution. The ether solution of *lactone* was washed twice with water and dried, then ether was evaporated and the lactone distilled to yield 2.10 g. of colorless liquid, b.p.

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(7) W. C. Percival, R. B. Wagner, and N. C. Cook, *J. Am. Chem. Soc.*, **75**, 3731 (1953).

(8) Melting points are corrected and boiling points are uncorrected. Distillations, unless otherwise specified, were through a half-meter column of the simple Podbielniak design which has been described in detail (J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., New York, 1950, p. 237). Infrared spectra were recorded on a Baird double beam spectrophotometer. Microanalyses are by the Microanalytical Division, Department of Chemistry, University of Calif.

(9) S. Skraup and S. Guggenheimer, *Ber.*, **58**, 2493 (1925).

(10) In another run, the organic extract was shaken in a separatory funnel with four successive portions of saturated aqueous sodium carbonate solution, then stirred overnight with an additional portion of carbonate solution. Work-up of the first four extracts yielded about two-thirds of the keto acid, while the remaining third was recovered from the overnight extraction.

(11) E. E. Blaise, *Compt. rend.*, **173**, 314 (1921).

(12) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, 1948, pp. 170, 171.

(13) E. W. Warnhoff and W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 494 (1953).

123°/10 mm., n_D^{25} 1.4614, single carbonyl band in the infrared spectrum at 5.79 μ.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.13; H, 10.33. Found: C, 69.19; H, 10.52.

Acidification of the carbonate extract of the lactone solution yielded 4 g. of colorless liquid, b.p. 130°/9 mm., n_D^{25} 1.4552. This index of refraction indicates a lactone content of about 30%, and the infrared spectrum indicates a mixture of lactone and acid.

Reaction of ethylmagnesium bromide with glutaryl dichloride. (*A*) *At 0°.* In a procedure parallel to that described for the reaction of succinyl dichloride,[3] reactants were 0.5 mole of distilled ethyl bromide, 0.5 g.-atom of magnesium turnings and 0.25 mole of glutaryl dichloride. Reaction time at 0°, after completion of addition, was 2 hr.

After the reaction mixture had been decomposed with ice and 12*N* sulfuric acid, the aqueous layer was separated and then extracted with three portions of ether. After the combined organic phases had been washed with water, they were stirred overnight with 450 ml. of saturated aqueous sodium carbonate solution. The material recovered from the carbonate extract, after acidification, proved to be a mixture of lactone III, unsaturated acid V, and δ-ketoenanthic acid. This mixture was distilled until there had been removed a top fraction of b.p. 98–140°/6 mm., weight 2.0 g., whose infrared spectrum was characteristic of the mixtures of lactone III and acid V frequently encountered in this investigation. The distillation residue, weight 16.0 g., solidified on cooling; crystallization from ether–petroleum ether yielded white crystals of m.p. 48.0–48.5°, no depression in melting point on admixture with an authentic sample of δ-ketoenanthic acid.

Fractional distillation of the neutral material remaining after carbonate extraction yielded no homogeneous components except for 1.5 g. of δ-ketoenanthic acid;[14] so the recombined fractions were heated under reflux for 3 hr. with 80 ml. of 10% aqueous sodium hydroxide. The products of alkali treatment were separated by the procedure described above under the cadmium reaction to yield 4.0 g. of ketonic material, b.p. 100–110°/18 mm.; 0.5 g. of lactone III; and 1.9 g. of the mixture of lactone III and unsaturated acid V, b.p. 120–121°/5 mm., n_D^{25} 1.4548.

The lactone-acid mixture (1.9 g. described above) was shaken out with a mixture of saturated aqueous sodium carbonate solution and ether, and the carbonate layer was carefully acidified to Congo Red with 12*N* sulfuric acid, then extracted with three portions of ether. The ether extracts were washed twice with water, dried over magnesium sulfate, then distilled to yield 1.0 g. of pure *unsaturated acid* (V), b.p. 117–118°/4.5 mm., n_D^{25} 1.4522, single carbonyl band in the infrared at 5.87 μ.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.13; H, 10.33; equiv. wt., 156. Found: C, 69.13; H, 10.31; equiv. wt., 153.

The ketonic material (4.0 g. described above) obtained in this reaction and other Grignard reactions exhibited an infrared spectrum which indicated a mixture of 2-methyl-3-ethyl-2-cyclohexenone (aldol product from 3,7-nonanedione) with about an equal amount of a saturated ketone. Repeated fractionation of this material yielded a product, b.p. 96–98°/10 mm., containing only small amounts of the cyclohexenone (as characterized by the intense infrared band at 6.03 μ). The infrared spectrum of this material was quite similar to that of 3,7-nonanedione except that the relative intensity of the carbonyl band at 5.84 μ was less and there was a weak broad band at 2.8 μ, characteristic of the hydroxyl group. The substance was inert to boiling 10% aqueous sodium hydroxide. Characterization of this material as 3-ethylnonan-3-ol-7-one seems reasonably safe, and further verification was not sought since its positive identification is not significant to the objectives of the present investigation.

(*B*) *Grignard reaction at −20°.* Grignard reagent from 0.5 mole of ethyl bromide in 165 ml. of ether was added to 0.24 mole of glutaryl dichloride dissolved in 100 ml. of ether. Addition was initiated at −50°, but it was soon necessary to allow the reaction to warm to about −20° in order to avoid plugging of the stirrer. Addition was completed in about 1.5 hr., then the reaction was stirred a few minutes as the temperature was allowed to rise to room temperature. Decomposition was with ice and 12*N* sulfuric acid.

Carbonate extraction of the reaction mixture and work-up as described for the run at 0° yielded 1.92 g. of lactone-unsaturated acid mixture, b.p. 105–143°/6 mm., and 8.14 g. of δ-ketoenanthic acid, b.p. 143–145°/6 mm., m.p. 46–48°.

The neutral material remaining after carbonate extraction was fractionally distilled at 10-mm. pressure to yield the following components:

Fraction	Weight, g.	B.P., °C.	n_D^{25}
1	1.23	83–98	1.4630
2	5.23	98–100	1.4557
3	0.81	100–117	
4	1.50	117–119	
5	0.33	119–133	
6	3.11	133–135	1.4593
7	0.55	(column stripped at 1 mm.)	

Fraction 2 has an infrared spectrum indicating an approximately equimolar mixture of 2-methyl-3-ethyl-2-cyclohexenone and 3-ethylnonan-3-ol-7-one (refer to investigation of run at 0°).

Fraction 4 solidified readily, m.p. 53°, no depression on admixture with an authentic sample of 3,7-nonanedione.

Fraction 6 has an infrared spectrum characteristic of the mixture of lactone III and acid V (refractive index indicates about 75% lactone).

(*C*) *Grignard reaction at −20° in presence of ferric chloride.* A reaction using 0.25 mole of glutaryl dichloride was carried out as described under (*B*) except that 0.75 g. of anhydrous ferric chloride was added to the ether solution of acid chloride.

Carbonate extraction of the products yielded 2.12 g. of lactone-unsaturated acid mixture, b.p. 120–144°/6 mm., and 4.13 g. of δ-ketoenanthic acid, b.p. 144–145°/6 mm., m.p. 48.0–48.5°.

Distillation of the neutral material at 10-mm. pressure yielded the following fractions:

Fraction	Weight, g.	B.P., °C.
1	1.61	40–92
2	3.35	92–95
3	2.42	95–110
4	2.79	110–118
5	0.90	118–132
6	2.53	132–134
7	1.29	134–145
8	1.89	(column stripped at 1 mm.)

The infrared spectrum of *Fractions 2 and 3* indicated an approximately equimolar mixture of 2-methyl-3-ethyl-2-cyclohexenone and 3-ethylnonan-3-ol-7-one.

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[14] This material had b.p. 143–145°/6 mm., m.p. 48–48.5°, no depression in melting point on admixture with an authentic sample of δ-ketoenanthic acid. Small quantities of δ-ketoenanthic acid were isolated at this point in all the runs with ethylmagnesium bromide. It is not clear why this material fails to appear in the fraction extracted with carbonate.

Fraction 4 is 3,7-nonanedione, m.p. 51-53°, no depression on admixture with an authentic sample. An additional 0.2 g. of dione was recovered from Fraction 5 by crystallization from ether-petroleum ether. The infrared spectra of the remainder of this fraction and of *Fractions 6 and 7* indicated a mixture of lactone and unsaturated acid.

Fraction 8 crystallized on standing, m.p. 48.0-48.5° after precipitation from ether-petroleum ether, no depression of melting point on admixture with an authentic sample of δ-ketoenanthic acid.

BERKELEY, CALIF.

[COMMUNICATION NO. 1748 FROM THE KODAK RESEARCH LABORATORIES]

Derivatives of Benzoylresorcinol

J. A. VANALLAN

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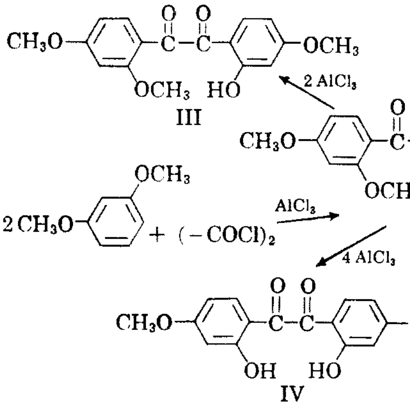
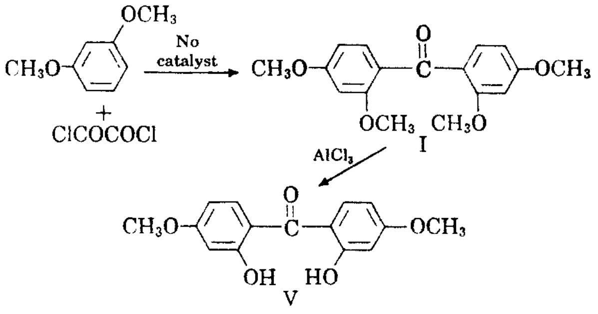
A new synthesis of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone is described. The substance stated by Staudinger to be 2,2',4,4'-tetramethoxybenzophenone has been shown to be 2,2',4,4'-tetramethoxybenzil. The ultraviolet absorption spectra of these materials are discussed.

In extending the investigation of derivatives of benzoylresorcinol,[1] we had occasion to synthesize a compound described[2] as 2,2',4,4'-tetramethoxybenzophenone (I). The ultraviolet absorption spectrum of this latter substance was at variance with that expected from our earlier work, so it was decided to re-examine this substance.

When *m*-dimethoxybenzene was allowed to react with oxalyl chloride in carbon disulfide[2] or ethylene chloride, with aluminum chloride as a catalyst, a substance melting at 129-130° was obtained, confirming Staudinger's result. However, methoxyl determination, Grignard analysis, and elementary analyses led to the conclusion that the substance melting at 129-130° was 2,2',4,4'-tetramethoxybenzil (II). To test this hypothesis, II was oxidized with alkaline hydrogen peroxide to 2,4-dimethoxybenzoic acid, a reaction typical of benzils. Selective demethylation of II with two and four equivalents of aluminum chloride gave 2-hydroxy-2',4,4'-trimethoxybenzil (III) and 2,2'-dihydroxy-4,4'-dimethoxybenzil (IV), respectively. The structures of III and IV are assigned on the basis of the Grignard analysis, on the known propensity of *o*-methoxyl groups to be demethylated, and the similarity of their ultraviolet curves to II.



It was noted that, on mixing oxalyl chloride and *m*-dimethoxybenzene, the solution became reddish yellow and hydrogen chloride was slowly evolved; heating accelerated this evolution of gas. In order to determine the nature of this reaction, the components were heated for a few hours, and the reaction mixture was distilled. The distillate was recrystallized from ethanol to give a substance having a melting point of 135-136° which, from its elementary analysis, methoxyl determination, and Grignard analysis, is 2,2',4,4'-tetramethoxybenzophenone (I). Its mixed melting point with II is 110-113°, and its 2,4-dinitrophenylhydrazone (m.p. 150°) differs from that of II (m.p. 185°). Moreover, demethylation of I with aluminum chloride gives 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (V), identical with that obtained from *m*-dimethoxybenzene and phosgene in the presence of aluminum chloride.[3]



The melting point of I has been reported as 130°[4] and as 137.2-139°.[5] It is evident, therefore, that the substance Staudinger describes as 2,2',4,4'-

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(1) J. A. VanAllan and J. F. Tinker, *J. Org. Chem.*, **19**, 1243 (1954).

(2) H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. Chim. Acta*, **4**, 334 (1921).

(3) General Aniline and Film Corp., Brit. Patent **706,151** (1954).

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