

*Anal.* Calcd. for  $C_{13}H_{10}O$ : C, 85.69; H, 5.53. Found: C, 85.70; H, 5.38.

The fluorenone was oxidized to fluorenone, m.p. 83–84°; no depression on admixture with an authentic sample.

Concentration of the fluorenone mother liquor gave an additional 13 g. of fluorenone azine, m.p. 270°, giving a total of 21.5 g. (0.06 mole, 28.2%) of this compound by both routes.

**9-Fluorenyllithium with 9-Diazofluorene.**—Fluorenone hydrazone<sup>31</sup> was oxidized with yellow mercuric oxide to 9-diazofluorene in 48% yield according to the method of

(31) H. Staudinger and O. Kupfer, *Ber.*, **44**, 2207 (1911).

Nenitzescu and Solomonica.<sup>32</sup>

A solution of 13 g. of 9-diazofluorene in 50 ml. of ether was added to a solution of 9-fluorenyllithium prepared from 10.5 g. of fluorenone and *n*-butyllithium in 200 ml. of ether.

There was isolated in the usual way 7.8 g. of fluorenone azine as a red-brown powder, m.p. 269–270° after crystallization from xylene. A mixed m.p. with an authentic sample showed no depression, and infrared spectra of the two samples were superimposable.

(32) C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 496.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Ketene Acetals. XXX. Alkylation of Dimethylketene Dimethylacetal

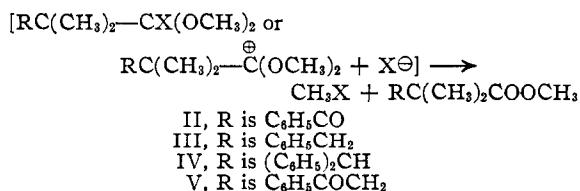
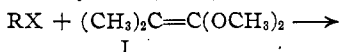
By S. M. McELVAIN AND CLYDE L. ALDRIDGE<sup>1</sup>

RECEIVED MARCH 13, 1953

Dimethylketene dimethylacetal (I) is readily converted to a trisubstituted acetic ester when heated with such halides as benzoyl chloride, benzyl bromide, benzhydryl bromide and phenacyl bromide. With triphenylmethyl bromide the thermal reaction with I produces triphenylmethane, methyl methacrylate and its dimer VIII. These products are shown to arise from a concerted intramolecular thermal decomposition of the initially formed methyl  $\beta,\beta,\beta$ -triphenylpivalate (VI), which may be prepared from I and triphenylmethyl bromide in the presence of small amounts of mercuric chloride at temperatures below its decomposition point. I is alkylated by butyl bromide in 74% yield in presence of zinc chloride. Stannic chloride causes a rapid methylation of I with methyl chloride, but dehydrohalogenates higher primary alkyl halides and the halogen acid produced reacts with I. Zinc chloride produces a similar dehydrohalogenation reaction with secondary and tertiary halides.

The dealcoholation of methyl orthoisobutyrate to dimethylketene dimethylacetal (I) with aluminum *t*-butoxide<sup>2</sup> and a new procedure, which is now reported, for the preparation of this orthoester in good (70%) yields have made this disubstituted ketene acetal available for a further study of its properties. Compared to the unsubstituted and monosubstituted ketene acetals, I is quite resistant to polymerization, *e.g.*, it may be distilled unchanged from aluminum chloride.<sup>3</sup> The reactions of I are further simplified by the absence of hydrogen on the methylene carbon.<sup>4</sup>

This paper reports the reactions of I with a variety of organic halides. Benzoyl chloride, benzyl bromide, benzhydryl bromide reacted smoothly and in the expected manner with I to give high yields (81–95%) of the trisubstituted acetic esters II, III and IV and the corresponding methyl halide. Phenacyl bromide, however, gave only a 25% yield of methyl benzoylpivalate (V) together with methyl isobutyrate (57%) and a viscous red oil which was



(1) U. S. Rubber Company Fellow 1951–1952; du Pont Summer Research Assistant 1951 and 1952.

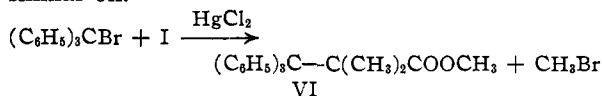
(2) S. M. McElvain and W. R. Davie, *THIS JOURNAL*, **73**, 1400 (1951).

(3) *Cf.* the polymerization of ketene diethylacetal with such metal salts as cadmium chloride (P. R. Johnson, H. M. Barnes and S. M. McElvain, *ibid.*, **62**, 964 (1940)).

(4) *Cf.* Reactions of other ketene acetals with alkyl and acyl halides (S. M. McElvain, *et al.*, *ibid.*, **64**, 254 (1942); **74**, 1811, 2662 (1953)).

not characterized; 35% of the phenacyl bromide was recovered. Evidently under the conditions of the reaction hydrogen bromide is generated and converts a major portion of I to methyl isobutyrate.

In contrast to the relatively simple reactions in which II–IV were produced, triphenylmethyl bromide reacted with I to give a group of unexpected reaction products; triphenylmethane (80%), methyl methacrylate (64%), dimethyl  $\alpha,\alpha$ -dimethyl- $\alpha'$ -methyleneglutarate (VIII) (24%), methyl bromide (78%) and a viscous, yellow oil, which boiled over a wide range, amounted to 14.5% of the weight of the reactants and was not further identified. Apparently the initially formed methyl  $\beta,\beta,\beta$ -triphenylpivalate (VI) was pyrolyzed into these products at the temperature (100–120°) required for the reaction of I with triphenylmethyl bromide. That VI was initially produced was shown when it was discovered that this ester could be formed in 89% yield at or below the boiling point of ether from the reaction of I with triphenylmethyl bromide in the presence of 1 mole per cent. of mercuric chloride. When VI was heated to the temperature required for its formation in the absence of the catalyst, it yielded triphenylmethane (61%), methyl methacrylate (40%), VIII (19%) and 34% of the yellow oil. This oil appears to be formed from the interaction of VI with oxygen of the air as a sample of this ester exposed to the air on a watch glass is transformed after several hours to a similar oil.



This unique pyrolysis of VI is doubtless related to its hexasubstituted ethane structure as the methyl diphenylpivalate (IV) is quite stable and

may be distilled (b.p. 137° (0.5 mm.)). Also ethyl  $\alpha$ -methyl- $\beta,\beta$ -triphenylpropionate,  $(C_6H_5)_3CCH(CH_3)COOC_2H_5$ , prepared by the reaction of triphenylmethyl bromide and methylketene diethylacetal, distills at 180° (0.4 mm.) without any detectable decomposition. However, when the latter ester was heated to 250° for an hour, it underwent partial pyrolysis into ethyl acrylate (7%) and triphenylmethane (13%); the remainder was recovered.

The manner in which the weak carbon-carbon bond of VI is ruptured by mild heating seemed of some interest. Conceivably, this bond could break homolytically to yield a pair of radicals or heterolytically into the triphenylcarbonium cation and the methyl isobutyrate anion. In either case the radicals or ions formed would be stabilized by resonance. In an effort to determine which of these processes was occurring, pyrolyses of VI were carried out in the presence of various solvents which seemed capable of trapping any intermediate radicals or ions. The results of these experiments are summarized in Table I.

TABLE I  
DECOMPOSITION OF VI IN VARIOUS SOLVENTS

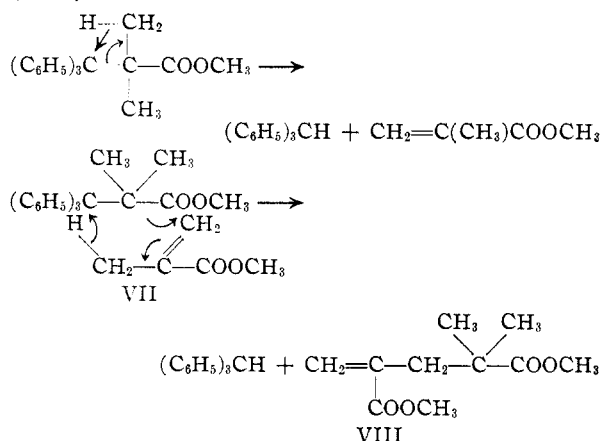
Run	Solvent	Reac- tion temp., °C.	Re- ac- tion time, hr.	Yields, % of —			
				(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> - CH	Methyl meth- acrylate	Dimer (VIII)	Oil <sup>a</sup>
1	None <sup>b</sup>	100–120	5	80	53	24	18.4
2	None	120	1	61	40	19	34
3	Methyl acetate	60	60	14	20	...	57
4	Methyl isobutyrate	95	5	75	63	Trace	17.5
5	Methyl methacry- late	100	0.5	82	..	76	..
6	Benzaldehyde	130	1	73	67	...	12
7	Benzyl alcohol	120	1	83	63	...	15
8	Toluene	110	2	81	63	...	17

<sup>a</sup> The unidentified, high-boiling, viscous oil expressed as weight % of the reactants. <sup>b</sup> This run shows the decomposition of VI as it was formed in the uncatalyzed reaction of I with triphenylmethyl bromide.

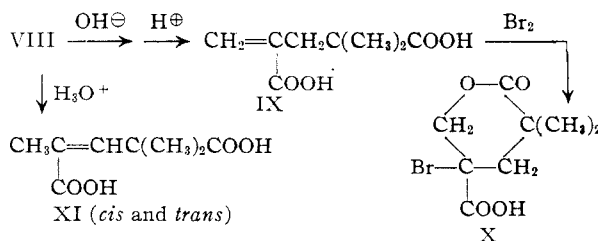
The data shown in Table I indicate that neither transient free radicals nor ions are formed in the pyrolysis of VI. If the methyl isobutyrate radical were formed, it would seem that it should propagate the polymerization of methyl methacrylate, but it is seen from run 5 that this solvent serves only to increase the yield of the dimer VIII. Also, this radical might be expected to attack the toluene solvent of run 8. If the methyl isobutyrate anion were formed, it would seem capable of reacting with either the esters (runs 3 and 4), the benzaldehyde (run 6) or with the benzyl alcohol of run 7. The fact that the yields of triphenylmethane and of methyl methacrylate are comparable in runs 4, 6, 7 and 8 indicates that the solvents used in these runs have no effect on the course of the pyrolysis other than to lower the yield of the dimer VIII. This fact together with the high yield of VIII in run 5 indicate that the dimer is the result of the interaction of VI with methyl methacrylate. The high yield of the oil at the expense of the other products in run 3 was doubtless due to the excessive length of reaction time and the lower reaction temperature.

These observations lead to the conclusion that VI undergoes pyrolysis *via* a concerted intramolecular process into triphenylmethane and methyl methacrylate.

The latter compound then reacts with VI in a similar manner *via* the six-membered cyclic complex VII to yield additional triphenylmethane and dimethyl  $\alpha,\alpha$ -dimethyl- $\alpha'$ -methyleneglutarate (VIII).



In addition to accommodating the experimental results of Table I, this mechanism predicts the structure of VIII, which was demonstrated in the following manner. Hydrogenation over palladium on carbon converted VIII, with the absorption of one equivalent of hydrogen, to a saturated ester, which yielded on saponification the known  $\alpha,\alpha,\alpha'$ -trimethylglutaric acid. A comparison of the ultraviolet absorption spectra of VIII with that of methyl methacrylate showed that the extinction coefficients of the two compounds were comparable in the low wave length regions where the absorption was rapidly approaching a maximum<sup>5</sup> (208–230 m $\mu$ ). The Kuhn-Roth C-methyl value of VIII was found to be 0.15, a value which is consistent with the observation that *gem*-dimethyl groups yield little if any distillable acid, under the conditions of this determination.<sup>6</sup> Hydrolysis of VIII under acidic conditions yielded an acid mixture of wide melting range which appeared to consist of IX and the *cis* and *trans* forms of the isomeric acid XI. Basic hydrolysis of VIII yielded a single acid, m.p. 123–124°, which appears to be IX; this acid on treatment with bromine yields a bromolactone,<sup>7</sup> m.p. 177–177.8°. The position of the carbonyl absorption band at 5.75  $\mu$  (no peak at 5.65  $\mu$ ) indicates that the bromolactone contains a six-membered



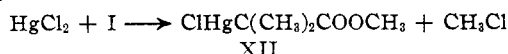
(5) Cf. R. B. Woodward, *THIS JOURNAL*, **63**, 1132 (1941); J. Cason and G. Sumrell, *J. Org. Chem.*, **16**, 1181 (1951).

(6) E. J. Eisenbraun, M.S. Thesis, University of Wisconsin (1951); the authors are indebted to Mr. Eisenbraun for the C-methyl determinations with VIII.

(7) Perkin and Smith (*J. Chem. Soc.*, **83**, 779 (1903); **85**, 157 (1904)) report the *cis* and *trans* forms of XI to melt at 125 and 150°, respectively; on treatment with bromine the *cis* acid yielded a dibromo acid, m.p. 168°, while the *trans* acid gave a dibromo acid, m.p. 205–207°.

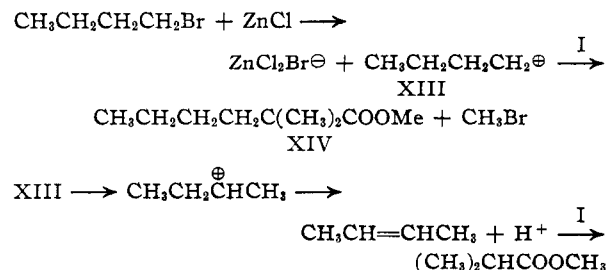
ring as represented by X. The facile formation of bromolactones as products of the bromination of similar  $\gamma,\delta$ -unsaturated acids has recently been reported.<sup>8</sup>

Inasmuch as the reaction of I with triphenylmethyl bromide was found to proceed at low temperatures in the presence of a catalytic amount of mercuric chloride, it seemed desirable to determine if an alkyl halide could be used to alkylate I to a trisubstituted acetic ester under the influence of similar catalysis. Mercuric chloride was ineffective as a catalyst for the butylation of I with butyl chloride even at the boiling point of this halide. At this temperature the mercuric chloride reacted quantitatively with I to yield methyl chloride and methyl  $\alpha$ -chloromercuri-isobutyrate (XII). The chloromercuri group of XII is quite resistant to replacement, e.g., when it is heated with butyl bromide only halogen exchange with the formation of butyl chloride resulted; the remaining bromomercuri-ester did not react with butyl iodide; with benzyl bromide XII produced polymers of this halide, presumably *via* a Friedel-Crafts type of reaction. For these reasons and also because mercuric chloride *does not* promote the reaction of trityl chloride with I, it is believed that XII is *not* an intermediate in the formation of VI from I and trityl bromide. This reaction appears to result from mercuric chloride ionizing the trityl bromide by an electrophilic attack on the halogen.



Stannic chloride produced a rapid reaction in a mixture of I and *n*-propyl chloride, but the reaction products were methyl chloride (67%) methyl isobutyrate (49%) and methyl pivalate (34%). Molar quantities of the stannic chloride are required for this reaction as the esters formed appear to deactivate the catalyst by formation of a stable coordination complex. It is not certain in this case whether the stannic chloride caused the rearrangement of I to methyl pivate, or first dehydrohalogenated the propyl chloride to yield hydrogen chloride, which converted I to methyl isobutyrate and methyl chloride and the latter compound then methylated some of I to the pivalic ester.

While zinc chloride did not produce any reaction between I and *n*-butyl chloride even after 19 hours at reflux, it did prove to be an effective catalyst for the butylation of I with *n*-butyl bromide. A 74% yield of methyl  $\alpha,\alpha$ -dimethylcaproate (XIV) along with 17% of the elimination products butene-2 and methyl isobutyrate were obtained. The fact that this butene rather than butene-1 was formed indi-



cates that the initial primary carbonium XIII formed from the halide and zinc chloride rearranges to a secondary carbonium ion before the proton is eliminated.

The reaction products from a series of runs of various primary halides and catalysts with I are summarized in Table II. An attempt to extend the alkylation of I to a secondary halide (2-bromooctane) in the presence of zinc chloride resulted only in the elimination of the halogen acid from the alkyl bromide and the reaction of this acid with I. Long heating (11 days) of I with *t*-amyl bromide without a catalyst also produced a large amount (71%) of dehydrohalogenation.

TABLE II  
CATALYZED ALKYLATIONS OF DIMETHYLKETENE DIMETHYLACETAL (I)

RX <sup>a</sup>	Catalyst	Mole % catalyst	CH <sub>3</sub> X	Yields, % of		
				Methyl isobutyrate	Methyl pivalate	XIV
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	None	...	No reaction <sup>b</sup>			
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl	SnCl <sub>4</sub>	100	67	49	34	..
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl	ZnCl <sub>2</sub>	3.7	No reaction			
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	ZnCl <sub>2</sub>	7.3	100	18	..	74
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	ZnBr <sub>2</sub>	3.7	112 <sup>c</sup>	9	..	70
<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	ZnCl <sub>2</sub>	7.3	63	11	21	67

<sup>a</sup> Generally 2.5 equivalents of RX used per equivalent of I. <sup>b</sup> After 24 hr. at reflux with a two molar excess of halide. <sup>c</sup> This product contained a considerable amount of butene-2.

### Experimental

**Isobutyronitrile.**<sup>9</sup>—A mixture of 1.6 g. of 5% palladium-on-carbon, 134 g. (2 moles) of methacrylonitrile (containing 0.5% of hydroquinone) and 60 ml. of glacial acetic acid was shaken in a 500-ml. bottle under 1–3 atmospheres of hydrogen. During the peak of the reaction the bottle was cooled by a jet of air. At the end of 2.5 hours 105–108% of a molar equivalent of hydrogen had been absorbed and the hydrogenation had effectively stopped. Several such runs were combined, the acetic acid neutralized with aqueous potassium hydroxide and the aqueous layer extracted with ether. The combined extracts were dried over magnesium sulfate and fractionated through a 25-cm. Heli-Pak column to yield isobutyronitrile, b.p. 101–102°, *n*<sub>D</sub><sup>20</sup> 1.3723. Fifteen runs (30 moles of methacrylonitrile) yielded 1594 g. (77%) of isobutyronitrile.

**Methyl Iminoisobutyrate Hydrochloride.**—This compound was prepared by the previously described procedure,<sup>10</sup> except that 1.5–2.0 instead of 1.1 equivalents of hydrogen chloride were used and the reaction time was lengthened from 2 to 14 days. With these alterations the reported 99% yields of the salt were obtained.

**Methyl Orthoisobutyrate.**—Two moles (275 g.) of methyl iminoisobutyrate hydrochloride, 6 moles (192 g.) of absolute methyl alcohol and 1800 ml. of dry petroleum ether (b.p. 35°) were placed in a 3-liter flask fitted with a stirrer and a reflux condenser. A calcium chloride tube was used to protect the system from moisture. Three phases: petroleum ether, methyl alcohol saturated with the salt, and undissolved iminoester hydrochloride were initially present in this reaction mixture. The mixture was stirred rapidly for two days at room temperature, at the end of which time the lower (alcohol) layer had been replaced by solid ammonium chloride. The liquid was filtered and then distilled through a 25-cm. Heli-Pak column. The excess methyl alcohol distilled as an azeotrope with the pentane at 27°. As the volume of the liquid was reduced some isobutyramide crystallized out. At this point the liquid was filtered into a smaller flask and the distillation continued with about five grams of sodium hydride in the pot to remove the last traces of water, alcohol and amide. A small forerun, b.p. 127–134°, was

(9) This preparation was developed by Mr. Roy Starn of this Laboratory.

(10) S. M. McElvain and J. T. Venerable, *THIS JOURNAL*, **72**, 1664 (1950).

(8) P. N. Craig and I. H. Witt, *THIS JOURNAL*, **72**, 4925 (1950).

taken before the main fraction, b.p. 134–136°, was collected. The yield of methyl orthoisobutyrate was 208 g. (70%). The amide which was obtained by filtration was combined with a small amount which was extracted from the ammonium chloride with ethyl acetate; the total yield of this product was 19.2 g. (11%), (m.p. after one crystallization from ethyl acetate 126–129°). The yield of ammonium chloride containing 64.9% chlorine (calcd. 66.3) was 91.0 g. (85%).

**Dimethylketene Dimethylacetal (I).**—This material was prepared by dealcoholation of methyl orthoisobutyrate by the procedure of McElvain and Davie.<sup>2</sup>

**Reactions of Dimethylketene Dimethylacetal (I).** (a) **With Benzyl Bromide.**—A mixture of 15.4 g. (0.09 mole) of benzyl bromide and 10.25 g. (0.088 mole) of dimethylketene dimethylacetal was placed in a 50-ml. round-bottom flask fitted with a spiral condenser leading to a Dry Ice-acetone trap. All joints were ground glass, and the opening to the air was through a calcium chloride tube. The flask was heated for 72 hours in an oil-bath at 150°. At the end of this time 6.8 g. (81%) of methyl bromide had collected in the trap; 77% had collected after 55 hours. Distillation of the reaction mixture through a 40-cm. Vigreux column yielded (a) 2.1 g. of benzyl bromide, b.p. 63–67° (10 mm.),  $n_D^{25}$  1.5551; (b) 2.3 g. of intermediate fraction, b.p. 67–102° (10 mm.),  $n_D^{25}$  1.5162; (c) 12.0 g. of methyl  $\alpha$ -benzylisobutyrate (III), b.p. 102–103° (10 mm.),  $n_D^{25}$  1.4945,  $d_4^{25}$  1.0043 (the boiling point of this material at 20 mm. was found to be 122–124°, reported<sup>11</sup> b.p. 121–122° (23 mm.)); and (d) 0.9 g. of viscous residue. With division of fraction (b) on the basis of refractive index the yield of methyl  $\alpha$ -benzylisobutyrate amounted to 81%, and recovered benzyl bromide to 18%.

Benzyl dimethylacetic acid, obtained by overnight saponification of the methyl ester in a solution of potassium hydroxide in alcohol-water, melted at 56.5–58.0°; reported<sup>12</sup> m.p. 57°; neut. equiv. 177 (calcd. 178). The amide was prepared by the action of thionyl chloride and pyridine on the acid followed by treatment with ammonium hydroxide; after two recrystallizations from pentane, it melted at 61–63°; reported<sup>13</sup> m.p. 62–63°.

(b) **With Phenacyl Bromide.**—A mixture of 11.6 g. (0.1 mole) of I and 19.9 g. (0.1 mole) of phenacyl bromide was refluxed in an oil-bath at 195–205° for 41 hours. At the end of this time 5.2 g. (55%) of methyl bromide had collected in the attached cold trap (54% had collected after 36 hours). The product was distilled through a 7-cm. Vigreux column to yield 6.65 g. of material boiling at 82–94° (743 mm.) together with fractions boiling up to 250° (0.1 mm.). The lower boiling fraction was redistilled and proved to be mainly methyl isobutyrate (57%). The higher boiling fractions were recrystallized from pentane and the following products separated: (a) 7.0 g. (35%) of recovered phenacyl bromide; (b) 4.5 g. of a red viscous residue (not characterized); (c) 5.7 g. (26%) of methyl  $\alpha$ -benzoylpivalate (V), m.p. after four crystallizations from pentane, 48–49°; reported<sup>13</sup> m.p. 46–47°.

Saponification of this ester in a refluxing alcohol-water solution of potassium hydroxide was found to be incomplete after 17 hours; however, the benzoylpivalic acid was obtained in the following manner: To 15 ml. of concentrated sulfuric acid was added 0.155 g. of methyl benzoylpivalate; a rose-colored solution resulted. Upon dilution with 75 ml. of water a white solid, m.p. 160–167°, precipitated. One crystallization from a mixture of benzene and petroleum ether gave benzoylpivalic acid, m.p. 168–171°, neut. equiv., 209 (calcd. 206); reported<sup>13</sup> m.p. 173°.

(c) **With Benzoyl Chloride.**—A mixture of 7.2 g. (0.062 mole) of I and 8.7 g. (0.062 mole) of benzoyl chloride was heated in an oil-bath at 200° for 4 hours. During this time 1.80 g. (58%) of methyl chloride condensed in the trap. The liquid in the pot was distilled through a 40-cm. Vigreux column to yield 1.02 g. (12%) of recovered benzoyl chloride and 10.6 g. (83%) of methyl  $\alpha$ -benzoylisobutyrate (II), b.p. 136–137° (14 mm.),  $n_D^{25}$  1.5100; reported<sup>14</sup> b.p. 140–142° (14 mm.).

Hydrolysis of 5.25 g. of this ester with a water-sulfuric acid-acetic acid mixture<sup>15</sup> gave 3 g. (83%) of isobutyrophen-

one, b.p. 220–224° (750 mm.),  $n_D^{25}$  1.5150; m.p. of oxime 59–61°, reported<sup>16</sup> m.p. 61°.

(d) **With Benzhydryl Bromide.**—A mixture of 11.6 g. (0.1 mole) of I and 23.7 g. (0.1 mole) of benzhydryl bromide, prepared from benzhydrol by the method of Courtot,<sup>17</sup> was heated for 15 hours at 110°; after this time, 8.1 g. (85%) of methyl bromide had collected in the cold trap (7.3 g. (77%) was evolved in 3.5 hr.). Distillation of the residue through a 45-cm. Vigreux column yielded after 1.0 g. of forerun, b.p. 128–136.5° (0.5 mm.), 24.4 g. (94.6%) of methyl  $\alpha,\alpha$ -dimethyl- $\beta,\beta$ -diphenylpropionate (IV), b.p. 136.5–137.5° (0.5 mm.), m.p. 50–56°. One recrystallization from petroleum ether raised the melting point to 56–57°.

*Anal.* Calcd. for  $C_{17}H_{17}O(OCH_3)_2$ : C, 80.56; H, 7.51; OCH<sub>3</sub>, 11.5. Found: C, 80.43; H, 7.66; OCH<sub>3</sub>, 10.8.

A 4.428-g. sample of IV was saponified by heating for 11 hours in 100 ml. of 0.3 N alcoholic potassium hydroxide. After replacement of the alcohol by water, extraction of the aqueous layer with ether, and acidification of the aqueous layer with concentrated hydrochloric acid, 3.908 g. (93%) of  $\alpha$ -benzhydrylisobutyric acid, m.p. 136.6–138°, was obtained. One recrystallization from benzene-petroleum ether (b.p. 65°) raised the melting point to 137–138°, reported<sup>18</sup> m.p. 134–135°.

(e) **With Triphenylmethyl Bromide.** (i).—A mixture of 48.5 g. (0.418 mole) of I and 135 g. (0.418 mole) of trityl bromide, in a flask attached to a spiral condenser leading to a Dry Ice-acetone trap, was immersed in an oil-bath at 140° until vigorous reflux occurred (15 minutes). The oil-bath was then lowered and the reaction allowed to proceed for 1.7 hours after which the oil-bath was reapplied for 1 hour at 100° and 2 hours at 120°. At the end of this time 30.9 g. (78%) of methyl bromide had collected in the cold trap. After removal of 38.9 g. of volatile material under vacuum there remained 109.6 g. of residue. Crystallization of this residue from benzene yielded a first crop, 72.5 g. (71%), of triphenylmethane, m.p. 92–94°, and a second crop, 9 g. (9%), m.p. 89.5–93°. Evaporation of the mother liquor left 26.5 g. of a dark residue.

Fractionation of the volatile material through a 25-cm. Heli-Pak column yielded fractions of methyl methacrylate totaling 27.0 g. (64%) which distilled at 92–99° (mainly 98.5–99°) and had refractive indices between 1.4082 and 1.4112, together with a fraction of dimethyl  $\alpha,\alpha$ -dimethyl- $\alpha$ -methyleneglutarate (VIII) totaling 10.0 g. (24%), b.p. 136–138° (50 mm.),  $n_D^{25}$  1.4439 to 1.4456. A sample boiling at 136.5–137.5° (50 mm.),  $n_D^{25}$  1.4440,  $d_4^{25}$  1.0428, was used for analysis.

*Anal.* Calcd. for  $C_8H_{10}O_2(OCH_3)_2$ : C, 59.98; H, 8.06; OCH<sub>3</sub>, 31.0. Found: C, 59.85; H, 8.30; OCH<sub>3</sub>, 27.0.

(ii) **With Mercuric Chloride.** Methyl  $\beta,\beta,\beta$ -Triphenylpivalate (VI).—A mixture of 51.7 g. (0.16 mole) of trityl bromide, 22.0 g. (0.176 mole) of dimethylketene dimethylacetal (I) and 75 ml. of dry ether was placed in a 250-ml. round-bottom flask connected to a 3-neck attachment which was fitted with a mechanical stirrer, a pressure equalized dropping funnel, and a spiral condenser leading to a Dry Ice-acetone trap. All joints were ground glass and the opening to the air was through a calcium chloride tube. Stirring was begun and a solution of 0.434 g. (1 mole %) of mercuric chloride in 100 ml. of dry ether was added one-half at a time with a 10-minute interval between additions. Immediately on addition of the mercuric chloride catalyst a yellow color appeared in the solution accompanied by an exothermic reaction. Stirring was continued until all the trityl bromide had gone in solution (ca. 15 minutes). During this time the temperature was kept below the boiling point of the ether solvent by periodic application of a cold water-bath. After 30 minutes the solution was heated momentarily to reflux and then allowed to stand for 2 hours. Cooling to 0° caused crystallization of 49 g. (89%) of product, m.p. 101.5–105.5°; one recrystallization from dry ether yielded 32.7 g. (60%) of VI, m.p. 105–107°. Further recrystallization narrowed the melting range to 106–107°.

*Anal.* Calcd. for  $C_{23}H_{21}O(OCH_3)_2$ : C, 83.69; H, 7.02; OCH<sub>3</sub>, 9.00. Found: C, 83.49; H, 7.08; OCH<sub>3</sub>, 8.55.

The infrared spectrum of this compound showed the characteristic strong ester carbonyl band at 5.80  $\mu$ , and the car-

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bon-oxygen-carbon bending absorption at 8.05 and 8.39  $\mu$ .

A 24.85-g. sample of VI, which had been kept in a glass stoppered bottle seven weeks without significant change, melted down to a yellow oil containing white solid dispersed throughout its volume upon being left unstoppered for 24 hours. A gain in weight of 0.95 g. (40% of a molecular equivalent of oxygen) accompanied this change. No further change occurred upon 3 weeks of additional standing. At the end of this time 4.50 g. of this material was dissolved in petroleum ether (b.p. 65°) and its absorption of oxygen measured volumetrically. After 6 hours at 28° and 15 hours at 65° the material had absorbed 61 ml. (after deduction of a 7 ml. blank) which corresponds to an additional 19% of a molecular equivalent of oxygen. Upon cooling the material separated from the petroleum ether as a clear yellow oil.

**Experiments Related to the Structure of Dimethyl  $\alpha,\alpha$ -Dimethyl- $\alpha'$ -methyleneglutarate (VIII).**—The ultraviolet spectra of VIII and methyl methacrylate were taken on a Cary recording ultraviolet spectrophotometer in 95% ethanol at dilutions of  $2 \times 10^{-4}$  and  $1 \times 10^{-4}$  mole per liter, respectively. In both cases the absorption was rapidly approaching a maximum at the lowest observable wave length, 208  $\mu$ . For VIII  $\log \epsilon$  208 was 3.86 and  $\log \epsilon$  210 was 3.83. For methyl methacrylate  $\log \epsilon$  208 was 3.94 and  $\log \epsilon$  210 was 3.88.

A mixture of 2.77 g. of VIII, 20 ml. of 95% ethanol and 0.6 g. of 5% palladium-on-carbon was shaken in a 60-ml. bottle attached to a conventional low pressure hydrogenation apparatus. In 2.5 hours the ester absorbed 110% of the amount of hydrogen required for saturation of one double bond. The liquid was filtered through a sintered glass funnel into a 10-ml. Claisen flask. After removal of the solvent there was obtained by distillation 2.46 g. (88.4%) of dimethyl  $\alpha,\alpha,\alpha'$ -trimethylglutarate, b.p. 112.5–113.5° (24 mm.),  $n_D^{25}$  1.4272,  $d_4^{25}$  1.0082.

*Anal.* Calcd. for  $C_{10}H_{18}O_4$ : C, 59.38; H, 8.97. Found: C, 59.29; H, 9.06.

Saponification of 0.783 g. of this product in an aqueous-alcoholic solution of potassium hydroxide for 24 hours yielded 0.578 g. (86%) of crude acid, m.p. 93.0–96.5°. One crystallization from petroleum ether (b.p. 60°) gave 0.438 g. (65%) of  $\alpha,\alpha,\alpha'$ -trimethylglutaric acid, m.p. 98.5–99.5°; reported<sup>19</sup> m.p. 97°. The anhydride was prepared by the procedure of Oddo and Manuelli as described by Auwers,<sup>20</sup> m.p. 95–96°; reported<sup>20</sup> m.p. 95–96°. The monoanilide melted at 164.5–165.5°; reported<sup>21</sup> m.p. 165°.

A mixture of 1.04 g. of VIII, 4 ml. of water, 1.5 ml. of ethyl alcohol and 2 g. of potassium hydroxide, was refluxed for two days. Evaporation to dryness followed by extraction with ether containing dry hydrogen chloride yielded 0.7 g. (86%) of crude acid. One crystallization from petroleum ether (b.p. 60°) yielded 0.4 g. (49%) of  $\alpha,\alpha$ -dimethyl- $\alpha'$ -methyleneglutaric acid, m.p. 120–122°. Repeated crystallizations from very small amounts of water brought the melting point up to 123–124°.

*Anal.* Calcd. for  $C_8H_{12}O_4$ : C, 55.80; H, 7.03; neut. equiv., 88.1. Found: C, 56.13; H, 7.11; neut. equiv., 88.4.

A mixture of 1.93 g. of VIII and 5 ml. of 48% hydrobromic acid was refluxed for 16 hours after which time an additional 2.5 ml. of the acid was put in and refluxing continued for 2 hours. Evaporation of the mixture to dryness and extraction of the residue with petroleum ether (65°) yielded 0.77 g. (46%) of solid acid, m.p. 98–115°. Sublimation (0.2 mm.) raised the melting point to 112–119°; subsequent crystallization from petroleum ether (b.p. 65°) raised the melting point to 118–120° whereas the use of water as solvent caused the melting point to rise to 145–152°. The neutral equivalent of this material was 86.7 (calcd. 86).

Exposure of 1.036 g. of  $\alpha,\alpha$ -dimethyl- $\alpha'$ -methyleneglutaric acid, m.p. 120–122°, to the action of bromine vapor in a desiccator for 18 hours, followed by removal of the excess bromine under vacuum over potassium hydroxide left 1.667 g. of product which after one crystallization from formic acid yielded 1.031 g. (68%) of  $\alpha,\alpha$ -dimethyl- $\gamma$ -carboxy- $\gamma$ -bromovalerolactone, m.p. 177.5–178.5°.

*Anal.* Calcd. for  $C_8H_{11}O_4Br$ : C, 38.26; H, 4.42; Br, 31.83. Found: C, 38.33; H, 4.51; Br, 32.22.

(19) K. Auwers and V. Meyer, *Ber.*, **23**, 300 (1890).

(20) K. Auwers, *ibid.*, **31**, 2113 (1898).

(21) K. Auwers, *Ann.*, **292**, 224 (1896).

**Pyrolyses of Methyl  $\beta,\beta,\beta$ -Triphenylpivalate (VI).** (a) **Without Solvent.**—A 11.1-g. sample of VI was placed in a 25-ml. round-bottom flask with ground glass joint connected by means of a U-shaped attachment to a Dry Ice-acetone trap. No material collected in the cold trap during 1 hour of evacuation at 0.2 mm. pressure. The sample then was heated at atmospheric pressure in an oil-bath at 120°. After 1 hour of heating, the pressure was reduced to 13 mm., whereupon 1.30 g. (40%) of methyl methacrylate,  $n_D^{25}$  1.4108, collected in the cold trap within ten minutes. Thirty minutes of additional heating at 120° (13 mm.) yielded no further distillate. The pressure then was reduced to 0.2 mm. and within 15 minutes 0.60 g. (19%) of VIII,  $n_D^{25}$  1.4472, was collected in the cold trap. Further heating for 2.5 hours at 120° and 0.2 mm. pressure yielded no additional distillate.

Crystallization of the 9.1 g. of solid remaining in the pot yielded 4.8 g. (61%) of triphenylmethane, m.p. 90.5–92.5°. When distilled from a 10-ml. Claisen flask, the 4.0 g. of material left in the mother liquor had a boiling range of 120–195° (0.1 mm.) and became, on cooling, a viscous yellow oil; only 0.6 g. of residue remained from the distillation.

(b) **In Toluene.**—A solution of 9.2 g. of VI in 20.0 g. of toluene, b.p. 109° (740 mm.),  $n_D^{25}$  1.4935, was refluxed for 2 hours. The solution became yellow immediately after refluxing began. Distillation of the reaction mixture through a 25-cm. Podbielniak column separated the toluene and methyl methacrylate from the non-volatile triphenylmethane and associated oil. Refractive index of the volatile material indicated the amount (1.69 g.) of methyl methacrylate indicated in run 8 of Table I. Refractionation of this material through a 96 plate true-bore annular space column at 740 mm. pressure permitted the separation of about 60% of the indicated methyl methacrylate from the associated toluene. Crystallization of the non-volatile material from benzene yielded 4.77 g. (73%) of triphenylmethane, m.p. 93.0–94.3°, and a second crop of 0.550 g. (8%), m.p. 91–93°. Evaporation of the solvent from the mother liquor yielded 1.57 g. (17% of the weight of the starting material) of yellow viscous residue.

(c) **In Methyl Isobutyrate.**—A mixture of 21.1 g. of VI and 58 g. of methyl isobutyrate soon became homogeneous when placed in an oil-bath at 100°. After 35 minutes of heating at 110–115°, the solution was yellow; refluxing was continued for a total of 5.25 hours. At this time the solution was cooled in a Dry Ice-acetone bath and seeded with VI; no crystallization occurred. The volatile material was removed through a 7-cm. Vigreux column leading to a Dry Ice-acetone trap at 12 mm. pressure. The volatile and non-volatile products were worked up as in (b) to yield the products shown in Table I.

(d) **In Methyl Acetate.**—A mixture of 3.4 g. of VI and 7.4 g. of methyl acetate,  $n_D^{25}$  1.3591, was refluxed for 15 hours, after which time the solvent was removed at 10 mm. pressure without heating; this distillate was found to have the boiling point and refractive index of methyl acetate and gave a negative unsaturation test with potassium permanganate. At room temperature an oil pump removed another 0.15 g. of solvent containing a trace of methyl methacrylate,  $n_D^{25}$  1.3618, which gave a positive unsaturation test. The 3.50 g. of material left as a residue melted at 94–105°. The 7.4 g. of solvent was replaced and reflux continued for an additional 45 hours. The solution was cooled and seeded with VI; 0.80 g. (23%) of starting material, m.p. 93–100°, was recovered. Removal of the solvent at atmospheric pressure was followed by collection of 0.2 g., of a mixture of solvent and methyl methacrylate,  $n_D^{25}$  1.3939, equivalent to 0.13 g. (13%) of the latter.

Crystallization of the 2.3 g. of residue from benzene yielded 0.35 g. (14%) of crude triphenylmethane, m.p. 86–91°. The remaining 1.95 g. (57% of starting material) was recovered from the mother liquor as a yellow sirup.

(e) **In Methyl Methacrylate.**—A solution of 10.3 g. of VI and 0.1 g. of hydroquinone in 9.0 g. of methyl methacrylate, b.p. 99.0–99.3°,  $n_D^{25}$  1.4122, was refluxed for 30 minutes, allowed to cool, and the solvent removed under 10 mm. pressure. This treatment yielded 7.0 g. of recovered methyl methacrylate, b.p. 98–99°,  $n_D^{25}$  1.4118. Further distillation without heating at 0.2 mm. pressure for 40 minutes yielded 2.3 g. (76%) of crude VIII,  $n_D^{25}$  1.4473. Redistillation of this material yielded 1.3 g. (43%) of VIII, b.p. 95–97° (10 mm.),  $n_D^{25}$  1.4450.

The 9.6 g. of residue in the reaction flask distilled at 120–

197° (0.1 mm.) and on crystallization from benzene yielded 6.0 g. (82%) of triphenylmethane, m.p. 88–91°.

(f) **In Benzaldehyde.**—A solution of 1.72 g. of VI in 5.88 g. of benzaldehyde was heated at 130° under an atmosphere of nitrogen for 1 hour. Distillation of the volatile material at 0.5 mm. pressure yielded 6.03 g. of material, b.p. 130–174° (740 mm.),  $n_D^{25}$  1.5362. Based on refractive index this recovered benzaldehyde contained 0.336 g. (67%) of methyl methacrylate.

Crystallization of the 1.402 g. of non-volatile material, m.p. 73–88°, from benzene yielded 0.865 g. (71%) of triphenylmethane, m.p. 91–93°. A second crop of 0.020 g. (2%), m.p. 82–89°, was obtained. Upon evaporation of the mother liquor there remained 0.200 g. (12% of the weight of the starting material) of viscous residue.

(g) **In Benzyl Alcohol.**—A solution of 10.30 g. of VI in 9.72 g. of benzyl alcohol,  $n_D^{25}$  1.5388, was heated at 120° for 1 hour. The pressure was then reduced to 9 mm. and 1.60 g. (53%) of methyl methacrylate, b.p. 97–99° (742 mm.),  $n_D^{25}$  1.4100, collected in the Dry Ice trap. Further distillation of the reaction mixture at 9 mm. through a 7-cm. Vigreux column yielded: (a) 8.00 g. of benzyl alcohol, b.p. 84°,  $n_D^{25}$  1.5350; (b) 1.90 g. of impure benzyl alcohol, b.p. ca. 85°,  $n_D^{25}$  1.5250; (c) 0.30 g. (10%) of methyl methacrylate (collected in the cold trap),  $n_D^{25}$  1.4113; (d) 7.80 g. of non-volatile residue.

Crystallization of fraction (d) from benzene yielded a first crop of 5.2 g. (71%), m.p. 92–93.5°, and a second crop of 0.85 g. (12%), m.p. 89–92°, of triphenylmethane. Evaporation of the mother liquor yielded 1.55 g. (15% of the weight of the starting material) of yellow viscous residue.

**Ethyl  $\alpha$ -Methyl- $\beta,\beta$ -triphenylpropionate.**—A mixture of 7.0 g. (0.054 mole) of methylketene diethylacetal<sup>2</sup> and 8.7 g. (0.027 mole) of trityl bromide was placed in a 50-ml. flask attached to a spiral condenser leading to a Dry Ice-acetone trap. Upon addition of 73 mg. (1 mole %) of mercuric chloride in 10 ml. of diethyl ether an exothermic reaction, which caused refluxing of the ether, resulted. The mercuric chloride in ether solution seemed to form a complex with the ketene acetal as a white precipitate formed immediately when this solution came into contact with a glass surface wet with the ketene acetal. When the initial reaction had subsided the mixture was refluxed for 1.25 hours.

After removal of the volatile material under vacuum, there remained 9.6 g. of yellow residue. Distillation of this material from a Claisen flask yielded after a 0.7 g. forerun, b.p. 60° (0.3 mm.) to 176° (0.4 mm.), 5.7 g. (60%) of ethyl  $\alpha$ -methyl- $\beta,\beta$ -triphenylpropionate, b.p. 176–182° (0.35 mm.); 2.9 g. of residue remained.

*Anal.* Calcd. for  $C_{22}H_{19}O(OC_2H_5)$ : C, 83.69; H, 7.02;  $OC_2H_5$ , 13.1. Found: C, 83.48; H, 7.24;  $OC_2H_5$ , 12.0.

When methylketene diethylacetal was treated with trityl bromide without catalyst or solvent at a temperature of 80° was necessary to initiate the reaction; ethyl bromide (76%), b.p. 38–40° and a 58% yield of the above tritylated propionic ester were obtained.

Pyrolysis of 14.1 g. of this ester for 1 hour in a Claisen flask at 250° and atmospheric pressure followed by distillation yielded: (a) 0.3 g. of forerun, b.p. < 204 (10 mm.); (b) 3.5 g. of a mixture of triphenylmethane and the ester, b.p. 204–215° (10 mm.); (c) 6.5 g. of the ester, b.p. 215–244° (10 mm.); (d) 3.4 g. of residue; 0.25 g. (7%) of ethyl acrylate,  $n_D^{25}$  1.3995 was caught in the Dry Ice-acetone trap.

Crystallization of fraction (b) from petroleum ether (b.p. 65°) yielded 1.0 g. (10%) of triphenylmethane, m.p. 88–90.5°. Crystallization of fraction (c) from benzene yielded an additional 0.3 g. (3%) of impure triphenylmethane, m.p. 73–82°.

**Alkylations of Dimethylketene Dimethylacetal (I) with Various Alkyl Halides and Catalysts.** (a) ***n*-Propyl Chloride and  $SnCl_4$ .**—A solution of 5.2 g. (0.02 mole) of anhydrous stannic chloride in 15.9 g. (0.2 mole) of *n*-propyl chloride was placed in a 200-ml. flask with three ground glass joints fitted with a stirrer, a dropping funnel and a spiral condenser leading to a Dry Ice-acetone trap. A solution of 23.2 g. (0.2 mole) of I in 15.9 g. (0.2 mole) of *n*-propyl chloride was added dropwise with stirring over a 30-minute period as reflux was maintained by application of heat. At this time 0.90 g. (9%) of methyl chloride and 0.25 g. of propyl chloride had collected in the cold trap. Further refluxing for 25 minutes yielded no additional distillate. Addition of another 5.2 g. (10 mole per cent.) of stannic chloride in one

portion caused the appearance of a yellow color in the reaction mixture accompanied by vigorous reflux. After 10 minutes the color had disappeared and 1.0 g. (10%) of methyl chloride had collected in the cold trap. After several minutes of additional reflux had failed to produce any further condensate, 41.6 g. (80 mole per cent.) of stannic chloride was added over a period of 15 minutes with no external heating. After standing overnight the mixture was refluxed for 1.75 hours. At this time the total volatile material which had been collected consisted of 6.80 g. (67%) of methyl chloride and 1.15 g. of propyl chloride.

Addition of 40 ml. of water to the reaction mixture followed by washing of the upper layer with 10 ml. of water yielded 49.2 g. of organic material. Distillation of this material through a 25-cm. Heli-Pak column yielded the following fractions: (a) 12.10 g. of *n*-propyl chloride, b.p. 43–45.8° (740 mm.),  $n_D^{25}$  1.3850; (b) 11.70 g. of *n*-propyl chloride, b.p. 45.8–46° (740 mm.),  $n_D^{25}$  1.3862; (c) 1.90 g. of intermediate fraction, b.p. 46–90° (740 mm.),  $n_D^{25}$  1.3847; (d) 8.30 g., b.p. 90–94° (740 mm.),  $n_D^{25}$  1.3822; (e) 6.55 g., b.p. 94–98° (740 mm.),  $n_D^{25}$  1.3849; (f) 2.75 g., b.p. 86° (170 mm.),  $n_D^{25}$  1.3879; (g) 4.1 g. residue. The presence of methyl pivalate in fractions (d, e and f) was shown by partial saponification to remove the methyl isobutyrate from this mixture. In this way 0.80 g. of methyl pivalate, b.p. 99.5–100.5 (741 mm.),  $n_D^{25}$  1.3870 was obtained. The composition of these fractions was then estimated on the basis of refractive index. In this way the yields of methyl isobutyrate and methyl pivalate were estimated to be 10.0 g. (49%) and 7.8 g. (34%), respectively.

(b) ***n*-Butyl Chloride with  $ZnCl_2$  and  $HgCl_2$ .** **Methyl  $\alpha$ -Chloromercuri-isobutyrate (XII).**—A mixture of 23.2 g. (0.2 mole) of I, 46.25 g. (0.5 mole) of *n*-butyl chloride, and 1.0 g. (3.7 mole per cent.) of fused zinc chloride, was placed in a 125-ml. flask fitted with a stirrer and spiral condenser leading to a Dry Ice-acetone trap. All joints were ground glass and the opening to the air was through a calcium chloride tube. After seven hours of reflux with stirring, during which time the zinc chloride remained insoluble, 0.15 g. (1.5%) of methyl chloride had collected in the cold trap; an additional 12 hours of reflux yielded only 0.05 g. (0.5%) of additional methyl chloride. To this mixture then was added 5.43 g. (10 mole per cent.) of mercuric chloride. After 2 hours of reflux 1.0 g. (10%) of methyl chloride had collected in the cold trap. Addition of another 5.43 g. (10 mole per cent.) of mercuric chloride was followed by the evolution of 1.0 g. (10%) of methyl chloride within 20 minutes as the mercuric chloride went into solution. The remaining 43.4 g. (80 mole per cent.) of mercuric chloride was added and after 40 minutes reflux 7.8 g. (77%) more methyl chloride (b.p. –22 to –15°, 740 mm.) had collected in the cold trap. This methyl chloride contained no butylene, as shown by negative unsaturation tests. Removal of the volatile material under reduced pressure left 66.8 g. (99%) of methyl  $\alpha$ -chloromercuri-isobutyrate (XII) (in addition to the 1.0 g. of zinc chloride) in the pot. One crystallization from diethyl ether gave an analytical sample, m.p. 97–98.2°. Analysis for mercury was carried out gravimetrically as follows: a weighed 1-gram sample was dissolved in 10 ml. of concentrated hydrochloric acid, in which it was immediately soluble. After standing overnight this solution was diluted to 200 ml. and the mercuric ions were precipitated with hydrogen sulfide.

*Anal.* Calcd. for  $C_5H_9O_2HgCl$ : Hg, 59.49. Found: Hg, 59.75.

A mixture of 33.7 g. (0.1 mole) of XII and 13.7 g. (0.1 mole) of *n*-butyl bromide was refluxed for 20 hours. After 4 hours the temperature at the stillhead had dropped to 78°. Distillation through a 25-cm. Podbielniak column yielded 8.7 g. (94%) of *n*-butyl chloride and 0.5 g. (5%) of methyl isobutyrate; 34.2 g. of solid residue remained in the reaction flask.

(c) ***n*-Butyl Bromide and  $ZnCl_2$ .**—A mixture of 23.2 g. (0.2 mole) of I, 68.5 g. (0.5 mole) of *n*-butyl bromide and 2.0 g. (7.3 mole per cent.) of zinc chloride was refluxed for 34 hours. After this time, 23.0 g. of a mixture of 2-butene and methyl bromide had collected in the cold trap. Titration of the butene in this condensate with bromine in carbon tetrachloride solution followed by slow reflux for 2 hours into a spiral condenser leading to a Dry Ice-acetone trap yielded in the cold trap 19.0 g. (100%) of methyl bromide, b.p. 4–10°. Distillation of the higher boiling material



through a 25-cm. Podbielniak column yielded 7.2 g. (17%), of 2,3-dibromobutane, b.p. (no decomposition) 153–155° (741 mm.),  $n_D^{25}$  1.5094; reported<sup>22</sup> b.p. of mixture of *dl* and *meso*, 157–158°. For comparison, a sample of dibromoisobutylene prepared from isobutylene showed a boiling point of 145–147° (738 mm.) with decomposition.

Removal of the volatile material from the reaction vessel at 0.5 mm. pressure yielded 66.3 g. of distillate and 3.7 g. of dark residue. Distillation of the volatile material through an efficient true-bore annular space column yielded, in addition to recovered *n*-butyl bromide, 2.8 g. (15%) of *n*-butyl chloride, 3.6 g. (18%) of methyl isobutyrate, and 23.4 g. (74%) of methyl  $\alpha,\alpha$ -dimethylcaproate, the major portion of which boiled at 164–167° (742 mm.),  $n_D^{25}$  1.4121. Refractionation through a 25-cm. Heli-Pak column yielded an analytical sample of methyl  $\alpha,\alpha$ -dimethylcaproate (XIV), b.p. 168.5° (740 mm.),  $n_D^{25}$  1.4124,  $d_4^{25}$  0.8707.

*Anal.* Calcd. for  $C_8H_{18}O_2$ : C, 68.31; H, 11.46;  $OCH_3$ , 19.6;  $M_{rD}$ , 44.73. Found: C, 68.25; H, 11.41;  $OCH_3$ , 16.1;  $M_{rD}$ , 45.22.

Overnight saponification of 5.5 g. of XIV in alcoholic potassium hydroxide yielded 3.0 g. (60%) of  $\alpha,\alpha$ -dimethylcaproic acid, b.p. 216–220° (726 mm.),  $n_D^{25}$  1.4240; reported<sup>23a</sup> b.p. 210–218°. Upon successive treatments with thionyl chloride and ammonium hydroxide 2.7 g. of this acid yielded 1.8 g. (66%) of  $\alpha,\alpha$ -dimethylcaproamide, m.p. 77–85°. One recrystallization from pentane raised the melting point to 92–93°; reported<sup>23a,b</sup> m.p. 88–89°, 92°.

The other butylations of I, which are listed in Table II, were carried out and worked up in a manner similar to that described in (c).

(d) **2-Bromoöctane and  $ZnCl_2$ .**—A mixture of 22.3 g. (0.192 mole) of I, 92.5 g. (0.480 mole) of 2-bromoöctane, b.p. 65.2–66.0° (11 mm.),  $n_D^{25}$  1.4482, and 1.92 g. (7.3 mole per cent.) of fused zinc chloride was refluxed for five hours. At this time 19.7 g. (108%) of methyl bromide, b.p. 1–7° (739 mm.), had collected in the cold trap, and all the catalyst had dissolved.

Distillation of the volatile material under reduced pressure gave 91.6 g. of distillate, which fumed from hydrogen bromide, and 3.8 g. of black residue. Distillation through an efficient true-bore annular space column of the material boiling below 137° and of the higher boiling material

through a 25-cm. Vigreux column yielded: (a) 8.15 g. (42%) of methyl isobutyrate, b.p. 88–95°; (b) 6.00 g. of intermediate fraction, b.p. 95–119.5°, containing, on the basis of refractive index, 3.9 g. (20%) of methyl isobutyrate and 2.1 g. (10%) of octylene, (c) 19.10 g. (89%) of a mixture of 1-octene and 2-octene the properties of which indicate a predominance of the latter, b.p. 119.5–122.1° (739 mm.), mainly at 121.0–122.1° (739 mm.),  $n_D^{25}$  1.4099,  $d_4^{25}$  0.735; reported<sup>24</sup> for 2-octene, b.p. 124.1–124.7 (745 mm.) (123–123.5°),  $n_D^{25}$  1.4149,  $d_4^{25}$  0.7248; (d) 8.70 g. of intermediate fraction, b.p. 47–63° (11 mm.), (e) 33.60 g. of recovered 2-bromoöctane, b.p. 63–70° (11 mm.), (f) 2.30 g. of intermediate fraction, b.p. 66–123° (11 mm.); (g) 1.90 g. of an unsaturated hydrocarbon, b.p. 123–125° (11 mm.),  $n_D^{25}$  1.4439,  $d_4^{25}$  0.7975; and (h) 1.6 g. of residue. Extraction of fraction (d) with base yielded 1.7 g. (10%) of isobutyric acid,  $n_D^{25}$  1.3928; neut. equiv., 92 (calcd. 88).

(e) ***t*-Amyl Bromide.**—A mixture of 11.6 g. (0.1 mole) of I and 15.1 g. (0.1 mole) of *t*-amyl bromide was refluxed for 11 days. After this time, 10.3 g. of a mixture of methyl bromide and amylenes had collected in the cold trap. Distillation of this cold trap material through a 25-cm. Podbielniak column yielded 6.1 g. of material in the cold trap and 1.5 g. (21%) of a mixture of amylenes, b.p. 31–34° (740 mm.),  $n_D^{25}$  1.3765. The material caught in the cold trap absorbed 3.6 g. of bromine, corresponding to an additional 1.5 g. (21%) of amylene. Distillation of the bromination mixture gave the dibromo derivative, b.p. 58–62° (16 mm.),  $n_D^{25}$  1.5071,  $d_4^{25}$  1.6642; reported<sup>25</sup> for 1,2-dibromo-2-methylbutane, b.p. 47.2–48.0° (9 mm.),  $n_D^{25}$  1.5088,  $d_4^{25}$  1.6711. Subtraction of the 3.0 g. of amylene from the 10.3 g. of volatile material leaves 7.3 g. (77%) of methyl bromide.

Distillation of the remaining reaction mixture through a 25-cm. Heli-Pak column yielded: (a) 9.20 g. of an azeotrope of methyl isobutyrate and *t*-amyl bromide, b.p. 88–91° (739 mm.),  $n_D^{25}$  1.3990; (b) 4.95 g. of a mixture of methyl isobutyrate, *t*-amyl bromide and I, b.p. 91–108°; and (c) 1.7 g. of liquid residue, b.p. 108–230°. The amount of I in fractions (a) and (b) was estimated by titration with bromine. The *t*-amyl bromide content was obtained by extraction of the other components with 85% phosphoric acid. On this basis the yields of products were estimated as: recovered I (18%), recovered *t*-amyl bromide (30%), and methyl isobutyrate (71%).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Ketene Acetals. XXXI. Dimethylketene Ethyleneacetal

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Dimethylketene ethyleneacetal (IV), prepared by the dealcoholation of methyl ethylene orthoisobutyrate (II), has extraordinary reactivity for a disubstituted ketene acetal. It reacts exothermically with benzyl bromide at room temperature to yield the benzylated ester V, and spontaneously with oxygen to form polymeric material containing one atom of oxygen per ketene acetal unit; smaller amounts of the cyclic dimer IX, acetone and ethylene carbonate are the other products of this autoxidation.

The unusual reactivities of ketene cyclic acetals (2-methylene-1,3-dioxolanes and 1,3-dioxanes) and certain of their halogen derivatives, which may be prepared by the dehydrohalogenation of the corresponding  $\alpha$ -haloacetals, were reported<sup>2</sup> in paper XIX of this series. It seemed of interest to prepare a cyclic analog of dimethylketene dimethylacetal<sup>3</sup> and compare its properties with those of the

latter compound as well as with those of the previously reported<sup>2</sup> ketene cyclic acetals. This paper describes the preparation and some of the remarkable properties of dimethylketene ethyleneacetal (IV).

McNall<sup>4</sup> in this Laboratory prepared some alkyl ethylene orthoesters,  $RC(OR')OCH_2CH_2O$ , in the

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