[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XVII. The Alkylation and Acylation of Substituted Ketene Acetals

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In the seventh paper[3] of this series it was shown that the methylene carbon of ketene diethylacetal (I) could be directly alkylated by heating the acetal with such halides as *n*-butyl bromide, allyl bromide and benzyl bromide. As would be expected, *n*-butyl bromide was the least reactive of these halides, and the conditions (seventy-two hours at 250°) necessary to cause it to react were so drastic that only 13% of the alkylated product, ethyl caproate, was obtained; the remainder of the ketene acetal was pyrolyzed to ethylene and ethyl acetate. With the more reactive allyl and benzyl bromides, however, reaction with the acetal occurred at lower temperatures (190 and 125°) and good yields of alkylated acetic esters were obtained, particularly when benzyl bromide was used.

An interesting feature of the alkylations with these more reactive bromides was that the dialkylacetic ester (VI) was found to be the principal product of the reaction. The formation of VI and of the smaller amount of the monoalkylacetic ester (III) were ascribed to the following reactions.

$$\underset{\text{I}}{CH_2{=}C(OC_2H_5)_2} \xrightarrow{RBr} \underset{\text{II}}{[RCH_2C(OC_2H_5)_2Br]} \longrightarrow \underset{\text{III}}{RCH_2COOC_2H_5} + C_2H_5Br$$

$$\underset{\text{II}}{[RCH_2C(OC_2H_5)_2Br]} \xrightarrow{-HBr} \underset{\text{IV}}{RCH{=}C(OC_2H_5)_2} \xrightarrow{RBr} \underset{\text{V}}{[R_2CHC(OC_2H_5)_2Br]} \longrightarrow \underset{\text{VI}}{R_2CHCOOC_2H_5} + C_2H_5Br$$

Since the reaction went preponderantly in the direction of VI, it appeared that the intermediate (II) preferentially underwent dehydrobromination to IV rather than decomposition into ethyl bromide and III. There was no indication that the presumed intermediate (V) similarly lost hydrogen bromide, as no trialkylacetic ester was found among the reaction products.

Nevertheless it seemed worth while to study the direct alkylation of certain monoalkylated ketene acetals to determine if such an intermediate as V could be caused to lose hydrogen bromide and yield a dialkylketene acetal, which then might be further alkylated to a trisubstituted acetic ester. The present paper reports the results of this study.

Exploratory experiments with the previously described[4] *n*-propylketene diethylacetal showed that the temperatures necessary to produce C-alkylation of the acetal were also sufficient to cause extensive pyrolysis of the acetal to ethyl valerate. Because of this tendency of the diethylacetals to pyrolyze, the dimethyl acetals were used in the subsequent work, since ketene dimethylacetal had been found[5] to be much more resistant to pyrolysis than the corresponding diethylacetal.

n-Propyl- and *n*-heptylketene dimethylacetals react with benzyl bromide at temperatures of 140 and 180°, respectively. After a few (three to five) hours the evolution of methyl bromide ceased in each case, and from the reaction mixtures methyl α-benzylvalerate and methyl α-benzylpelargonate were obtained in 83 and 87% yields, respectively. There was no indication of the formation of a trisubstituted acetic ester from either of these monoalkylketene dimethylacetals. These results confirm the postulated mechanism by which disubstituted acetic esters are formed from ketene diethylacetal[3] (II → IV → V → VI) and furnish further evidence that intermediates of the structure V lose bromine only in the form of ethyl (or methyl) bromide.

It seemed that such an intermediate as V would be more likely to lose the elements of hydrogen bromide and form a disubstituted ketene acetal if at least one of the R groups were phenyl which would serve to activate the hydrogen to be eliminated. The facile pyrolysis of triethyl and trimethyl phenylacetates to the corresponding phenylketene acetals[6] are examples of such α-hydrogen activation by the phenyl group. Phenylketene diethylacetal gave more satisfactory results than *n*-propylketene diethylacetal when alkylated with benzyl bromide. The monoalkylated product, ethyl α,β-diphenylpropionate was obtained in 59% yield along with 39% of ethyl phenylacetate, the pyrolysis product of the acetal. Phenylketene dimethylacetal under the same conditions of reaction yields 68% of methyl α,β-diphenylpropionate. There was, however, no indication that any of the trisubstituted acetic esters, ethyl or methyl α,β,β′-triphenylisobutyrate, were formed in these reactions.

Diethyl sulfate also was studied as an alkylating agent in the hope that it would be more active

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(3) McElvain and Kudinger, THIS JOURNAL, **64**, 254 (1942).

(4) McElvain, Clarke and Jones, *ibid.*, **64** 1966 (1942).

(5) McElvain, Anthes and Shapiro, *ibid.*, **64**, 2525 (1942).

(6) Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922); see also ref. 8.

than the alkyl bromides. When heated with *n*-propylketene dimethylacetal (VII) for fifteen hours at 145°, diethyl sulfate produced a 65% yield of an alkylated product, which, surprisingly, proved to be methyl *α-methyl*valerate (XI); 20% of the ketene acetal was recovered unchanged. None of the expected methyl *α*-ethylvalerate (IX) was isolated. These results indicate that the following sequence of reactions probably had occurred:

$$C_3H_7CH{=}C(OCH_3)_2 + (C_2H_5)_2SO_4 \longrightarrow$$
$$\underset{\text{VII}}{[C_3H_7CHC_2H_5C(OCH_3)_2SO_4C_2H_5]} \longrightarrow$$
$$\underset{\text{VIII}}{C_3H_7CHC_2H_5COOCH_3} + \underset{\text{X}}{CH_3SO_4C_2H_5}$$
$$\underset{\text{IX}}{}$$

$$C_3H_7CH{=}C(OCH_3)_2 + CH_3SO_4C_2H_5 \longrightarrow$$
$$[C_3H_7CHCH_3C(OCH_3)_2SO_4C_2H_5] \longrightarrow$$
$$\underset{\text{XI}}{C_3H_7CHCH_3COOCH_3} + CH_3SO_4C_2H_5$$

The conversion of VII to XI instead of IX is due to the greater reactivity of methyl ethyl sulfate as a methylating agent than as an ethylating agent. The preferential methylating action of this reagent has been observed by Thayer[7] in the alkylation of phenol. It is, however, rather surprising that the selective methylation of the ketene acetal should persist in the presence of the large excess of diethyl sulfate that exists in the reaction mixture. If the above reaction course is valid, it seemed that the ketene acetal should be alkylated by catalytic amounts of dimethyl sulfate, which would serve merely as a carrier of one of the methoxyl-methyl groups of the acetal from the oxygen to the *α*-carbon

$$C_3H_7CH{=}C(OCH_3)_2 \longrightarrow C_3H_7CHCH_3COOCH_3$$

When an experiment in this direction was tried, it was possible to isolate a 30% yield of *α*-methylvaleric acid from the saponification of the ester fraction obtained from the interaction of *n*-propylketene dimethylacetal with 0.05 of an equivalent of dimethyl sulfate. This result demonstrates the validity of the suggested mechanism for the methylation of the dimethylacetal with diethyl sulfate. While the alkyl sulfates are definitely more active than the alkyl halides as alkylating agents for the ketene acetals (*cf.* reactivity of *n*-butyl bromide, ref. 3), their use is limited by the alkyl interchange that may result between the acetal and the alkyl sulfate.

The acyl chlorides, acetyl and benzoyl chlorides, were shown in the earlier work[8] to react with ketene diethylacetal to yield the corresponding O-acyl-acylacetic esters, $RC(OCOR){=}CHCOOC_2H_5$ (R is CH_3 or C_6H_5). In the present work *n*-propylketene dimethylacetal was found to react exothermically with benzoyl chloride to yield a dibenzoylvaleric ester. The exact structure of this product was not determined, but it is assumed to be methyl O-benzoyl-*α*-benzoylvalerate (XII) from analogy to the product obtained from the reaction of ketene diethylacetal with benzoyl chloride. The over-all reaction between the acetal and benzoyl chloride is

$$2CH_3CH_2CH_2CH{=}C(OCH_3)_2 + 2C_6H_5COCl \longrightarrow$$
$$2CH_3Cl + \underset{\text{XII}}{C_6H_5C(OCOC_6H_5){=}C(CH_2CH_2CH_3)COOCH_3} + CH_3(CH_2)_3COOCH_3$$

The ester XII was obtained in 60% yield as a viscous oil which crystallized after standing for about two months. Recrystallization gave XII as a fine white powder, which melted at 61–63°. Alkaline hydrolysis converted XII to valerophenone and benzoic acid.

The experiments described above show that an alkyl or phenyl substituent does not greatly modify the reactivity of the anionoid center of a ketene acetal toward C-alkylation with such a reactive halide as benzyl bromide. However, with these monosubstituted ketene acetals there is no evidence of any of the dialkylation that is the preponderant reaction with the unsubstituted ketene acetal.

In view of these results, it seemed of interest to determine the effect of a halogen substituent on the reactivity of a ketene acetal in this type of reaction. When chloroketene diethylacetal was treated with either benzyl or benzoyl chloride under the conditions used for the alkylketene acetals, an insignificant amount of reaction, as measured by the evolution of ethyl chloride, occurred. In each case the reactants were recovered unchanged and in good yields. This behavior indicates that the halogen substituent depresses the anionoid reactivity of the ketene acetal to such an extent that even the very reactive benzoyl chloride fails to acylate it.

Experimental

n-Propyl- and *n*-heptylketene dimethylacetals were prepared as described below from the corresponding *α*-bromo-orthoesters.[4] Phenylketene dimethyl- and diethylacetals were obtained by the pyrolysis of the corresponding esters of orthophenylacetic acid.[8]

Methyl Orthovalerate.—A solution of 166 g. (2 moles) of valeronitrile and 90 ml. (2.2 moles) of anhydrous methanol in 750 ml. of anhydrous diisopropyl ether (this ether as a diluent gave a more satisfactory reaction and product than did diethyl ether) was cooled in an ice-bath and treated with dry hydrogen chloride until 78 g. (2.2 moles) had been absorbed. The container was stoppered tightly and allowed to stand in a refrigerator for forty-eight hours. The white, crystalline precipitate that formed was filtered off and the mother liquors concentrated to yield a second crop of crystals. The total yield of **methyl imidovalerate hydrochloride**, after trituration with diisopropyl ether and drying in a vacuum desiccator, amounted to 240 g. (79%).

Anal. Calcd. for $C_6H_{14}ONCl$: Cl, 23.4. Found: Cl, 23.2.

A mixture of 151 g. (1 mole) of methyl imidovalerate hydrochloride and 400 ml. of anhydrous methanol was stirred vigorously at room temperature in a flask, fitted with reflux condenser protected with a calcium chloride tube, until the salt was dissolved. Then 1300 ml. of anhydrous diethyl ether was added, and the resulting fine salt suspension stirred and refluxed gently for eighteen hours. After this time the ethereal solution was cooled

(7) Thayer, THIS JOURNAL, **46**, 1044 (1924).

(8) McElvain and Stevens, *ibid.*, **68**, 1917 (1946).

in ice and the precipitated ammonium chloride (48 g., 90%) filtered off and washed with a small amount of ether. The combined ether solutions were distilled to remove the solvent and the residue fractionated through a 20-cm. modified Widmer column; 129 g. (79%) of methyl orthovalerate, b. p. 164–166°; d^{27}_4 0.9413; $n^{24}D$ 1.4090, was obtained.

Anal. Calcd. for $C_6H_{13}O_3$: C, 59.23; H, 11.18. Found: C, 59.42; H, 10.80.

The residue from the distillation of the orthoester consisted of 10 g. (10%) of valeramide, which after one recrystallization from an ethyl acetate–petroleum ether (60–68°) mixture, melted at 101–105°.

Methyl Orthopelargonate.—This ester was prepared in the same manner as methyl orthovalerate. The intermediate **methyl imidopelargonate hydrochloride** was obtained in 79% yield.

Anal. Calcd. for $C_{10}H_{22}ONCl$: Cl, 17.1. Found: Cl, 17.1.

Methanolysis of this hydrochloride gave 5% of pelargonamide, m. p. 96–98°, and a 78% yield of methyl orthopelargonate, b. p. 138–140° (45 mm.); d^{23}_4 0.8985; $n^{21}D$ 1.4255.

Anal. Calcd. for $C_{12}H_{26}O_3$: C, 66.01; H, 12.01. Found: C, 65.78; H, 11.92.

Methyl Ortho-α-bromovalerate.—To a mixture of 162 g. (1 mole) of methyl orthovalerate, 87 g. (1.1 moles) of dry pyridine and 150 ml. of carbon tetrachloride, contained in a 1-liter flask fitted with a stirrer, dropping funnel and a reflux condenser, was added dropwise and with stirring a solution of 160 g. (1 mole) of bromine in 200 ml. of carbon tetrachloride. The reaction was cooled at first, but toward the end of the bromine addition was allowed to come to room temperature; after the addition was completed, the reaction mixture was warmed to 50° in a water-bath. The orange salts (there was always some unreacted pyridine perbromide or pyridine hydrobromide perbromide present to color the white pyridine hydrobromide) were filtered off and thoroughly triturated with dry ether. The pale green ether–carbon tetrachloride solution then was distilled through a 20-cm. modified Widmer column. The main fraction distilled at 85–98° (14 mm.); this on refractionation gave 191 g. (79%) of methyl ortho-α-bromovalerate, b. p. 93–96° (14 mm.); d^{27}_4 1.2681; $n^{25}D$ 1.4507.

Anal. Calcd. for $C_6H_{17}O_3Br$: C, 39.84; H, 7.11; Br, 33.2. Found: C, 39.72; H, 6.98; Br, 33.5.

When the previously reported procedure,[9] which used no carbon tetrachloride as a solvent and washed the bromoester with aqueous sodium carbonate before distillation was followed in this preparation, the maximum yield of methyl orthobromovalerate was 63% of the theoretical.

Methyl Ortho-α-bromopelargonate.—This bromoester was prepared from methyl orthopelargonate as described above. It was obtained in 65% yield and boiled at 110–112° (0.7 mm.); d^{23}_4 1.1526; $n^{25}D$ 1.4528.

Anal. Calcd. for $C_{12}H_{25}O_3Br$: C, 48.49; H, 8.48; Br, 26.8. Found: C, 48.60; H, 8.52; Br, 26.6.

n-Propylketene Dimethylacetal.—To a vigorously stirred suspension of 25.3 g. (1.1 atom) of fine sodium sand in 400 ml. of gently refluxing benzene was added dropwise 120 g. (0.5 mole) of methyl ortho-α-bromovalerate. The addition required about four hours, after which the reaction mixture was stirred and refluxed for an additional six hours. After the first few minutes the reaction mixture turned the deep blue color that is characteristic of this type of reaction. After centrifuging and thoroughly washing the precipitated sodium salts with dry ether, the combined ether–benzene solution was distilled. The *n*-propylketene dimethylacetal so obtained boiled at 67–68° (47 mm.); d^{27}_4 0.8834; $n^{24}D$ 1.4235; and weighed 44 g. (68%).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.60; H, 10.84; CH_3O, 47.7. Found: C, 64.85; H, 10.46; CH_3O, 46.1.

(9) Walters and McElvain, This Journal, **62**, 1482 (1940).

A 2-g. sample of this ketene acetal, when treated with the theoretical amount of water containing a trace of hydrochloric acid, spontaneously warmed to 70°. Distillation of the resulting homogeneous product gave methyl valerate, b. p. 125–128°; $n^{20}D$ 1.3981; sapn. equiv., 116 (calcd. 116).

***n*-Heptylketene Dimethylacetal.**—This acetal was prepared from methyl ortho-α-bromopelargonate in the manner described above. It boiled at 100–105° (10 mm.); d^{23}_4 0.8655; $n^{20}D$ 1.4370; and was obtained in 87% yield.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.91; CH_3O, 33.3. Found: C, 70.69; H, 11.79; CH_3O, 32.1.

Reaction of Benzyl Bromide with *n*-Propyl- and *n*-Heptylketene Dimethylacetals.—A mixture of 34 g. (0.2 mole) of benzyl bromide and 26 g. (0.2 mole) of *n*-propylketene dimethylacetal was heated in a flask connected through a 20-cm. still head to a Dry Ice trap. When the temperature of the heating bath reached 140°, methyl bromide, b. p. 4–5°, began to distil from the reaction mixture and collect in the Dry Ice trap. After five hours, no more of the methyl bromide appeared to be leaving the reaction mixture; 14.5 g. (77%) had collected in the trap. Fractionation of the remaining material in the reaction flask yielded 4.5 g. of benzyl bromide and 33.8 g. (83%) of **methyl α-benzylvalerate,** b. p. 108–110° (1.5 mm); d^{27}_4 0.9809; $n^{25}D$ 1.4897.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79; CH_3O, 15.10; sapn. equiv., 206. Found: C, 75.55; H, 8.82; CH_3O, 15.15; sapn. equiv., 204.

Saponification of this ester gave, after acidification, **α-benzylvaleric acid,** b. p. 164–165° (8 mm.); d^{27}_4 1.0185; $n^{25}D$ 1.5042. After standing for four months this acid solidified; recrystallization gave the solid acid, m. p. 40–42°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; neut. equiv., 192. Found: C, 75.09; H, 8.34; neut. equiv., 194.

Conversion of this acid to the amide *via* the acid chloride (thionyl chloride) gave **α-benzylvaleramide** as silky, white needles, m. p. 122–123°.

Anal. Calcd. for $C_{12}H_{17}ON$: C, 75.35; H, 8.96. Found: C, 75.03; H, 8.79.

When *n*-heptylketene dimethylacetal was used instead of the *n*-propylketene acetal in the above experiment, a temperature of 180° was required to initiate the reaction and only three hours of heating were necessary to complete the evolution of methyl bromide. From 12.8 g. (0.07 mole) of *n*-heptylketene dimethylacetal and 11.7 g. (0.07 mole) of benzyl bromide, 4.1 g. (63%) of methyl bromide was collected and 15.7 g. (87%) of **methyl α-benzylpelargonate,** b. p. 156–158° (1.5 mm.); d^{23}_4 0.9455; $n^{20}D$ 1.4846 was obtained from the fractionation of the reaction mixture.

Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.81; H, 9.99; sapn. equiv., 262. Found: C, 77.48; H, 9.88; sapn. equiv., 264.

Saponification of this ester gave **α-benzylpelargonic acid** as a viscous, pale yellow oil, b. p. 160–165° (0.1 mm.); $n^{22}D$ 1.4940.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74; neut. equiv., 248. Found: C, 77.00; H, 9.78; neut. equiv., 249.

α-Benzylpelargonamide, prepared from this acid *via* the acid chloride, melted at 90–92°.

Anal. Calcd. for $C_{16}H_{25}ON$: N, 5.66. Found: N, 5.66.

Reaction of Benzyl Bromide with Phenylketene Diethyl- and Dimethylacetals.—Each of these acetals was heated with benzyl bromide until the evolution of the alkyl bromide ceased. This required four hours at 160° for the diethylacetal and four hours at 200° for the dimethylacetal. Fractionation of the reaction mixture from 22.5 g. of the diethylacetal and 20 g. of benzyl bromide yielded 7.5 g. (39%) of ethyl phenylacetate, b. p. 120–125° (24 mm.) and 17.7 g. (59%) of ethyl α,β-diphenyl-

propionate,[10] b. p. 134–136° (1 mm.); d^{27}_4 1.0585; $n^{27}D$ 1.5428. Fractionation of the reaction mixture from 10 g. of the dimethylacetal and 10.5 g. of benzyl bromide gave 9.9 g. (68%) of methyl α,β-diphenylpropionate,[10] b. p. 125–127° (0.5 mm.); d^{24}_4 1.0825; $n^{24}D$ 1.5562; OCH_3, 13.6% (calcd., 13.0%).

Saponification of each of the above esters gave α,β-diphenylpropionic acid,[10] b. p. 178–179° (2 mm.); m. p., 85–87°. The amide prepared from this acid melted at 160–161°.[11]

Reaction of Diethyl Sulfate with *n*-Propylketene Dimethylacetal.—A mixture of 30.8 g. (0.2 mole) of freshly distilled diethyl sulfate and 26 g. (0.2 mole) of *n*-propylketene dimethylacetal was heated under a reflux condenser for fifteen hours at 145°. Fractionation of the reaction mixture through a 20-cm. Widmer column gave: (a) 5.6 g. (20%) of unchanged ketene acetal, b. p. 40–65° (50 mm.); (b) 17 g. (65%) of methyl α-methylvalerate, b. p. 65–80° (50 mm.); and (c) 26 g. of alkyl sulfates, b. p., 62–120° (0.6 mm.).

Fraction (b) could not be completely freed of alkyl sulfates by further fractionation, but a product with a saponification equivalent of 132 (calcd. 130) was obtained. A 14-g. sample of this material was saponified and the α-methylvaleric acid isolated by acidification and steam distillation; 9.3 g. of the acid, b. p. 190–195° (740 mm.); $n^{21}D$ 1.4135; neut. equiv. 116.5 (calcd. 116), was obtained. This acid has previously been reported[12] as boiling at 192–194°; $n^{20}D$ 1.4136.

Conversion of this acid to its amide gave a product that melted at 78–82° after one recrystallization from ethyl acetate. Recrystallization of this product from an ethyl acetate–petroleum ether (60–68°) mixture gave an amide that melted at 90–91°. The melting point of this amide has been reported as 80[12] and 85°.[13]

The toluidide of this α-methylvaleric acid melted at 88–89° (previously reported,[12] 80°).

A mixture of 4 g. (0.03 mole) of *n*-propylketene dimethylacetal and 0.2 g. (0.0015 mole) of dimethyl sulfate was refluxed on a hot plate for six hours. Saponification of the reaction product and isolation of the acid as described above gave 1.0 g. (30%) of α-methylvaleric acid, neut. equiv. 115.

Reaction of Benzoyl Chloride with *n*-Propylketene Dimethylacetal. Methyl O-Benzoyl-α-benzoylvalerate.—A mixture of 14 g. (0.1 mole) of benzoyl chloride and 13 g. (0.1 mole) of the ketene acetal gave no indication of reaction when first mixed, but after standing for about ten minutes, the temperature of the mixture began to rise and ultimately reached 70°. Then the mixture was heated for three hours in an oil-bath at 130–140°. During this time 4 g. (80%) of methyl chloride was evolved and collected in a cold trap. Distillation of the remaining material gave 11 g. of a fraction boiling at 60–84° (0.2 mm.), which was a mixture methyl valerate, methyl benzoate and benzoyl chloride. The remaining residue (11 g.) could not be distilled in the ordinary manner, but on evaporative distillation[14] at 0.2 mm. and a jacket temperature of 200–225°, it was obtained as a colorless, very viscous liquid ($n^{26}D$ 1.5560) that weighed 10.5 g. (60%) and which, after standing for about two months, set to a mass of crystals. Recrystallization from anhydrous methanol at −70° gave methyl O-benzoyl-α-benzoylvalerate (XII) as a fine white powder, m. p. 61–63°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.20; CH_3O, 9.57. Found: C, 73.96; H, 6.01; CH_3O, 9.54.

Saponification of the enol-benzoate (XII) in 10% sodium hydroxide solution, followed by steam distillation of the alkaline solution, gave valerophenone (2,4-dinitrophenylhydrazone, m. p. 163–165°; semicarbazone, m. p. 162–164°). Acidification of the alkaline saponification solution gave benzoic acid, m. p. 120–122°.

Attempted Reaction of Chloroketene Diethylacetal with Benzyl Chloride and with Benzoyl Chloride.—A mixture of 12.6 g. (0.1 mole) of benzyl chloride and 16.5 g. (0.11 mole) of chloroketene diethylacetal[15] was heated for 27 hours in an oil-bath at 150–160°; less than 1 g. of ethyl chloride collected in a Dry Ice trap. Repeated distillation of the reaction mixture through a 20-cm. Widmer column failed to separate it into its components. The refractive index, methoxyl and chlorine content of this mixture indicated that it was approximately an equi-molecular mixture of the two starting materials.

A mixture of 15 g. (0.1 mole) of chloroketene diethylacetal and 14 g. (0.1 mole) of benzoyl chloride was heated for five hours at 160°; only 0.5 g. (8%) of ethyl chloride collected in the cold trap. Fractionation of the reaction mixture gave 7.6 g. (51%) of the chloroketene acetal, 12.8 g. (91%) of benzoyl chloride and 5 g. of an undistillable tar.

Summary

A study of the alkylation of monosubstituted ketene acetals is reported. *n*-Propyl- and *n*-heptylketene dimethyl acetals are readily alkylated with benzyl bromide to form methyl bromide and methyl α-benzylvalerate and methyl α-benzylpelargonate, respectively. The corresponding diethylacetals are not satisfactory for this reaction because of the readiness with which they are pyrolyzed into ethylene and the corresponding normal esters. Both phenylketene dimethyl- and diethylacetals are alkylated by benzyl bromide to form methyl and ethyl α,β-diphenylpropionate in 68 and 59% yields, respectively. In none of these alkylations is there any evidence of dialkylation to produce a trisubstituted acetic ester.

The alkylation of *n*-propylketene dimethylacetal with ethyl sulfate yields methyl *α-methylvalerate*, the formation of which is explained. It also is shown that this ketene acetal may be alkylated by catalytic amounts of dimethyl sulfate.

n-Propylketene dimethylacetal reacts with benzoyl chloride to yield methyl O-benzoyl-α-benzoylvalerate. Chloroketene diethylacetal fails to react with either benzyl bromide or benzoyl chloride.

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(10) Meyer, *Ber.*, **21**, 1313 (1888).

(11) The melting point of this amide is reported by Meyer (ref. 10) as 133–134°. The higher melting amide obtained in the present work contained 6.0 N (calcd. 6.2).

(12) Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933); *C. A.*, **27**, 5306 (1933).

(13) Guerbet, *Bull. soc. chim.*, **11**, 168 (1912).

(14) See McElvain, Jelinek and Rorig, THIS JOURNAL, **67**, 1578 (1945), for a description of the apparatus used.

(15) Magnani and McElvain, *ibid.*, **60**, 2210 (1938).