Reaction of XIII with Phenylglyoxal (IV). Preparation of ***cis-*** **and** ***trans*****-2,2,2-Trimethoxy-4-acetyl-5-benzoyl-4-phenyl-1,-3,2-dioxaphospholane (XIXa and XIXb).**—The phospholene XIII (4.4 g, 16 mmoles) and the ketoaldehyde IV (2.2 g, 16 m-moles) were dissolved in methylene chloride (16 ml) at 20°, under N_2. The infrared and the H^1 nmr spectra of aliquots were examined after 1, 18, 42, and 54 hr. Two H^1 nmr signals began to appear at τ 7.75 and 8.25 in a 40:60 proportion. Reaction had proceeded to about 70% of completion in 54 hr. In addition to the signals listed in Table I, the H^1 nmr spectrum (CCl_4) of the crude mixture showed signals at τ 2.10 and 2.75 (aromatic protons). The ring proton of the major (XIXa) and the minor (XIXb) isomers each showed a doublet at τ 4.92, J_{HP} = 21 cps, and at τ 4.56, J_{HP} = 24 cps. The two nine-proton doublets, J_{HP} = 12.8 cps, due to the CH_3O- groups attached to the P, were centered at τ 6.63 (major, XIXa) and 6.57 (minor, XIXb). The infrared spectrum (CCl_4) had bands at 5.82 (acetyl) and 5.92 μ (benzoyl).

Attempted Reaction of XIII with 1-Phenylpropanedione.—The reagents were kept at 20° in CH_2Cl_2 solution in a 1:1 mole ratio. The H^1 nmr spectrum after 4 months showed little evidence of formation of the expected dioxaphospholanes. No appreciable reaction was noted after 20 days when the reagents were kept at 20° in a 1:3 mole ratio.

Polymethyleneketene Dimers and Trimers

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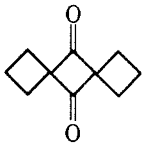
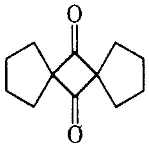
Polymethyleneketene dimers were converted by a base-catalyzed process to polymethyleneketene trimers. This conversion involves the formation of 1,3,5-cyclohexanetriones from 1,3-cyclobutanediones. The dimers, dispiro[3.1.3.1]decane-5,10-dione (I), dispiro[4.1.4.1]dodecane-6,12-dione (II), and dispiro[5.1.5.1]tetradecane-7,14-dione (III), were converted to the corresponding trimers, trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (IV), trispiro[4.1.4.1.4.1]octadecane-6,12,18-trione (V), and trispiro[5.1.5.1.5.1]heneicosane-7,14,21-trione (VI). These diones and triones were completely reduced to diols and triols, respectively. Dodecahydrotriphenylene (XX) was obtained by the dehydration of trispiro[4.1.4.1.4.1]octadecane-6,12,18-triol (XVIII). Alcoholysis of the dimers and trimers gave the corresponding esters (IX–XIV). Alkaline hydrolysis of IV resulted in cleavage followed by decarboxylation to the β-diketone VII. The formation of unsaturated δ-lactone trimers, isomeric with the normal trimers, has been discussed.

In a recent investigation[3] it was shown that dimethylketene and its dimer, tetramethyl-1,3-cyclobutanedione, were converted by a base-catalyzed process to the trimer, hexamethyl-1,3,5-cyclohexanetrione. We now report the conversion of several polymethyleneketene dimers to polymethyleneketene trimers, and some of their reactions. No polymethyleneketene monomers, with the exception of pentamethyleneketene, have been reported, and only two polymethyleneketene dimers, tetramethyleneketene dimer (II) and pentamethyleneketene dimer (III), have been described in the literature, whereas the polymethyleneketene trimers are apparently unknown.


I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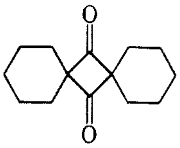
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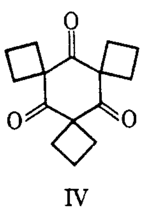
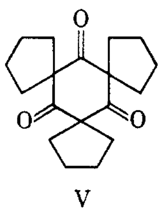
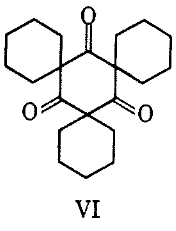
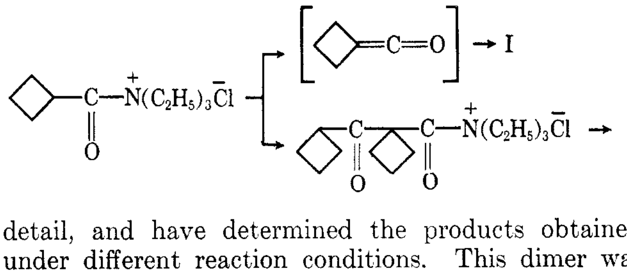

IV


V


VI

The polymethyleneketene dimers were prepared by a well-known reaction—the dehydrohalogenation of cycloalkanecarbonyl chlorides with triethylamine. In some cases the initial step in the reaction between the acyl halide and a tertiary amine is evidenced by the formation of an insoluble acyl quaternary ammonium halide. Such salts have been obtained by Minunni,[4] Adkins and Thompson,[5] Doering and McEwen,[6] and Baumgarten,[7] from various acyl halides and bases. Walborsky[8] treated cyclopropanecarbonyl chloride with triethylamine and obtained a solid product which was designated as an acyl quaternary ammonium salt, and which acylated aniline to give cyclopropanecarboxanilide. The failure of this salt to yield dimethyleneketene was attributed to I strain. In view of such evidence, it appears that an acyl quaternary ammonium salt is the initial product resulting from the reaction of an acyl halide with a tertiary amine.

The dimer of trimethyleneketene, dispiro[3.1.3.1]decane-5,10-dione (I), was first prepared by Walborsky.[9] We have studied this reaction in greater detail, and have determined the products obtained under different reaction conditions. This dimer was prepared in 70% yield from the reaction of cyclobutanecarbonyl chloride and triethylamine at 50°. When the reaction was carried out below room temperature, a precipitate was formed, presumably cyclobutanecarbonyltriethylammonium chloride. This high-melting salt, a powerful acylating agent, reacted



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[1] Cities Service Research Fellow, 1964–1965.

[2] Esso Research Fellow, 1962–1963.

[3] J. L. E. Erickson and G. C. Kitchens, *J. Org. Chem.*, **27**, 460 (1962).

[4] G. Minunni, *Gazz. Chim. Ital.*, **22**, 213 (1892).

[5] H. Adkins and Q. E. Thompson, *J. Am. Chem. Soc.*, **71**, 2242 (1949).

[6] W. v. E. Doering and W. E. McEwen, *ibid.*, **73**, 2104 (1951).

[7] H. E. Baumgarten, *ibid.*, **75**, 1239 (1953).

[8] H. M. Walborsky, *ibid.*, **74**, 4962 (1952).

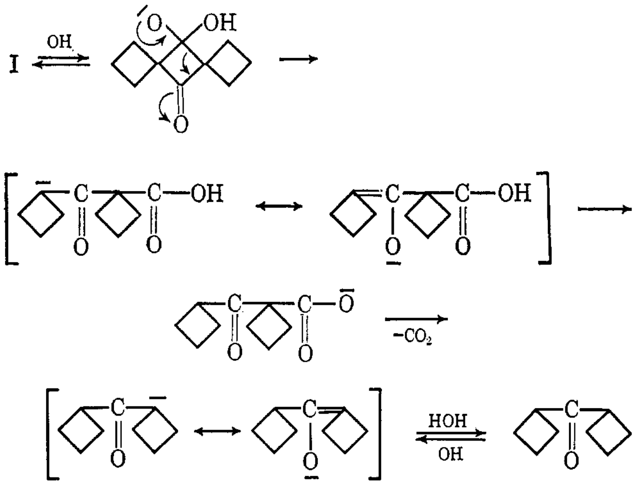
[9] H. M. Walborsky, Ph.D. Thesis, The Ohio State University, 1949.

with aniline to give cyclobutanecarboxanilide, and it was hydrolyzed to yield cyclobutanecarboxylic acid. This salt, suspended in refluxing benzene for 24 hr, gave trimethyleneketene dimer (I) and triethylammonium chloride.

It is generally regarded that the dehydrohalogenation process results in the formation of the ketene monomer which then dimerizes. An alternate route to the dimer, which would involve acylation of the acylammonium chloride, followed by an intramolecular acylation to give the ketene dimer and triethylammonium chloride, would demand no additional internal strain in the cyclopropane ring and permit the formation of dimethyleneketene dimer. The failure to obtain dimethyleneketene dimer,[8] and the fact that some heating seems necessary for the formation of trimethyleneketene dimer (I), whereas higher members of cycloalkanecarbonyl chlorides dehydrohalogenate readily at room temperature, suggests that bond-angle strain is probably an important factor, so that this route to the ketene dimer is not favored.

Two other diones were prepared for study in this investigation. Tetramethyleneketene dimer (II)[10,11] and pentamethyleneketene dimer (III)[12] were obtained by the dehydrohalogenation of the corresponding acyl halides, cyclopentanecarbonyl chloride and cyclohexanecarbonyl chloride, with triethylamine.

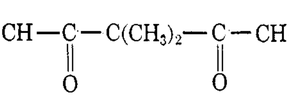
Trimethyleneketene dimer (I), upon hydrolysis with 20% sodium hydroxide solution followed by steam distillation, gave a 67% yield of dicyclobutyl ketone. It is of interest to note that the ketone was obtained without acidification of the alkaline solution. Cleavage of I by alkali with subsequent decarboxylation of the resulting anion may be interpreted as shown.



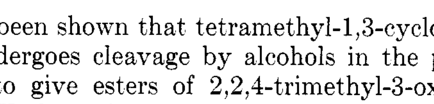
Similarly, II and III, upon alkaline hydrolysis, gave dicyclopentyl ketone and dicyclohexyl ketone,[10,12] respectively.

It was found in this study that the dimer of trimethyleneketene, dispiro[3.1.3.1]decane-5,10-dione (I), was converted to the trimer of trimethyleneketene, trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (IV), by a base-catalyzed process similar to that described by Erickson and Kitchens.[3] Tetramethyleneketene dimer (II) gave an analogous reaction which resulted in the formation of trispiro[4.1.4.1.4.1]octadecane-6,12,18-trione (V), and pentamethyleneketene dimer (III) was converted by the same process to trispiro[5.1.5.1.5.1]heneicosane-7,14,21-trione (VI). Trispiro compounds of this type have not been reported in the literature, and they represent unusual chemical structures. Identification of IV, V, and VI was made on the basis of elemental analyses and molecular weight determinations, which indicated trimers of trimethyleneketene, tetramethyleneketene, and pentamethyleneketene. The infrared spectra of these trimers were characterized by $C{=}O$ absorption at 5.88 μ, a value identical with the one obtained from the infrared spectrum of dimethylketene trimer, prepared either by the trimerization of dimethylketene[3] or by the methylation of phloroglucinol.[13]

Trimethyleneketene trimer (IV) underwent cleavage and decarboxylation when treated with barium hydroxide solution to give both 1,1-di(cyclobutanecarbonyl)cyclobutane (VII) and dicyclobutyl ketone. This result is in harmony with the cleavage product, 2,4,4,6-tetramethylheptane-3,5-dione (VIII) obtained by the alkaline hydrolysis of the trimer of dimethylketene, hexamethyl-1,3,5-cyclohexanetrione. The acquisition of these β-diketones may be accounted for by the same mechanism suggested for the alkaline cleavage and decarboxylation of trimethyleneketene dimer (I).



VII



$$(\mathrm{CH_3})_2\mathrm{CH}-\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{C(CH_3)_2}-\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH(CH_3)_2}$$

VIII

It has been shown that tetramethyl-1,3-cyclobutanedione undergoes cleavage by alcohols in the presence of base to give esters of 2,2,4-trimethyl-3-oxovaleric acid.[14] We have found that this base-catalyzed alcoholysis may be applied not only to the dimers (I–III), but also to the trimers (IV–VI) of polymethyleneketenes. Thus, trimethyleneketene dimer (I), tetramethyleneketene dimer (II), and pentamethyleneketene dimer (III) underwent alcoholysis in the presence of a catalytic amount of sodium ethoxide to give excellent yields of ethyl 1-(cyclobutanecarbonyl)cyclobutanecarboxylate (IX), ethyl 1-(cyclopentanecarbonyl)cyclopentanecarboxylate (X), and ethyl 1-(cyclohexanecarbonyl)cyclohexanecarboxylate (XI), respectively. Upon treatment with the same reagent, trimethyleneketene trimer (IV) underwent cleavage to give ethyl 1-[1-(cyclobutanecarbonyl)cyclobutanecarbonyl]cyclobutanecarboxylate (XII). Similarly, tetramethyleneketene trimer (V) and pentamethyleneketene trimer (VI) gave ethyl 1-[1-(cyclopentanecarbonyl)cyclopentanecarbonyl]cyclopentanecarboxylate (XIII) and ethyl 1-[1-(cyclohexanecarbonyl)cyclohexanecarbonyl]cyclohexanecarboxylate (XIV).

Tetramethyleneketene dimer (II) has been reduced to dispiro[4.1.4.1]dodecane-6,12-diol[11] with lithium

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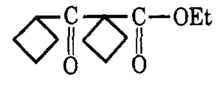
[10] A. J. Bilbo, M.S. Thesis, Louisiana State University, 1950.

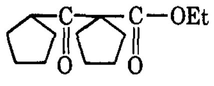
[11] H. M. Walborsky, *J. Org. Chem.*, **18**, 702 (1953).

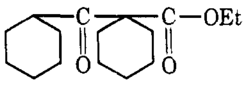
[12] C. M. Hill, Ph.D. Thesis, Cornell University, 1941; C. M. Hill and M. E. Hill, *J. Am. Chem. Soc.*, **75**, 2765 (1953).

[13] J. Herzig and B. Erthal, *Monatsh.*, **32**, 505 (1911).

[14] R. H. Hasek, E. U. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, **26**, 700 (1961).


IX


X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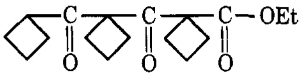
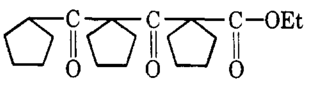
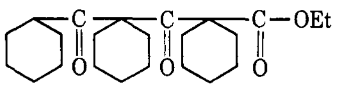
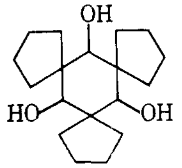

XII

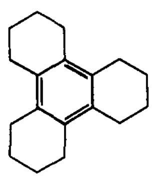

XIII


XIV

aluminum hydride, a reagent which was found useful in this work for the reduction of I and III to dispiro[3.1.3.1]decane-5,10-diol (XV) and dispiro[5.1.5.1]-tetradecane-7,14-diol (XVI), respectively. In the same manner, the trimers, IV, V, and VI, were reduced to the corresponding triols, trispiro[3.1.3.1.3.1]-pentadecane-5,10,15-triol (XVII), trispiro[4.1.4.1.4.1]-octadecane-6,12,18-triol (XVIII), and trispiro[5.1.5.-1.5.1]heneicosane-7,14,21-triol (XIX). Complete reduction was evidenced by strong hydroxy absorption at 2.86–3.05 μ and absence of carbonyl absorption in the infrared spectra of these compounds. Ayers and Hauser[15] have shown that 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetriol, the reduction product of dimethylketene trimer, undergoes dehydration and rearrangement when treated with cold, concentrated sulfuric acid to yield hexamethylbenzene. It was found that XVIII gave an analogous reaction when dissolved in cold, concentrated sulfuric acid to yield an aromatic hydrocarbon, dodecahydrotriphenylene (XX), which had an infrared spectrum identical with that of XX, prepared[16] by the action of sulfuric acid on cyclohexanone.



XVIII


XX

The rearrangement of XVIII to XX probably involves three reactions, each consisting of the removal of a hydroxyl group to form a carbonium ion, the 1,2 shift of one end of a tetramethylene group with its attached electron pair, and the loss of a proton to form the double bond, resulting in ring expansion and the formation of dodecahydrotriphenylene (XX). Attempts to isolate the corresponding aromatic hydrocarbons by the action of sulfuric acid on the triols, XVII and XIX, were unsuccessful.

It is known that disubstituted ketenes dimerize spontaneously upon standing to form tetrasubstituted 1,3-cyclobutanediones. Catalytic dimerization of two disubstituted ketenes, however, has recently been shown to yield unsaturated β-lactones. Dimethylketene and its dimer, tetramethyl-1,3-cyclobutanedione, in the presence of catalytic amounts of aluminum chloride gave high yields of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone.[17] Diphenylketene with small amounts of sodium methoxide gave a mixture of products from which 3-hydroxy-2,2,4,4-tetraphenyl-3-butenoic acid β-lactone[18] was isolated.

It is interesting to note that the mechanisms[3,17,18] proposed for the base-catalyzed dimerization and trimerization of disubstituted ketenes can accommodate the formation of both 1,3-cyclobutanediones and β-lactone dimers, with the product determined by C-acylation or O-acylation in the ring closure. Such mechanisms may be extended to account for the formation of both 1,3,5-cyclohexanetriones and δ-lactone trimers. Cookson and co-workers[19] have noted the equilibration of cyclic nonenolizable β-diketones with the isomeric enol lactones by irradiation with ultraviolet light. When the trimerization reaction was carried out with dimethylketene dimer, tetramethyleneketene dimer (II), or pentamethyleneketene dimer (III) in the molten state, the corresponding trimers sometimes showed very weak infrared absorption bands suggesting contamination (less than 1%) by cyclic δ-lactone trimer formation. In the case of trimethyleneketene dimer (I), a small quantity of the δ-lactone XXI was isolated.

It has been reported[3] that sodium methoxide accelerated the polymerization of diphenylketene to yield both tetraphenyl-1,3-cyclobutanedione and another polymer melting at 176°, a result Staudinger[20] obtained many years earlier by heating diphenylketene–quinoline. On the basis of analysis, molecular weight, and analogy to the structure of the trimer of dimethylketene, hexamethyl-1,3,5-cyclohexanetrione, this polymer was assigned the structure of the trimer, hexaphenyl-1,3,5-cyclohexanetrione. Subsequent studies of its infrared spectrum, however, showed absorption bands at 5.62, 5.90, 6.04, and 8.42 μ, suggesting the structure of the δ-lactone, 5-hydroxy-3-oxo-2,2,4,4,6,6-hexaphenyl-5-hexenoic acid δ-lactone. We have repeated this work and have not been able to confirm the formation of this δ-lactone when diphenylketene was heated in the presence of sodium methoxide. Instead, Anet's β-lactone[18] dimer, 3-hydroxy-2,2,4,4-tetraphenyl-3-butenoic acid β-lactone, was formed in excellent yield.

Higher members of this series of polymethyleneketenes and their dimers and trimers are under investigation.

Experimental Section[21]

The Reaction of Cyclobutanecarbonyl Chloride with Triethylamine.—Cyclobutanecarbonyl chloride, bp 137° (lit.[22] bp 137–139°), was prepared in 89% yield by the action of thionyl chloride on cyclobutanecarboxylic acid. To 8.8 g (0.074 mole) of this acyl chloride in 25 ml of ether at −15° was added 9 g (0.09 mole) of cold triethylamine; a light precipitate formed immediately. The suspension was allowed to stand for 48 hr during which time

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(15) E. B. Ayers and C. R. Hauser, *J. Am. Chem. Soc.*, **64**, 2461 (1942).

(16) C. Mannich, *Ber.*, **40**, 153 (1907).

(17) R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962); R. H. Hasek, R. D. Clark, E. U. Elam, and R. G. Nations, *ibid.*, **27**, 3106 (1962).

(18) R. Anet, *Chem. Ind.* (London), **33**, 1313 (1961).

(19) R. C. Cookson, A. G. Edwards, J. Hudec, and M. Kingsland, *Chem. Commun.* (London), **No. 6**, 98 (1965).

(20) H. Staudinger and H. Goller, *Ber.*, **44**, 530 (1911); H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, pp 39, 145.

(21) Melting points are corrected and boiling points are uncorrected. Microanalyses were determined by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Mr. R. L. Seab, of this laboratory. Spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer.

(22) W. H. Perkin, *J. Chem. Soc.*, **61**, 41 (1892).

it warmed to room temperature. The precipitate was separated by filtration and washed with three 100-ml portions of ether. Care was taken to prevent air from being drawn through the solid. A total of 14 g (81%) of cyclobutanecarbonyltriethylammonium chloride, mp 225–230° dec, was obtained. The solid was very hygroscopic and reacted with water to give cyclobutanecarboxylic acid. Cyclobutanecarboxanilide, mp 113–113.5°, mmp 113–113.5° (lit.[23] mp 112.5–113°), was obtained in 81% yield upon treatment of 3 g of the salt with aniline.

Decomposition of the acyl quaternary ammonium salt occurred when it was suspended in refluxing benzene for 24 hr. From 5.3 g of the salt there was obtained 0.7 g (35%) of dispiro[3.1.3.1]decane-5,10-dione (I), mp 86–87°, mmp 86–87°.

Dispiro[3.1.3.1]decane-5,10-dione (I).—To 103 g (0.87 mole) of cyclobutanecarbonyl chloride, bp 137°, in 800 ml of a benzene–ether mixture, under an atmosphere of dry nitrogen, was added 145 g (1.4 moles) of triethylamine, and the resulting suspension was stirred and refluxed at 50° for 25 hr. The triethylammonium chloride (116 g, 97%) was removed by filtration and the filtrate was washed with 400 ml of cold 10% hydrochloric acid solution to remove the excess amine. The filtrate was then washed with 200 ml of water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature, and the residual solid was recrystallized from a benzene–pentane mixture to yield 50 g (70%) of I, mp 84–86°. A second recrystallization raised the melting point to 86–87° (lit.[9] mp 86–86.5°): $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.41, 5.77, 7.02, 7.92, 8.34, and 10.93 μ.

Dispiro[4.1.4.1]dodecane-6,12-dione (II).[10,11]—To a stirred solution of 52.8 g (0.4 mole) of cyclopentanecarbonyl chloride, bp 161° (lit.[22] bp 160°), in 500 ml of ether under nitrogen was added 63.5 g (0.62 mole) of triethylamine over a period of 1.5 hr. The reaction mixture was stirred 18 hr, then worked up as described in the procedure for the preparation of I to give 30.3 g (85%) of II: mp 75–76° (from pentane); $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.37, 3.47, 5.72, 6.91, 8.03, and 8.73 μ (lit. mp 74–75°,[10] 70–70.5°[11]).

Dispiro[5.1.5.1]tetradecane-7,14-dione (III).[12]—From 73 g (0.5 mole) of cyclohexanecarbonyl chloride, bp 179° (lit.[24] bp 179°), in 500 ml of ether under an atmosphere of dry nitrogen, and 75.9 g (0.75 mole) of triethylamine, there was obtained after stirring for 18 hr 54 g (82%) of III: mp 163.5–165°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.38, 3.47, 5.72, 6.88, 7.16, 8.47, and 10.13 μ (lit.[12] mp 164–165°).

The Alkaline Hydrolysis of Dispiro[3.1.3.1]decane-5,10-dione (I).—To 50 ml of a 20% sodium hydroxide solution was added 5 g (0.031 mole) of dispiro[3.1.3.1]decane-5,10-dione (I), and the resulting suspension was refluxed 0.5 hr and then steam distilled. The distillate was extracted with 10 ml of benzene. After removal of the benzene from the extract by distillation, the odorous residue was distilled to give 2.8 g (67%) of dicyclobutyl ketone, bp 201–202°, $n^{25}\mathrm{D}$ 1.4682 (lit.[25] bp 201°, $n^{21}\mathrm{D}$ 1.4678).

The alkaline hydrolysis of dispiro[4.1.4.1]dodecane-6,12-dione (II), by the procedure used for the hydrolysis of I, gave a 72% yield of dicyclopentyl ketone, bp 244–246°, $n^{25}\mathrm{D}$ 1.4768 [lit.[26] bp 113–116° (14 mm), $n^{20}\mathrm{D}$ 1.4812]. Vapor phase chromatographic analysis indicated a very pure compound.

Trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (IV).—To 16.4 g (0.1 mole) of dispiro[3.1.3.1]decane-5,10-dione (I) dissolved in 20 ml of toluene was added 0.12 g of sodium methoxide, and the suspension was stirred and heated rapidly to reflux when a vigorous reaction occurred that lasted 5 min. Heating was continued for 1 hr during which time three 0.06-g portions of catalyst were added. The reaction mixture was cooled to room temperature, and the toluene solution was decanted into a distillation flask. The toluene was removed under reduced pressure and the residual oil was distilled to yield 11.1 g (68%) of IV, bp 139–140° (2 mm), mp 27°, and a small amount of solid residue. The infrared spectrum of IV had $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.38, 5.88, 7.70, 8.03, 8.23, 8.74, and 10.27 μ.

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37; mol wt, 246.3. Found: C, 73.21, 73.17; H, 7.55, 7.54; mol wt (benzene), 238.

The residue from the distillation was extracted with pentane from which 1.1 g of an isomeric δ-lactone trimer (XXI), mp 83–88°, was obtained. A second recrystallization raised the melting point to 91.2–93°: $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.40, 5.65, 5.72, 5.86, 7.78, 7.93–8.28, 9.24, and 9.27 μ.

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.29, 73.07; H, 7.52, 7.61.

Trispiro[4.1.4.1.4.1]octadecane-6,12,18-trione (V).—To a stirred melt of 10 g (0.052 mole) of dispiro[4.1.4.1]dodecane-6,12-dione (II) at a temperature of 80° and under an atmosphere of nitrogen was added 0.2 g of sodium methoxide. A vigorous reaction followed, and the temperature rose to 195° over a period of 2 min. The mixture was allowed to cool to room temperature and then was dissolved in 25 ml of ether. The catalyst was destroyed by the addition of 0.24 g of glacial acetic acid, and the solution was washed with three 50-ml portions of water and dried over anhydrous magnesium sulfate. Upon cooling, 6.1 g of product, mp 104–110°, was obtained. Recrystallization from pentane yielded 5.7 g (57%) of V: mp 112.5–113.5°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.37, 3.46, 5.88, 7.69, 7.89, 8.28, 8.38, and 8.67 μ. The separate filtrates were combined and evaporated to dryness and gave a residue of 2.3 g of a dark brown oil which failed to crystallize and was not identified.

Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39; mol wt, 288. Found: C, 74.86; H, 8.36; mol wt (benzene), 280, 276.

Trispiro[5.1.5.1.5.1]heneicosane-7,14,21-trione (VI).—To 20 g of dispiro[5.1.5.1]tetradecane-7,14-dione (III), stirred at a temperature of 170° under an atmosphere of nitrogen, was added 0.3 g of sodium methoxide. An exothermic reaction resulted, and the temperature rose to 230°. The reaction mixture was allowed to cool to room temperature, and 50 ml of ether containing 0.4 ml of glacial acetic acid was added. The ethereal solution was washed with water, dried, concentrated, and upon cooling yielded 17.2 g of solid, mp 135–144°. Recrystallization of this material from benzene gave 15.6 g (78%) of VI: mp 147°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.39, 3.48, 5.88, 6.87, 7.66, 8.12, 8.33, 8.83, 8.94, and 10.20 μ. Evaporation of the mother liquor yielded 1.8 g of a dark brown oil which failed to crystallize.

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15; mol wt, 330. Found: C, 76.43; H, 9.18; mol wt (benzene), 332, 315.

The Alkaline Hydrolysis of Trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (IV).—To 7.4 g (0.03 mole) of IV at 80° was added dropwise with vigorous stirring 3 g (0.0165 mole) of barium hydroxide dissolved in 187 ml of water. The stirring and heating were continued until the reaction mixture was neutral to litmus paper. The precipitate (2.5 g) that formed was separated by filtration and the filtrate was extracted with 50 ml of benzene. Drying was accomplished by azeotropic removal of the water. The last traces of benzene were removed at 3 mm pressure, leaving 5.3 g of a clear residual oil which was fractionated to yield 1 g of dicyclobutyl ketone, bp 56–58° (3 mm), $n^{25}\mathrm{D}$ 1.4713, semicarbazone mp 129.5–130° (lit.[25] bp 201°, $n^{21}\mathrm{D}$ 1.4678, semicarbazone mp 129–130°), 2.5 g (38%) of 1,1-di(cyclobutanecarbonyl)cyclobutane (VII), bp 129–135° (3 mm), $n^{25}\mathrm{D}$ 1.4994, and 1.6 g of material, bp 135–139° (3 mm). Redistillation of VII gave material: bp 130–134° (3 mm); $n^{25}\mathrm{D}$ 1.4986; $d^{25}{}_4$ 1.0572; MR 61.10 (calcd 61.71); $\lambda_{\max}$ 3.37, 3.47, 5.88, 6.92, 7.39, 7.68, 8.03, 8.60, 9.02, 10.27, and 10.33 μ.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 75.88, 75.82; H, 9.15, 9.07.

The alkaline hydrolysis of dimethylketene trimer gave similar results. To 15.8 g (0.075 mole) of hexamethyl-1,3,5-cyclohexanetrione, suspended in 50 ml of water at 80°, was added dropwise with vigorous stirring 7.4 g (0.0375 mole) of barium hydroxide dissolved in 426 ml of water. The suspension was stirred 15 min and then cooled to room temperature. The barium carbonate (7 g) was separated by filtration, and the filtrate was extracted with 50 ml of benzene, which was distilled to yield 7.7 g (56%) of 2,4,4,6-tetramethylheptane-3,5-dione (VIII), bp 95–100° (10 mm). Redistillation of VIII gave 6.1 g: bp 212–214°; $n^{25}\mathrm{D}$ 1.4356; $\lambda_{\max}$ 3.36, 5.82, 6.78, 7.22, 7.30, 7.92, 9.27, 9.47, 9.67, 9.84, and 10.03 μ. The product was shown to be 95% pure by vapor phase chromatographic analysis.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.84; H, 10.79.

Alcoholysis of Polymethyleneketene Dimers and Trimers.—The dimers I–III and the trimers IV–VI underwent cleavage when treated with ethanol containing a catalytic amount of sodium ethoxide to give the corresponding keto esters IX–XIV. The reactions were carried out using the same procedure. To a solution of 12 ml of absolute ethanol containing 0.03 g of sodium ethoxide was added 5 g of the dimer or trimer in portions, and the

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[24] V. Meyer, *Ber.*, **30**, 1941 (1897).

[25] B. A. Kasansky and W. P. Golmov, *Compt. Rend. Acad. Sci. URSS*, **34**, 196 (1942); *Chem. Abstr.*, **37**, 1703 (1943).

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resulting solution was allowed to stand 0.5 hr before it was acidified with 0.2 ml of glacial acetic acid. The solvent was removed under reduced pressure and the esters were purified by distillation.

Ethyl 1-(cyclobutanecarbonyl)cyclobutanecarboxylate (IX) was obtained in 86% yield: bp 99.5° (2 mm); $n^{25}\text{D}$ 1.4646; $d^{25}{}_4$ 1.0419; MR 55.73 (calcd 55.84); $\lambda_{\max}^{\text{CCl}_4}$ 3.38, 5.75, 5.85, 6.92, 7.32, 7.40, 7.87, 8.03, 8.22, 8.95, and 10.32 μ.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.26, 68.28; H, 8.75, 8.71.

Ethyl 1-(cyclopentanecarbonyl)cyclopentanecarboxylate (X) was obtained in 72% yield: bp 123 (2 mm); $n^{25}\text{D}$ 1.4723; $d^{25}{}_4$ 1.0250; MR 64.21 (calcd 64.11); $\lambda_{\max}$ 3.44, 3.52, 5.76, 5.87, 6.91, 7.35, 7.73, 8.10, 8.33, 8.61, 8.91, 9.20, 9.75, 10.53, and 11.65 μ.

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.55; H, 9.48.

Ethyl 1-(cyclohexanecarbonyl)cyclohexanecarboxylate (XI) was obtained in 92% yield: bp 143–144° (2 mm); $n^{25}\text{D}$ 1.4786; $d^{25}{}_4$ 1.0200; MR 73.93 (calcd 73.35); $\lambda_{\max}^{\text{CCl}_4}$ 3.43, 3.51, 5.77, 5.85, 6.90, 7.34, 7.70, 8.27, 8.83, 9.02, 9.17, 9.38, 9.78, and 10.15 μ.

Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 71.94; H, 10.01.

Ethyl 1-[1-(cyclobutanecarbonyl)cyclobutanecarbonyl]cyclobutanecarboxylate (XII) was obtained in 85% yield: bp 148–149° (2 mm); $n^{25}\text{D}$ 1.4934; $d^{25}{}_4$ 1.1057; MR 76.88 (calcd 77.22); $\lambda_{\max}^{\text{CCl}_4}$ 3.38, 5.72, 5.92, 7.77, 8.04, 8.23, 8.36, 8.65, and 9.07 μ.

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.00, 69.94; H, 8.29, 8.23.

Ethyl 1-[1-(cyclopentanecarbonyl)cyclopentanecarbonyl]cyclopentanecarboxylate (XIII) was obtained in 76% yield: bp 187° (2 mm); $n^{25}\text{D}$ 1.4964; $\lambda_{\max}$ 3.42, 3.50, 5.75, 5.85, 5.92, 6.90, 7.34, 7.72, 8.10, 8.62, 9.00, and 9.75 μ.

Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.70; H, 8.81.

Ethyl 1-[1-(cyclohexanecarbonyl)cyclohexanecarbonyl]cyclohexanecarboxylate (XIV) was obtained in 68% yield: bp 190° (0.5 mm); $n^{25}\text{D}$ 1.5018; $\lambda_{\max}$ 3.43, 3.51, 5.75, 5.84, 5.94, 6.90, 7.33, 7.68, 8.25, 8.84, 8.95, 9.13, 9.77, 10.05, and 10.17 μ.

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.49; H, 9.50.

Reduction of Polymethyleneketene Dimers and Trimers.—The dimers I and III, and the trimers IV–VI were reduced with lithium aluminum hydride, using essentially the same procedure for each. A solution of 0.5 g of ketone in 25 ml of ether was slowly added to a stirred slurry of 0.241 g of lithium aluminum hydride in 25 ml of ether, and the suspension was stirred 2 hr. The excess lithium aluminum hydride was destroyed with ethyl acetate, followed by addition of 25 ml of cold 10% sulfuric acid solution. The ether layer was separated and washed with 5% sodium carbonate, then dried over anhydrous magnesium sulfate. The ether was evaporated and the residue was recrystallized from benzene.

Dispiro[3.1.3.1]decane-5,10-diol (XV) was obtained in 89% yield: mp 99.5–101°; $\lambda_{\max}^{\text{KBr}}$ 2.95, 3.40, 6.98, 7.13, 7.75, 8.06, 8.93, 9.13, 9.50, and 9.78 μ.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; 9.59. Found: C, 70.89, 70.91; H, 9.61, 9.61.

Dispiro[5.1.5.1]tetradecane-7,14-diol (XVI) was obtained in 86% yield: mp 179–182°; $\lambda_{\max}^{\text{KBr}}$ 2.97, 3.45, 3.52, 6.90, 7.10, 8.77, 9.15, 9.55, and 9.76 μ.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 74.95; H, 10.78. Found: C, 75.16; H, 10.76.

Trispiro[3.1.3.1.3.1]pentadecane-5,10,15-triol (XVII) was obtained in 54% yield: mp 191–192.5°; $\lambda_{\max}^{\text{KBr}}$ 2.86, 3.02, 3.24, 3.40, 7.00, 8.06, 8.46, 9.10, 9.63, and 10.27 μ.

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.36; H, 9.59. Found: C, 71.01, 70.67; H, 9.69, 9.61.

Trispiro[4.1.4.1.4.1]octadecane-6,12,18-triol (XVIII) was obtained in 80% yield: mp 189–190° (two recrystallizations from methanol); $\lambda_{\max}^{\text{KBr}}$ 3.05, 3.42, 3.50, 6.84, 9.48, 9.80, 10.05, 10.38, and 10.55 μ.

Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.32; H, 10.18.

Trispiro[5.1.5.1.5.1]heneicosane-7,14,21-triol (XIX) was obtained in 62% yield: mp 229–231°; $\lambda_{\max}^{\text{KBr}}$ 2.97, 3.45, 6.85, 6.87, 7.96, 9.91, and 11.03 μ.

Anal. Calcd for $C_{21}H_{36}O_3$: C, 74.95; H, 10.78. Found: C, 75.20; H, 10.87.

Dehydration of Trispiro[4.1.4.1.4.1]octadecane-6,12,18-triol (XVIII).—To 10 ml of cold, concentrated sulfuric acid was added 1 g (0.0034 mole) of XVIII. The mixture was stirred for 45 min and then allowed to stand for an additional 30 hr. During this period the temperature was not allowed to rise over 10°. The mixture was extracted with 100 ml of pentane. The extract was washed with 5% sodium bicarbonate solution. The solvent was removed by distillation to yield a residue consisting of 0.18 g (22%) of dodecahydrotriphenylene (XX), mp 231–233°, mmp 232–233°. The infrared spectrum was identical with that of an authentic sample of XX, prepared[16] from cyclohexanone. The sulfuric acid layer was poured over ice, and the resulting mixture was extracted with ether. After the ether extract was washed, dried, and concentrated, a yellow oil remained which was not identified.

Polymerization of Diphenylketene.—To 10 g of diphenylketene, under an atmosphere of dry nitrogen, was added 0.1 g of sodium methoxide, and the resulting suspension was stirred and heated slowly. When the temperature reached 80°, an exothermic reaction occurred and the temperature increased rapidly to 146°. The reaction was complete in 5 min, and the product solidified. The solid was dissolved in hot benzene, and the catalyst was neutralized with 0.2 ml of glacial acetic acid. After washing the benzene solution with five 20-ml portions of water, it was concentrated by evaporation. Upon addition of an equal volume of pentane, 7 g of 3-hydroxy-2,2,4,4-tetraphenyl-3-butenoic acid β-lactone, mp 147–148° (lit.[18] mp 148°), was obtained. The mother liquor was concentrated and pentane was added again to yield 2.1 g of the same compound, making a total of 9.1 g (91%) of the β-lactone dimer: $\lambda_{\max}^{\text{CCl}_4}$ 3.29, 5.39, 6.02, 6.73, 6.95, and 8.60 μ.

It was found that the reaction temperature was critical for consistant results. When the catalyst was added to diphenylketene at 160°, a mixture of products was obtained from which 0.5 g of tetraphenyl-1,3-cyclobutanedione, mp 244–245° (lit.[20] mp 244–245°), and 4.5 g of the β-lactone dimer, mp 147–148°, were isolated.