

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

Ketene Acetals. XXXIV. Tetra- and Pentamethylene Ketene AcetalsBY S. M. McELVAIN AND R. E. STARN, JR.¹

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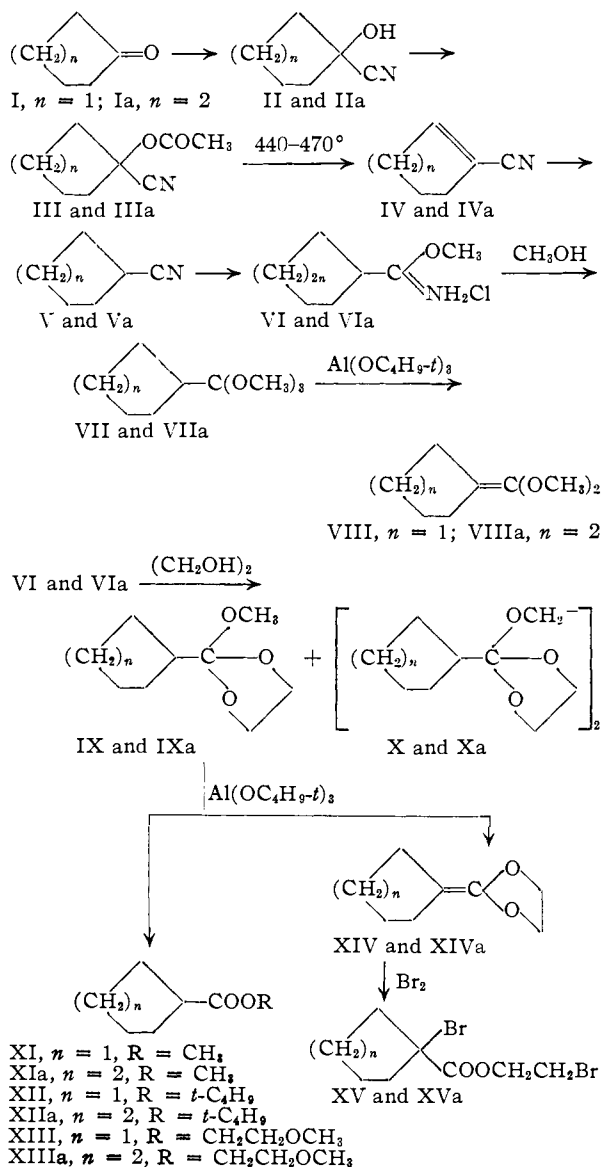
Ketene acetals VIII and VIIIa with the nucleophilic center in a cyclopentane and cyclohexane ring have been prepared by the dealcoholation of the corresponding orthoesters VII and VIIa. These dealcoholations proceed in satisfactory yields only with *sublimed* aluminum *t*-butoxide. Methyl and *t*-butyl normal esters are significant reaction products and evidence is presented as to their mode of formation. Some reactions of these ketene acetals are described. Attempts to prepare the bicyclic ketene acetals XIV and XIVa by dealcoholation of the ortho esters IX and IXa yielded principally normal esters; these ketene acetals were formed in yields too low (5%) to permit their purification.

An improved method of preparation of the α,α -disubstituted orthoester, methyl orthoisobutyrate,^{2a} and the unusual reactivity associated with the cyclic dimethyl ketene ethyleneacetal^{2b} prompted the preparation and study of the properties of tetra- and pentamethylene ketene dimethylacetals (VIII and VIIIa) and the corresponding ethyleneacetals (XIV and XIVa). In the former pair the nucleophilic center of the ketene acetal is a part of the cycle while in the latter pair both the unsaturated carbons of the ketene acetal are in a cyclic structure.

The nitriles, which were required for this work, were prepared from cyclopentanone and cyclohexanone *via* the sequence³ I \rightarrow V. The first three steps of this sequence proceeded in high yields,⁴ but the hydrogenation of IV and IVa to V and Va required considerable study⁵ before satisfactory conditions were found. The saturated nitriles V and Va eventually were obtained in high (93–98%) and reproducible yields under the following conditions: (a) palladium-on-strontium carbonate as catalyst, (b) ether as solvent containing 2 mole per cent. of acetic anhydride to destroy any catalyst-poisoning amine that resulted from the hydrogenation of the nitrile group, and (c) the use of freshly distilled IV and IVa.⁶ Even under these conditions the hydrogenation of the cyanocyclohexene (IVa)

was relatively slow and required about seven times the amount of catalyst that was used for the cyanocyclopentene (IV).

The nitriles V and Va were converted quantitatively to the respective iminoester salts VI and VIa, the structures of which were confirmed by pyrolyses to the corresponding amides.⁷ The reactivities

(7) S. M. McElvain and B. E. Tate, *ibid.*, **73**, 2233 (1951).

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(2) (a) S. M. McElvain and C. L. Aldridge, *THIS JOURNAL*, **75**, 3987 (1953); (b) **75**, 3993 (1953).

(3) This sequence was studied first with model compounds prepared from acetone since methacrylonitrile, corresponding to IV and IVa, was commercially available. This nitrile, however, could be prepared readily in 83% yield by passage of the acetate of acetone cyanohydrin through a glass-packed column at 440–470°. The unsaturated nitrile could be hydrogenated to isobutyronitrile in 85% yield in glacial acetic acid over 5% palladium-on-carbon (*cf.* ref. 2, p. 3989).

(4) The two-step conversion of cyclohexanone cyanohydrin *via* the acetate could be circumvented by the direct dehydration of the cyanohydrin to IVa with thionyl chloride and pyridine (*cf.* B. K. Bhattacharya, *J. Indian Chem. Soc.*, **22**, 85 (1945)). A similar preparation of IV in 60% yield has been reported (A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934)), but this method was found to be capricious in the present work. The preparation of IV *via* III, which was prepared in 91% yields and pyrolyzed in 96% yields, seemed preferable.

(5) The use of palladium-on-carbon in glacial acetic acid, which was effective for the hydrogenation of methacrylonitrile (ref. 2 and 3) caused absorption of 1.2 equivalents of hydrogen and left about 40% of IVa unreacted.

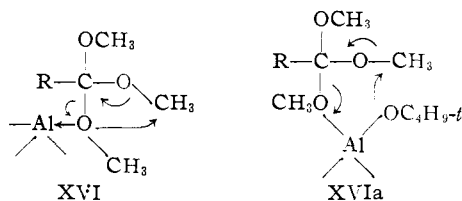
(6) This requirement seems essential but for no apparent reason. The efficiency of the distillation was not important and there was no observable differences in the physical properties of the distilled material. Similar observations have been made on the reduction of certain cyanohydrins to amino alcohols (A. C. Cope, *et al.*, *THIS JOURNAL*, **72**, 1123 (1950)).

of these salts, however, were found to be quite different toward both hydrolysis⁸ and alcoholysis. The application of the improved alcoholysis procedure² to VI gave the orthoester VII in 76–84% yields, but with VIa the alcoholysis was incomplete after 11 days. With some modifications of this procedure it was possible to prepare the orthoester VIIa in 45–58% yields after 6 days of reaction; hexahydrobenzamide (17–27%) was a significant side product. When ethylene glycol was used instead of methanol for the alcoholysis of the salts VI and VIa, the ethylene orthoesters IX and IXa were obtained in *ca.* 58% yields; in each case 13% of the dimeric product X or Xa was isolated.

There was little if any indication of an ester carbonyl band at 5.76 μ in the infrared spectra of these α,α -disubstituted orthoesters. Each of these orthoesters, as well as methyl orthoisobutyrate,² have two recurring strong bands at 8.03 ± 0.03 and $9.34 \pm 0.04 \mu$ and medium bands at 8.67 ± 0.03 and $10.06 \pm 0.06 \mu$ (see Table I). These spectra, together with the analytical data, established the purity of the orthoesters.

The dealcoholation of the methyl orthoesters VII and VIIa with ordinary aluminum *t*-butoxide⁹ gave low yields (43–49%) of *t*-butyl alcohol (as distillate from the reaction) and mixtures of the ketene acetals VIII and VIIIa with the corresponding methyl (XI and XIa) and *t*-butyl (XII and XIIa) normal esters. The latter esters were shown to be the result of an alkyl exchange between the methyl esters and aluminum *t*-butoxide. This side reaction, which had not been observed previously in such dealcoholations,⁹ greatly complicated the separation of the ketene acetals from the reaction mixtures. The use of aluminum methoxide, in order to eliminate this reaction, gave poorer yields of the ketene acetals, increased yields of the methyl esters XI and XIa, and dimethyl ether in amounts equivalent to the normal esters. The production of normal ester in these dealcoholations is reminiscent of the extensive conversion of methyl orthophenylacetate to the normal ester by alumina¹⁰ and prompted the use of sublimed aluminum *t*-butoxide for the dealcoholations. With this reagent the yield of *t*-butyl alcohol rose to 98% with the orthoester VII; the other products were the methyl ester XI (11%), the *t*-butyl ester XII (6%) and the ketene acetal VIII (64%). With the orthoester VIIa, 79% of *t*-butyl alcohol containing less than 2% of methyl *t*-butyl ether, and 18% of dimethyl ether distilled from the reaction; the other products were methyl (13%) and *t*-butyl (10%) hexahydrobenzoates XIa and XIIa, and the ketene acetal VIIIa (58%). The presence of dimethyl ether among the reaction products in an amount approximately equivalent to the two normal esters indicates that the mode of formation of the latter compounds involves the decomposition of the aluminum *t*-butoxide-orthoester complex as indicated in XVI

rather than *via* XVIa. It is apparent, therefore, that the unsublimed aluminum *t*-butoxide contains an impurity, probably alumina, which promotes the formation of normal ester by elimination of the ether at the expense of dealcoholation to form the ketene acetal.



The purities of the ketene acetals were established and their separations from the esters in the distillation foreruns were effected with lithium aluminum hydride. Each of these ketene acetals may be distilled unchanged from this hydride, or the metal salts formed by its reduction of the normal esters.¹¹ The product so obtained gave no reaction with 2,4-dinitrophenylhydrazine reagent—showing the absence of an enol ether from the reduction of the ketene acetal or of any acetal from the reduction of an orthoester—and showed no ester carbonyl band in the infrared spectrum.

Substitution of the methylene carbon of a ketene acetal by alkyl groups shifts the characteristic absorption peak in the infrared from 6.10 to 5.86 μ ; substitution by phenyl groups, however, does not produce any significant change in the absorption (see Table I). The spectra of the disubstituted ketene acetals VIII and VIIIa correspond at this absorption frequency with the other dialkylsubstituted compound, dimethylketene dimethylacetal.

The reaction of the ethylene orthoesters IX and IXa with sublimed aluminum *t*-butoxide gave mainly normal esters. From IX the products were: *t*-butyl alcohol (23%), methyl (36%) and *t*-butyl (42%) cyclopentanecarboxylates (IX and XIII), tetramethyleneketene ethyleneacetal (XIV) (5%), and the β -methoxyethyl ester XIII (4%). The formation of the latter compound is analogous to the formation of dimethyl ether from the trimethyl orthoesters VII and VIIa. From the orthoester IXa the reaction products were: *t*-butyl alcohol (20%), XIa (38%), XIIa (36%), Xa (2%) and XIIIa (2%).

The ketene acetals VIII and VIIIa react with 2,4-dinitrophenylhydrazine in dioxane solution containing zinc chloride to yield crystalline methyl N-2,4-dinitrophenylhydraziminocarboxylates XVII and XVIIa in 43 and 69% yields, respectively. These structures were assigned on the basis of analyses, infrared and ultraviolet spectra, and analogy to the reaction of ketene diethylacetal with aniline.¹²

Both VIII and VIIIa were converted to the corresponding solid 1-benzhydryl methyl esters XVIII

(8) For example, VI was hydrolyzed rapidly to the methyl ester XI (88%) while some of VIa, which has a much lower solubility, remained after an hour of stirring with water; the ester XIa, however, eventually was produced in 91% yield.

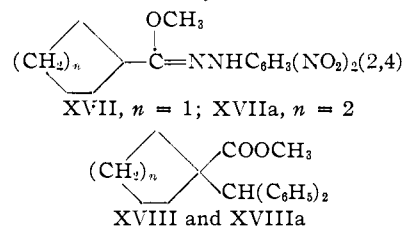
(9) S. M. McElvain and W. R. Davie, *THIS JOURNAL*, **73**, 1400 (1951).

(10) S. M. McElvain and J. T. Venerable, *ibid.*, **73**, 1661 (1950).

(11) The temperatures used for these distillations never exceeded 35°. Higher temperatures were found unsafe, *e.g.*, an explosion and fire resulted from heating phenylketene dimethylacetal with lithium aluminum hydride at 85°, which is about 35° below the reported decomposition point of this hydride (*cf.* W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 484).

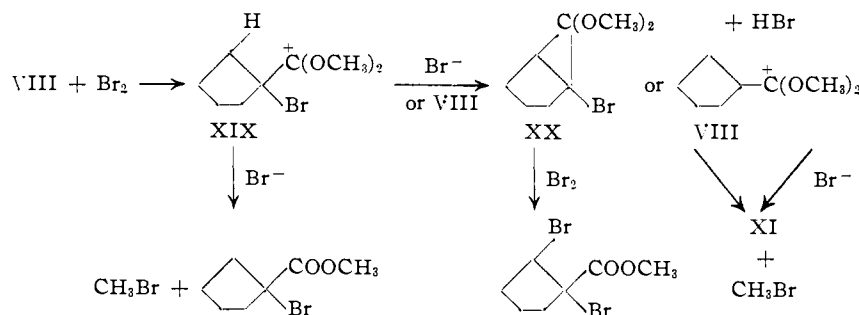
(12) H. M. Barnes, D. Kundiger and S. M. McElvain, *THIS JOURNAL*, **62**, 1281 (1940).

(64%) and XVIIIa (75%), by heating with benzhydryl bromide at 125°. VIIIa also was converted to phenyl cyclohexyl ketone *via* methyl 1-benzoyl-1-cyclohexanecarboxylate, which was obtained from heating VIIIa with benzoyl chloride.



The addition of bromine to VIII at 25° consumed 85% of an equivalent and produced the normal methyl ester XI (10%), the 1-bromoester XXI (73%) and a dibromoester (8%). The latter compound was shown to be the 1,2-dibromoester XXII by debromination with sodium iodide in ethanol to methyl cyclopentene-1-carboxylate. When this bromination was run in carbon tetrachloride solution the absorption amounted to 93% of the theoretical and the products were XI (3%), XXI (91%) and XXII (2%).

The formation of the dibromoester XXII was quite unexpected and at first was thought to be the result of the dehydrobromination of the monobromoester by the ketene acetal; however, these compounds showed no sign of reaction when mixed and allowed to stand at room temperature for several days. It was concluded, therefore, that the dibromoester resulted from the bromination of the cyclopropane structure XX, which could result from the loss of a proton from the cation XIX formed in the first step of the bromination of VIII. The bromide anion or a molecule of VIII would be expected to be of assistance in the removal of the proton. This mechanism requires, as was found, that the unbrominated ester XI and the dibromoester XXII be formed in equivalent amounts.



The ketene acetal VIIIa absorbed 93% of an equivalent of bromine at 0–5° to give the normal ester XIa (6%), methyl 1-bromocyclohexane-carboxylate (85%) and a higher boiling product with a high refractive index, which indicated the dibromoester corresponding to XXII.

The absorption of oxygen by VIIIa was much slower (69% after 161 hr.) than by dimethylketene ethyleneacetal.^{2a} The only products isolated were cyclohexanone (7%) and dimethyl carbonate (28%). The remaining material distilled over a wide range (54° (13 mm.) to 61° (0.05 mm.)) and left

a non-crystalline, ether-soluble residue (*cf.* the ether-insoluble polymer obtained from dimethylketene ethyleneacetal^{2a}).

Experimental

Cyanohydrins II and IIa.—These cyanohydrins were prepared by the procedure of Cox and Stormont¹³ using cyclopentanone and cyclohexanone instead of acetone. II was obtained in 78–88% yields, b.p. 102–106° (9 mm.), n_D^{25} 1.4560¹⁴; IIa was obtained in 88% yields, b.p. 109–113° (9 mm.), n_D^{25} 1.4613.¹⁵

Cyanohydrin Acetates III and IIIa.—These cyanohydrin acetates were prepared by the following procedure: To a well-stirred mixture of 564 g. (5.25 moles) of 95% acetic anhydride and 20 ml. of acetyl chloride at reflux was added cautiously over a period of 70 minutes 455 g. (4.10 moles) of cyclopentanone cyanohydrin (II). The refluxing mixture was stirred 15 minutes longer. Acetic acid and acetic anhydride were removed through a 45 × 1.4 cm. Vigreux column at reduced pressure. Distillation gave 568 g. (91%) of 1-acetoxy-1-cyanocyclopentane (III), b. p. 101–102° (8 mm.), n_D^{25} 1.4458. A center cut was analyzed.

Anal. Calcd. for C₈H₁₁O₂N: C, 62.70; H, 7.24. Found: C, 63.03; H, 7.33.

From the pot residue there was isolated 29.2 g. (3.4%) of N-acetyl-1-acetoxycyclopentanecarboxamide, m.p. 108.5–110° after two recrystallizations from 60–70° petroleum ether. The analytical sample (m.p. 108.5–109.5°) was recrystallized twice more and sublimed.

Anal. Calcd. for C₁₀H₁₅O₄N: C, 56.33; H, 7.09. Found: C, 56.61; H, 6.82.

The infrared spectrum shows an associated NH band at 3.16 μ, a carbonyl band at 5.81 μ, another broad band at 5.93 μ and a shoulder at 6.01 μ. The third carbonyl band required by this structure was not resolved and could be either the broad 5.93 band or the 6.01 shoulder.

The acetate IIIa was obtained by the above procedure in 63–70% yields, b.p. 117–118° (13 mm.), m.p. 47–49°.¹⁶

Preparation of Nitriles IV and IVa. (a) **Pyrolysis of Cyanohydrin Acetates.**—A 32-mm. o.d. Pyrex tube, 80 cm. long, was drawn to an 8 mm. orifice at the lower end and packed with 5 to 10-cm. lengths of 4 mm. Pyrex rod. The tube was surrounded with a 65-cm. heating jacket with a 500° thermometer at its inner surface. The tube was clamped in a vertical position and the constricted lower end connected to a suction-flask cooled in an ice-bath; this first receiver was connected to a smaller suction flask cooled in a Dry Ice-acetone mixture. The top of the tube carried a dropping funnel. Maximum yields were obtained only after the packing had been used several times.

In a typical run 185 g. (1.11 moles) of 1-acetoxy-1-cyanocyclohexane (IIIa) was dropped over a period of 3 hours into the pyrolysis tube maintained at 480–500°. The condensate was neutralized with 61 g. of potassium hydroxide in 100 ml. of water, the aqueous layer extracted with three 100-ml. portions of ether and the combined ether layer dried over magnesium sulfate. After removal of the ether through a 35-cm. Vigreux column, distillation of the residue from a 250-ml. Claisen flask gave 104 g. (88%) of 1-cyanocyclohexene, b.p. 74–

76° (12 mm.), n_D^{25} 1.4791 (reported¹⁶ b.p. 73.8–74.2° (11.5 mm.), n_D^{25} 1.4823).

Similarly 1-cyanocyclopentene (IV) was prepared in 93–96% yields, b.p. 53–54° (11 mm.), n_D^{25} 1.4701.¹⁴

(b) **Dehydration of Cyclohexanone Cyanohydrin.**¹⁷—To a mixture of 21 g. (0.168 mole) of cyclohexanone cyanohydrin (IIa) and 27 ml. of pyridine at 0° was added dropwise

(13) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 7.

(14) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).

(15) R. Van Coillie, *Bull. soc. chim. Belg.*, **42**, 419 (1933).

(16) R. Burns, *et al.*, *J. Chem. Soc.*, 400 (1935).

(17) This reaction was mentioned but not described in detail by B. K. Bhattacharyya (see ref. 4).

over a period of 30 minutes 21.4 g. (0.180 mole) of thionyl chloride. After 4 hours stirring, the sirupy mixture was poured onto 100 g. of ice, the organic layer diluted with 15 ml. of ether and separated. The aqueous layer was extracted three times with 25-ml. portions of ether, and the combined ether extracts dried over magnesium sulfate. The ether was removed through a 14-cm. Vigreux column and the residue distilled from a 25-ml. Claisen flask to give 16.2 g. (90%) of 1-cyanocyclohexene, b.p. 65–67° (9 mm.), n_D^{25} 1.4796. The yield from a similar run using 4 moles of the cyanohydrin was 81%.

Preparation of Nitriles V and Va. Palladium-on-Strontium Carbonate Catalyst.¹⁸—To a well-stirred suspension of 61.5 g. of strontium carbonate in 960 ml. of warm (60°) water was added a palladium chloride solution prepared by heating 6.55 g. of palladium chloride, 6.4 ml. of concentrated hydrochloric acid and 40 ml. of water on a steam-bath. To this suspension then was added 6.4 ml. of 37% formaldehyde. The suspension was made slightly alkaline to litmus with 30% sodium hydroxide solution and stirred 5 minutes. The catalyst was washed twice by decantation, collected on a Büchner funnel, washed with ten 100-ml. portions of water, dried in an oven at 80°, and stored in a glass stoppered bottle.

A solution of 100 g. (1.08 moles) of 1-cyanocyclopentene (IV) and 2.0 ml. of acetic anhydride in 100 ml. of ether was shaken over 1.25 g. of palladium-on-strontium carbonate at one to three atmospheres of hydrogen. The reaction bottle was cooled by a stream of air. Shaking was discontinued when the temperature rose to 45–50°. Hydrogen absorption ceased after 1.09 moles had been absorbed (1.5 hr.). The catalyst was removed by filtration, the solution thoroughly washed with potassium carbonate solution and dried over magnesium sulfate. Distillation through a 10-cm. Vigreux column gave 100.5 g. (98%) of cyclopentyl cyanide (V), b.p. 43–44° (7 mm.), n_D^{25} 1.4409 (reported¹⁹ b.p. 74.5–75° (30 mm.), n_D^{25} 1.4404).

A solution of 210 g. (1.96 moles) of 1-cyanocyclohexene (IVa) and 4.5 ml. of acetic anhydride in 210 ml. of ether was shaken over 13.5 g. of catalyst at one to three atmospheres of hydrogen. The temperature was kept below 45–50° by blowing air on the bottle. After 7.5 hours the hydrogen absorption (1.7 moles) had virtually stopped. After removal of the catalyst by filtration, the mixture was washed four times with 10-ml. portions of 20% potassium hydroxide solution, once with saturated sodium chloride solution, and dried over magnesium sulfate. After removal of the ether, rapid distillation at 12 mm. through a 10-cm. Vigreux column gave 208 g. of liquid, n_D^{25} 1.4559, which was mixed with 0.4 ml. of acetic anhydride in 105 ml. of ether and shaken with 6.3 g. of catalyst until hydrogen absorption ceased (0.52 mole). Distillation through a 1.4 × 17 cm. Heli-Pak column gave 198 g. (93%) cyclohexyl cyanide, b.p. 69–70° (12 mm.), n_D^{25} 1.4493 (reported²⁰ b.p. 187–188°, n_D^{25} 1.4500); after redistillation from phosphorus pentoxide, n_D^{25} 1.4497.

Preparation of Iminoester Hydrochlorides VIa and VI.—To 164 g. (1.50 moles) of cyclohexyl cyanide (Va), 76 ml. of anhydrous methanol and 450 ml. of ether cooled in an ice-bath was added 96 g. (2.64 moles) of anhydrous hydrogen chloride. The mixture was cooled in an ice-bath for 6 hr. and shaken periodically to prevent the formation of a solid cake. After the mixture had stood for 2 weeks in a refrigerator, 300 ml. of ether was added and the mixture kept in the refrigerator for 2 more days. After filtration and storage in a vacuum desiccator over sodium hydroxide for one week, the white, flaky methyl iminocyclohexanecarboxylate hydrochloride (VIa) amounted to 266 g. (100%).

Anal. Calcd. for C₈H₁₆ClNO: Cl, 20.0. Found: Cl, 19.7, 19.9.

A 2.98-g. sample of this iminoester hydrochloride was heated under an air condenser in an oil-bath at 140° for 4.5 hours, and the temperature then raised until the solid melted. The solid formed on cooling was recrystallized from ethanol to yield 1.88 g. (88%) of hexahydrobenzamide, m.p. 186.0–187.5°, undepressed on admixture with an authentic sample. Concentration of the mother liquors and recrystallization from water gave 0.12 g. (6%) more amide, m.p. 184.5–186.0°.

When 61 ml. of water was added to 43.5 g. (0.245 mole) of VIa, the solid did not go into solution immediately. After one hour an organic layer had been formed but some solid still remained. After 5 hr. the organic layer was separated, the aqueous layer extracted three times with 50-ml. portions of ether, the combined ether layers washed with saturated sodium chloride solution, and dried over magnesium sulfate. Distillation through a 1.6 × 17 cm. Heli-Pak column gave 31.7 g. (91%) of methyl cyclohexanecarboxylate (XIa), b.p. 54.5° (7 mm.), n_D^{25} 1.4412 (reported²¹ b.p. 54–54.5° (6 mm.), n_D^{25} 1.4433).

Methyl iminocyclopentanecarboxylate hydrochloride (VI) was prepared by the above procedure in 97% yield.

Anal. Calcd. for C₇H₁₄ClNO: Cl, 21.7. Found: Cl, 21.7.

When 16.4 g. of this iminoester hydrochloride was hydrolyzed with the same molar ratio of water as above, the salt went into solution immediately and the solution became warm. There was obtained from the reaction 11.3 g. (88%) of methyl cyclopentanecarboxylate (XI), b.p. 38–39° (7 mm.), n_D^{25} 1.4338 (reported²² b.p. 158.1–160.1° (760 mm.), n_D^{18} 1.4367). A mixture of 1.023 g. of VI and 5 ml. of dry dimethyl formamide was refluxed for 15 minutes and the hot solution filtered and evaporated. Recrystallization of the residue from acetone gave 546 mg. (78%) of cyclopentanecarboxamide, m.p. 176–177° (reported²³ 179°). The filtrate gave a second crop (from water) of 29 mg. (4%), m.p. 173.5–175°.

Preparation of Orthoesters. (a) **Methyl Orthocyclopentanecarboxylate (VII).**—This ester was prepared in 76–84% yield from VI by the procedure of Aldridge and McElvain,² except that a four to one molar ratio of methanol to salt was used. The analytical sample boiled at 64° (7 mm.), 76° (18 mm.), n_D^{25} 1.4366. There also was obtained 7–8% methyl cyclopentanecarboxylate (XI) and 4–5% of cyclopentanecarboxamide, m.p. 173.5–176°.

Anal. Calcd. for C₆H₁₀O₃: C, 62.04; H, 10.41; OCH₃, 53.3. Found: C, 61.84; H, 10.18; OCH₃, 52.7.

(b) **Methyl Orthocyclohexanecarboxylate (VIIa).**—A mixture of 120 g. (0.675 mole) of methyl iminocyclohexanecarboxylate hydrochloride (VIa) and 164 ml. (4.05 mole) of dry methanol was stirred with a glass stirrer for 15 minutes, then 600 ml. of petroleum ether, b.p. 65°, added and the stirring continued for 6 days. After the ammonium chloride was filtered off and most of the solvent removed by distillation 14.3 g. (17%) of hexahydrobenzamide, m.p. 180–183°, was collected on a filter. Distillation of the filtrate through a 1.6 × 17 cm. Heli-Pak column gave (a) 9.8 g. of forerun, b.p. 66.5–84° (13 mm.), n_D^{25} 1.4436 and (b) 74.0 g. (58%) of VIIa, b.p. 87–88° (13 mm.), n_D^{25} 1.4432.

Anal. Calcd. for C₁₀H₂₀O₃: C, 63.97; H, 10.71; OCH₃, 49.4. Found: C, 63.87; H, 10.50; OCH₃, 44.2.

To 774 mg. of this orthoester was added 750 mg. of a 90% water-methanol solution and five drops of acidified methanol. The solution warmed immediately. After standing for 3 hr. the solution was warmed on a steam-bath for 5 minutes, 0.3 g. of anhydrous hydrazine added, and the solution refluxed for 19 hr. The hydrazide was precipitated by the addition of petroleum ether and recrystallized from benzene-petroleum ether to give 340 mg. (58%) of cyclohexanecarboxylic acid hydrazide, m.p. 156–156.5° (reported²⁴ 159°) undepressed when mixed with an authentic sample. A second crop of 189 mg. (32%), m.p. 155–155.5°, was obtained from the mother liquors.

(c) **Methyl Ethylene Orthocyclopentanecarboxylate (IX).**—A mixture of 82 g. (0.50 mole) of VI and 62 g. (1.00 mole) of ethylene glycol was stirred 10 minutes. After the addition of 300 ml. of petroleum ether (b.p. 35°) stirring was continued for 44 hours. The precipitated solid was removed by filtration, washed with acetone, and dried to give 22.3 g. (84%) of ammonium chloride. The petroleum ether layer was separated and distilled through a 1.6 × 17 cm. Heli-Pak column to give, after removal of the solvent: (a) 3.7 g. of forerun, b.p. 75–81° (7 mm.), n_D^{25} 1.4547

(21) G. Natta, *et al.*, *Gazz. chim. ital.*, **80**, 680 (1950).

(22) K. W. Kohlrausch and R. Skrabal, *Monatsh.*, **70**, 44 (1937).

(23) N. Zelinski, *Ber.*, **41**, 2627 (1908).

(24) S. Olson and E. Enkemeyer, *ibid.*, **81**, 359 (1948).

(18) The preparation of this catalyst was furnished by Dr. D. K. Banerjee, formerly in this laboratory, now at the Indian Institute of Science, Bangalore.

(19) J. D. Roberts and M. T. Rogers, *THIS JOURNAL*, **68**, 843 (1946).

(20) C. L. Stevens and T. H. Coffield, *ibid.*, **73**, 104 (1951).

and (b) 49.4 g. (58%) of IX, b.p. 81–82.5° (7 mm.), n_D^{25} 1.4545.

Anal. Calcd. for $C_8H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 63.06; H, 9.46.

The pot residue was distilled through a 10-cm. Vigreux column to give (c) 5.8 g. of intermediate cut, b.p. 42–152° (0.2 mm.), and (d) 13.0 g. (13%) of ethylene glycol di-(ethylene orthocyclopentane)-carboxylate (X), b.p. 152–155° (0.2 mm.). Part of (d) was redistilled from sodium hydride and a center cut b.p. 154–157° (0.2 mm.), m.p. 31.5–33°, analyzed.

Anal. Calcd. for $C_{18}H_{30}O_6$: C, 63.11; H, 8.83. Found: C, 63.22; H, 8.93.

(d) Methyl Ethylene Orthocyclohexanecarboxylate (IXa) was prepared in a similar manner to IX using a 3:1 glycol to salt ratio. The yield was 57% of a product, b.p. 100–101° (17 mm.), n_D^{25} 1.4606.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.47; H, 9.74. Found: C, 64.25; H, 9.62.

There was also isolated 13% of ethylene glycol di-(ethylene orthocyclohexanecarboxylate) (Xa), b.p. 166–169° (0.2 mm.), m.p. 52.0–55.0°.

Anal. Calcd. for $C_{20}H_{34}O_6$: C, 64.82; H, 9.25. Found: C, 65.11; H, 9.32.

The recurring bands in the infrared spectra of the orthoesters VII, VIIa, IX, IXa and methyl orthoisobutyrate are assembled in Table I. Bergmann has studied the spectra of acetals and ketals and assigned four bands to the C–O–C–O–C grouping. He also has assigned²⁵ the same bands to orthoesters on the basis of three compounds (the structure of one of which rests upon its spectrum). All of the spectra of the orthoesters of Table I have bands falling within his limits. Since his assignments are broad (8.51 ± 0.12, 8.81 ± 0.07, 9.24 ± 0.12, and 9.54 ± 0.09) and his orthoester spectra stretch these limits even more, these four bands in the frequently complex fingerprint region are of limited utility. It is apparent that the 8.67 and 9.34 bands of Table I correspond to Bergmann's 8.81 and 9.24 bands. While the spectra of Table I fall within more closely defined limits, any conclusions should be drawn with caution since the cases studied are limited both in number and type (*i.e.*, α,α -disubstituted orthoesters). This latter factor doubtless accounts for the narrow limits observed.

TABLE I
RECURRING BANDS IN INFRARED SPECTRA OF α,α -DISUBSTITUTED ORTHOESTERS

Compound	8.03 μ (S) ^a	8.67 μ (MS)	9.34 μ (S)	10.05 μ (M) ^b
VII	8.00	8.70	9.36	10.12
VIIa	8.04	8.67	9.38	10.04
IX	8.00	8.68	9.31	10.07
IXa	8.06	8.67	9.32	10.01
$(CH_3)_2CHC(OCH_3)_2$	8.02	8.65	9.36	10.00

^a Strong. ^b Medium.

Dealcoholation of the Orthoesters to Ketene Acetals.
(a) Tetramethyleneketene Dimethylacetal (VIII).—A mixture of 68.0 g. (0.279 mole) of sublimed aluminum *t*-butoxide and 48.5 g. (0.279 mole) of the orthoester VII, was heated at 175–190° in a magnetically stirred flask surmounted by a 12-cm. Vigreux column and still-head. After 40 minutes 20.4 g. (98%) of *t*-butyl alcohol, n_D^{25} 1.3859, had been collected. Slow reduction of the pressure gave a distillate of 37.9 g., n_D^{25} 1.4487, which was redistilled from a magnetically stirred pot through a nitrogen-filled 1.6 × 25 cm. Heli-Pak column and collected under 19 mm. pressure: (1) 3.2 g., b.p. 65–69.5°, n_D^{25} 1.4450; (2) 3.1 g., b.p. 69.5–70.5°, n_D^{25} 1.4519; (3) 5.3 g., b.p. 70.5–70.8°, n_D^{25} 1.4540; (4) 4.0 g., b.p. 70.8–71.1°, n_D^{25} 1.4540; (5) 4.8 g., b.p. 71.1°, n_D^{25} 1.4541; (6) 6.6 g., b.p. 71.1–71.4°, n_D^{25} 1.4541; (7) 3.6 g., b.p. 71.4–71.8°, n_D^{25} 1.4531; (8) 3.6 g., b.p. above 72°, n_D^{25} 1.4384. Fractions 3 to 6

(25) E. D. Bergmann, *et al.*, *Rec. trav. chim.*, **70**, 161 (1952); *THIS JOURNAL*, **73**, 2352 (1951).

(26) Ordinary aluminum *t*-butoxide (ref. 9) was sublimed at 165° (0.1 mm.) in 6 to 10 g. batches from a 3.75 × 20 cm. test-tube onto a cold finger; *cf.* also S. M. McElvain and A. N. Bolstad, *THIS JOURNAL*, **73**, 1988 (1951), footnote (6).

amount to a 52% yield of VIII. Fractions 1, 2 and 3 were added slowly to 0.9 g. of lithium aluminum hydride in 25 ml. of ether and allowed to stand overnight. The ether was removed at 20 mm. and the remaining ketene acetal at 0.1 mm. The temperature of the pot was never raised over 35°. Redistillation of VIII through a nitrogen filled 25-cm. Podbielniak column gave 10.1 g. of pure VIII, b.p. 68.0° (18 mm.), n_D^{25} 1.4541, d_4^{25} 0.9571. The total yield of pure VIII amounted to 64%.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.52; H, 9.92; OCH_3 , 43.6; *MRD*, 39.76. Found: C, 67.72; H, 10.03; OCH_3 , 39.4; *MRD*, 40.24.

(b) Pentamethyleneketene Dimethylacetal (VIIIa).—A mixture of 77.2 g. (0.314 mole) of sublimed aluminum *t*-butoxide and 59.0 g. (0.314 mole) of methyl orthocyclohexanecarboxylate (VIIa) was heated at 180–185° in a magnetically stirred flask surmounted by a 10-cm. Vigreux column and still-head. After 1.3 hours 18.4 g. (79%) *t*-butyl alcohol had been collected and there was 3.8 g. of liquid in a cold trap connected to the receiver. The 43.5 g. of liquid, n_D^{25} 1.4508, obtained by slowly reducing the pressure was fractionated under nitrogen through a 1.6 × 25 cm. Heli-Pak column to yield the following fractions under 19 mm. pressure: (1) 2.9 g., b.p. 79–81°, n_D^{25} 1.4432; (2) 6.6 g., b.p. 81–82°, n_D^{25} 1.4510; (3) 2.5 g., b.p. 82–83°, n_D^{25} 1.4561; (4) 10.0 g., b.p. 83°, n_D^{25} 1.4588; (5) 5.9 g., b.p. 83–83.5°, n_D^{25} 1.4590; (6) 4.1 g., b.p. 83.5–84°, n_D^{25} 1.4589; (7) 3.1 g., b.p. 84–98°, n_D^{25} 1.4556; (8) 5.5 g., b.p. 98–99.5°, n_D^{25} 1.4389.

Fractions 4, 5 and 6 amount to a 40% yield of the ketene acetal VIIIa. On the basis of index of refraction, fractions 1, 2 and 3 contain 13% of the normal ester XIa and 12% of the ketene acetal VIIIa.

Fraction 5 was added to 0.25 g. of lithium aluminum hydride and 20 ml. of ether. This mixture was allowed to stand for 30 minutes, the ether was removed at 20 mm. pressure and VIIIa distilled off at 0.1 mm.; the pot was never heated over 35°. The distillate was redistilled through a nitrogen filled 25-cm. Podbielniak column to give 4.80 g. of pure VIIIa, b.p. 83.0° (19 mm.), n_D^{25} 1.4592, d_4^{25} 0.9475.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32; OCH_3 , 39.7; *MRD*, 44.38. Found: C, 69.39; H, 10.37; OCH_3 , 35.4; *MRD*, 45.09.

The 3.8 g. of trap material was brominated at –76° to a definite bromine color with 0.44 ml. of bromine (to remove the isobutylene). Distillation gave 2.65 g. (18%) of dimethyl ether, b.p. –23°.

The 18.4 g. of *t*-butyl alcohol initially obtained from the reaction was redistilled through a 1.6 × 25 cm. Heli-Pak column to give (a) 2.50 g., b.p. 61–81° and (b) 14.9 g. of pure *t*-butyl alcohol, m.p. 25.2°. The water-insoluble portion of (a) was distilled from calcium hydride to give 0.52 g. of liquid, b.p. (micro) 68.5°, n_D^{25} 1.3789 (*cf.* b.p. 55.2°, n_D^{25} 1.3667 reported²⁷ for *t*-butyl methyl ether).

(c) Dealcoholation of IX.—When 43.5 g. (0.253 mole) of methyl ethylene orthocyclopentanecarboxylate (IX) and 65.9 g. (0.267 mole) of sublimed aluminum *t*-butoxide was heated with magnetic stirring in an oil-bath at 180–188° for 40 minutes there was obtained 4.37 g. (23%) of *t*-butyl alcohol, n_D^{25} 1.3847. No more alcohol was obtained after an additional 15 minutes of heating. A Dry Ice-acetone trap connected to the still-head contained 1.32 g. of liquid, presumably isobutylene, since no distillate was obtained after the liquid was brominated and allowed to warm to room temperature. The volatile material was removed from the alkoxide under reduced pressure and redistilled through a nitrogen-filled 1.6 × 25 cm. Heli-Pak column to give (a) 9.52 g. of methyl cyclopentanecarboxylate (XI), b.p. 48.5–50° (10 mm.), n_D^{25} 1.4340; (b) 2.20 g. of intermediate fraction, b.p. 50–68.5° (10 mm.), n_D^{25} 1.4335; (c) 15.5 g. of *t*-butyl cyclopentanecarboxylate²² (XII), b.p. 68.5–71.5° (10 mm.), n_D^{25} 1.4304; (d) 1.90 g. of less pure *t*-butyl ester, b.p. 71.5–89° (10 mm.), n_D^{25} 1.4328; (e) 0.66 g. of an intermediate cut, b.p. 89–95° (10 mm.), n_D^{25} 1.4547 (the presence of some of the ketene acetal XIV in both (d) and (e) was indicated by decolorization of a bromine in carbon tetrachloride solution); (f) 0.38 g., b.p. 95–96° (10 mm.), n_D^{25} 1.4779; and (g) 2.85 g., b.p. 96–99° (10 mm.), n_D^{25} 1.4683.

(27) J. F. Norris and G. W. Rigby, *ibid.*, **54**, 2098 (1932).

An attempt was made to separate the ketene acetal IV from (f) by use of the lithium aluminum hydride technique, but no distillate was obtained at 35° and 0.1 mm. pressure. Titration of (g) to a faint bromine color required 10.0 ml. (45%) of 0.914 *M* bromine in carbon tetrachloride solution. Distillation of the bromination products through a 25-cm. Podbielniak column gave (h) 1.00 g. of β -methoxyethyl cyclopentanecarboxylate (XIII), b.p. 43–44° (0.04 mm.), n_D^{25} 1.4430; (i) 0.39 g. of an intermediate cut, b.p. 68–75° (0.04 mm.), n_D^{25} 1.4722; and (j) 2.07 g. (75% based on the bromine absorption) of β -bromoethyl 1-bromocyclopentanecarboxylate, b.p. 75–76° (0.04 mm.), n_D^{25} 1.5150.

The infrared spectrum of (h) showed ester bands at 5.80 and 8.04 μ . Refluxing (h) with a twofold excess of hydrazine in dioxane solution for 22 hr. converted it in a 28% yield to cyclopentanecarboxylic acid hydrazide, m.p. 104–110.5°. Several recrystallizations from benzene-petroleum ether gave material, m.p. 118–118.5° (reported²⁸ m.p. 110–111°) undepressed by an authentic sample of the hydrazide, prepared in 89% yield from the methyl ester XI.

The elemental analysis (Found: C, 60.93; H, 9.14) indicate that (h) is not pure β -methoxyethyl cyclopentanecarboxylate (Calcd. for $C_8H_{16}O_3$: C, 62.76; H, 9.36).

The infrared spectrum of the dibromoester showed ester bands at 5.79 and 8.01 μ .

Anal. Calcd. for $C_8H_{12}Br_2O_3$: C, 32.03; H, 4.03; Br, 53.30. Found: C, 32.82; H, 3.75; Br, 53.21.

Extrapolation of the index of refraction on the basis of the bromine titer of (g) gives for the ketene acetal IV the value n_D^{25} 1.4964, which may be used to calculate the ketene acetal content of (d), (e) and (f). These values, together with proration of (b) on the basis of index of refraction, give the following total yields: (1) 36% methyl cyclopentanecarboxylate (XI), (2) 42% *t*-butyl cyclopentanecarboxylate (XII), (3) 5% pentamethyleneketene ethyleneacetal (XIV) and (4) 4% β -methoxyethyl cyclopentanecarboxylate (XIII).

(d) **Dealcoholation of IXa.**—When 43.2 g. (0.227 mole) of methyl ethylene orthocyclohexanecarboxylate (IXa) and 56.0 g. (0.227 mole) of sublimed aluminum *t*-butoxide was magnetically stirred in a flask surmounted by a 10-cm. Vigreux column and still-head and heated in an oil-bath at 184–188°, 3.30 g. (20%) of *t*-butyl alcohol was obtained in 20 minutes. No more alcohol was obtained after an additional 85 minutes of heating. The volatile material was removed from the alkoxide under reduced pressure and redistilled through a 1.6 \times 25 cm. Heli-Pak column to give: (a) 10.67 g. of the normal methyl ester XIa, b.p. 63.5–64° (9 mm.), n_D^{25} 1.4414; (b) 2.37 g. of an intermediate fraction, b.p. 64–82.5° (9 mm.), n_D^{25} 1.4400; (c) 12.25 g. of *t*-butyl cyclohexanecarboxylate (XIIa), b.p. 82.5–85.5° (9 mm.), n_D^{25} 1.4370; (d) 2.04 g. of less pure *t*-butyl ester, b.p. 85.5–102.5° (9 mm.), n_D^{25} 1.4378; and (e) 1.36 g., b.p. 114–117° (9 mm.), n_D^{25} 1.4771.

Anal. Calcd. for $C_{11}H_{20}O_2$ (XIIa): C, 71.40; H, 11.02. Found: C, 71.69; H, 10.85.

Titration of 1.14 g. of (e) to a faint bromine coloration required 4.25 ml. (51%) of 0.881 *M* bromine-carbon tetrachloride solution. The bromination mixture was combined with the brominated column washings and distilled through a 25-cm. Podbielniak column to give: (f) 1.14 g. of β -methoxyethyl cyclohexanecarboxylate (XIIIa), b.p. 51–52° (0.04 mm.), n_D^{25} 1.4469; (g) 0.53 g. of an intermediate fraction, b.p. 52–86° (0.04 mm.), n_D^{25} 1.4597; and (h) 1.18 g., b.p. 86–88° (0.04 mm.), n_D^{25} 1.5154.

Anal. Calcd. for $C_{10}H_{18}O_3$ (XIIIa): C, 64.49; H, 9.74. Found: C, 64.21; H, 9.44.

The infrared spectra of (f) showed ester bands at 5.78 and 8.03 μ . Refluxing (f) with a twofold excess of hydrazine in dioxane solution for 22 hr. converted it to cyclohexanecarboxylic acid hydrazide, m.p. 147–151.5°, in 16% yield. Several recrystallizations from benzene-petroleum ether gave material, m.p. 156–156.5° (reported²⁴ m.p. 159°) undepressed by an authentic sample.

The bromine analysis (Found: Br, 49.69) for fraction (h) suggest that it is β -bromoethyl 1-bromocyclohexanecarboxylate (Calcd.: Br, 50.90) contaminated by some of XIIIa.

Estimation of the yields in the same manner as described above for the dealcoholation of methyl ethylene orthocyclo-

pentanecarboxylate (IX) give the following total yields: (1) 38% of methyl cyclohexanecarboxylate (XIa), (2) 36% of *t*-butyl cyclohexanecarboxylate (XIIa), (3) 2% of pentamethyleneketene ethyleneacetal (XIVa) and (4) 2% β -methoxyethyl cyclohexanecarboxylate (XIIIa).

The infrared spectra of the ketene acetals have two recurring bands in the region of 6 and 10 μ . The position of these bands for some representative ketene acetals is shown in Table II. The band in the 6 μ region, representing the $<C=C>$ stretching frequency, is the more characteristic and pronounced. It is of interest to note that while mono- (no. 2 and 3) and dialkyl (no. 6, 7 and 8) substitution shifts this 6 μ absorption band of the unsubstituted ketene acetal (no. 1) to lower wave lengths, mono- and diaryl substitution (no. 4 and 5) are without effect.

TABLE II
RECURRING INFRARED ABSORPTION BANDS OF KETENE ACETALS $R_1R_2C=C(OR)_2$

No.	R ₁	R ₂	R	Bands in the region of	
				6 μ	10 μ
1	H	H	CH ₃	6.10	9.65
2	CH ₃	H	C ₂ H ₅	5.97	9.82
3	<i>n</i> -C ₃ H ₇	H	CH ₃	5.97	9.84
4	C ₆ H ₅	H	CH ₃	6.12	9.78
5	C ₆ H ₅	C ₆ H ₅	CH ₃	6.12	10.01
6	CH ₃	CH ₃	CH ₃	5.86	10.07
7	(CH ₂) ₄		CH ₃	5.84	10.02
8	(CH ₂) ₅		CH ₃	5.88	10.05

Reactions of the Ketene Acetals. (a) VIII and VIIIa with Bromine.—Titration of 12.85 g. of the tetramethyleneketene acetal VIII, maintained at 25–35°, required 3.96 ml. (85%) of liquid bromine. Distillation of the bromination mixture through a 0.8 \times 20 cm. glass tube column gave the following fractions at 7 mm. pressure: (1) 0.67 g., b.p. 54–64°, n_D^{25} 1.4471; (2) 1.17 g., b.p. 64–68°, n_D^{25} 1.4629; (3) 2.18 g., b.p. 68–80°, n_D^{25} 1.4772; (4) 8.86 g., b.p. 80–82°, n_D^{25} 1.4848; (5) 2.18 g., b.p. 82.5–87°, n_D^{25} 1.4866. The pot residue was distilled from a modified Claisen distilling flask to give (6) 1.27 g., b.p. 44–46° (0.1 mm.), n_D^{25} 1.5231; (7) 0.53 g., b.p. 46–48° (0.1 mm.), n_D^{25} 1.5271.

Fractions 2 to 5 were redistilled through a 25-cm. Podbielniak column and the center cut of a constant-boiling, constant-index fraction of methyl 1-bromocyclopentanecarboxylate (XXI), b.p. 81° (9 mm.), (reported²⁹ b.p. 122–125° (60 mm.)), n_D^{25} 1.4825, was analyzed.

Anal. Calcd. for $C_7H_{11}BrO_2$: C, 40.61; H, 5.36; Br, 38.60. Found: C, 40.70; H, 5.49; Br, 38.21.

The analytical data for fraction 6 (Found: Br, 54.2; OCH₃, 9.2) showed the presence of two bromine and one methoxyl substituents in the molecule; however, these values do not closely correspond to those of methyl 1,2-dibromocyclopentanecarboxylate (XXII) (calcd.: Br, 55.8; OCH₃, 10.8).

A mixture of 219 mg. of fraction 6, 5 ml. of absolute ethanol and 300 mg. of sodium iodide was refluxed for 20 minutes, the liberated iodine was removed from the solution with aqueous sodium thiosulfate and the methyl cyclopentene-1-carboxylate saponified by the addition of 0.5 g. of potassium hydroxide followed by reflux for one hour. The ethanol was removed from the solution in a stream of nitrogen, the remaining material acidified with hydrochloric acid and extracted with two 20-ml. portions of ether, and the ether washed with a saturated sodium chloride solution. Evaporation of the ether gave 82 mg. (95%) of cyclopentene-1-carboxylic acid, m.p. 113–116° (reported³⁰ m.p. 119–120°).

Proration of fractions 1 to 7 on the basis of index of refraction, assuming the low-boiling, low-index material in fractions 1 to 3 to be methyl cyclopentanecarboxylate and using the index of fraction 7 to calculate the yield of methyl 1,2-dibromocyclopentanecarboxylate, gives the following total yields: XI (10%), methyl 1-bromocyclopentanecarboxylate (XXI) (73%) and methyl 1,2-dibromocyclopentanecarboxylate (XXII) (8%).

A solution prepared by filtering 133 g. of carbon tetrachloride directly from calcium hydride into a flame-dried

(29) E. Haworth and W. H. Perkin, *J. Chem. Soc.*, **65**, 101 (1894).

(30) J. Kenner and W. L. Wain, *Ber.*, **72B**, 456 (1939).

(28) H. L. Yale, *et al.*, *THIS JOURNAL*, **75**, 1933 (1953).

flask containing 11.23 g. of VIII was titrated at 0–5° to a faint bromine coloration with 98.1 ml. (88%) of a 0.709 *M* bromine-carbon tetrachloride solution. Distillation of the bromination mixture through a 25-cm. tantalum-spiral Podbielniak column gave: (a) 0.86 g., b.p. 74–88° (11.5 mm.), n_D^{25} 1.4695; (b) 7.96 g. of methyl 1-bromocyclohexanecarboxylate (XXI), b.p. 88–89° (11.5 mm.), n_D^{25} 1.4838; (c) an additional 6.43 g. of this bromoester, b.p. 89–90° (11.5 mm.), n_D^{25} 1.4842; and (d) 0.27 g. of α -bromoester, n_D^{25} 1.4838, recovered by heating the pot to 100° at 0.1 mm. There was a black, tarry pot-residue amounting to only 0.153 g.

Since (b) and (c) have a higher refractive index than the analytical sample of XXI described above, it is possible that they contain some of the dibromoester. If this assumption is made, and if it is again assumed that (a) is a mixture of normal ester XI and XXI, proration on the basis of index of refraction gives the following total yields: XI (3%), XXI (91%) and XXII (2%).

Titration of 12.40 g. (0.0795 mole) of the pentamethylene ketene acetal VIIa cooled in an ice-bath required 3.81 ml. (93%) of liquid bromine to produce a faint coloration. Distillation of this material through a 25-cm. tantalum-spiral Podbielniak column gave (a) 1.48 g., b.p. 90–117° (21 mm.), n_D^{25} 1.4668; (b) 13.94 g. of methyl 1-bromocyclohexanecarboxylate, b.p. 115–116° (19 mm.), n_D^{25} 1.4908; (c) 0.25 g. of less pure bromoester, n_D^{25} 1.4920, which distilled when the pressure was reduced to 0.1 mm.; and (d) 0.145 g. of liquid, b.p. 40–52° (0.1 mm.), n_D^{25} 1.5033. If (a) is prorated as being a mixture of the normal ester XIa and α -bromoester, the total yields of XIa and methyl 1-bromocyclohexanecarboxylate are 6 and 85%, respectively.

Anal. Calcd. for $C_6H_{10}BrO_2$ (fraction b): C, 43.46; H, 5.93; Br, 36.15. Found: C, 43.62; H, 5.59; Br, 36.22.

(b) VIII and VIIa with 2,4-Dinitrophenylhydrazine.—A mixture of 112 mg. of VIII, 156 mg. (0.788 mmole) of 2,4-dinitrophenylhydrazine, 5 mg. of fused zinc chloride and 5 ml. of dioxane was refluxed 5 minutes. After cooling, 103 mg. (43%) of methyl 2,4-dinitrophenylhydrazinocyclohexanecarboxylate (XVII), m.p. 203.5–207.5°, was collected. Recrystallization from benzene raised the m.p. to 213–214°. The ultraviolet spectrum had a single peak, $\lambda_{max}^{CHCl_3}$ 377 μ , $\log \epsilon$ 4.36. The infrared spectrum had a single NH band at 3.01 μ and a C=N band at 6.15 μ .

Anal. Calcd. for $C_{13}H_{16}N_4O_6$: C, 50.64; H, 5.23; OCH₃, 10.1. Found: C, 50.76; H, 5.06; OCH₃, 8.6.

A mixture of 767 mg. (4.91 mmoles) of VIIa, 937 mg. of 2,4-dinitrophenylhydrazine, 52 mg. of fused zinc chloride and 20 ml. of dioxane was refluxed five minutes. After cooling, 1.063 g. (69%) of methyl N-2,4-dinitrophenylhydrazinocyclohexanecarboxylate (XVIIa), as golden needles, m.p. 192–194°, was removed by filtration. One recrystallization from benzene raised the m.p. to 194.5–195°, unchanged by three more recrystallizations. The ultraviolet spectra showed a single peak, $\lambda_{max}^{CHCl_3}$ 376 μ , $\log \epsilon$ 4.38.

Anal. Calcd. for $C_{14}H_{18}N_4O_6$: C, 52.17; H, 5.63; OCH₃, 9.6. Found: C, 51.96; H, 5.44; OCH₃, 9.6.

(c) VIII and VIIa with Benzhydryl Bromide.—A sealed, nitrogen-filled, capillary tube containing 84 mg. of tetramethyleneketene dimethylacetal (VIII) and 174 mg. of benzhydryl bromide was heated in an oil-bath at 105° for 12.5 hours. The mixture was dissolved in isopropyl alcohol, decolorized with Norite and the solvent evaporated. The residue was dissolved in 8 ml. of petroleum ether (b.p. 65°), cooled to –78° for 24 hr. and the supernatant liquid decanted to leave 153 mg. of crude methyl 1-benzhydrylcyclohexanecarboxylate (XVIII), m.p. 36–61°. Recrystalliza-

tion from isopropyl alcohol-water gave 92 mg. of product, m.p. 61.5–62.5°, and a second crop of 20 mg., m.p. 58.5–60° (total yield 64%). Two more recrystallizations gave material, m.p. 64.0–64.5°, unchanged by one more recrystallization.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.66; H, 7.60.

A sealed, nitrogen-filled, capillary tube containing 201 mg. of VIIa and 316 mg. of benzhydryl bromide was heated in an oil-bath at 125° for 12.5 hours. Recrystallization of the reaction mixture from petroleum ether (b.p. 65°) gave, in two crops, 295 mg. (75%) of methyl α -benzhydrylcyclohexanecarboxylate (XVIIa), m.p. 74.5–76.5°. The analytical sample, m.p. 77–77.5°, was recrystallized four times from isopropyl alcohol-water. The infrared spectrum had bands at 5.82 and 8.17 μ .

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.50; H, 7.71.

(d) VIIa with Benzoyl Chloride.—A sealed, nitrogen-filled, capillary tube containing 87 mg. of VIIa and 98 mg. of benzoyl chloride was heated for 3 hours in a metal-bath at 225°. After the contents of the tube were refluxed for 2 hours with 5 ml. of a hydrolysis mixture consisting of 10 ml. of sulfuric acid, 5 ml. of water and 30 ml. of acetic acid, the cooled hydrolysis solution was treated with 3.0 ml. of a 0.135 *M* 2,4-dinitrophenylhydrazine solution. The 190 mg. of crude hydrazone, m.p. 170–175°, that separated was recrystallized from chloroform-ethanol to give 111 mg. (53%) of the 2,4-dinitrophenylhydrazone of phenyl cyclohexyl ketone, m.p. 199–199.5°, raised by one more recrystallization to 200–200.5° (reported³¹ m.p. 192°). This hydrazone was undepressed in m.p. by that prepared from authentic phenyl cyclohexyl ketone, synthesized by the method of Sidorova.³²

(e) VIIa with Oxygen.—A flask containing 4.97 g. (0.0318 mole) of pentamethyleneketene dimethyl acetal (VIIa) was connected to a pressure-equalized, calibrated reservoir containing dry oxygen and the liquid magnetically stirred. After an induction period of one hour, oxygen absorption proceeded at a slowly decreasing rate; 536 ml. (69%) was absorbed after 161 hours. Distillation through a 25-cm. Podbielniak column gave the following fractions: (1) 0.46 g., b.p. 54–84° (13 mm.), n_D^{25} 1.4458; (2) 0.57 g., b.p. 84–94° (13 mm.), n_D^{25} 1.4512; (3) 0.25 g., b.p. 94–96° (13 mm.), n_D^{25} 1.4521; (4) 0.26 g., b.p. 96–103° (13 mm.), n_D^{25} 1.4502; (5) 0.46 g., b.p. 54–56° (0.05 mm.), n_D^{25} 1.4538; (6) 0.23 g., b.p. 56–61° (0.05 mm.), n_D^{25} 1.4554. There was 2.29 g. of ether-soluble, viscous pot-residue which did not crystallize from small amounts of ether or petroleum ether.

A trap connected to the still-head contained 0.903 g. of a mixture of dimethyl carbonate and cyclohexanone, m.p. –4°, n_D^{25} 1.3752. A 279-mg. aliquot of this mixture gave 81 mg. (91% of the amount calculated on the basis of refractive index) of crude cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 157–159.5°. Two recrystallizations from chloroform-ethanol gave material, m.p. 160.5–161.5° undepressed by an authentic sample. Treatment of fractions 1 and 2 with 2,4-dinitrophenylhydrazine reagent gave 406 mg. more hydrazone, m.p. 156–159°. Proration of the trap material on the basis of refractive index and allowance for the 406 mg. of hydrazone from (1) and (2) indicates yields of 7% cyclohexanone and 28% dimethyl carbonate.

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