isocyanate or phosphorus oxychloride as dehydrating agents, the former providing some small advantages in yields, the latter some advantages in isolation of product.

Experimental

3a,4,4a,7a,8,8a-Hexahydro-3-propyl-4,8-methano-5H-indeno-[5,6,*d*]isoxazole.—Seventy-five milliliters of dry benzene was placed in a round-bottomed flask equipped with a mechanical stirrer and a reflux condenser fitted with a calcium chloride drying tube. To this were added 47.6 g. (0.4 mole) of phenyl isocyanate, 20.6 g. (0.2 mole) of 1-nitrobutane, 13.2 g. (0.1 mole) of cyclopentadiene dimer, and 10 drops of triethylamine. The reaction mixture was stirred 1 hr. at room temperature, followed by a 1-hr. reflux period. The solution was cooled and filtered. The *sym*-diphenylurea obtained was recrystallized from ethanol to yield 36.90 g. (86.9% conversion), m.p. 235–236°. The solvent was removed with a water aspirator and the residue triply distilled under vacuum, yielding 7.38 g. (26.23% conversion) of the isoxazoline, b.p. 122° (0.7 mm.); $n^{24}\text{D}$ 1.5209.

Anal. Calcd. for $C_{14}H_{19}NO$; C, 77.37; H, 8.81; N, 6.45. Found: C, 77.42; H, 8.79; N, 6.48.

Attempted Preparation of an Isoxazoline from Hexachlorocyclopentadiene and 1-Nitrobutane.—To 40 ml. of benzene was added 16.7 g. (0.14 mole) of phenyl isocyanate, 7.2 g. (0.07 mole) of 1-nitrobutane, 19.1 g. (0.07 mole) of hexachlorocyclopentadiene, and 5 drops of triethylamine. The reaction mixture was stirred 3 days at room temperature and the reflux period omitted. It was then cooled and the *sym*-diphenylurea filtered and recrystallized from ethanol, m.p. 232–235°. The filtrate was distilled and yielded 18.42 g. of hexachlorocyclopentadiene, b.p. 59–60° (0.8 mm.), and a few grams of dipropylfuroxane, b.p. 82–85° (0.8 mm.); $n^{24}\text{D}$ 1.4785. Identification was made by infrared analysis.

Similar results were obtained with cholesteryl acetate, cyclohexene, dimethyl itaconate, β-nitrostyrene, benzoquinone, 1,4-naphthoquinone, and 2,3-dichloro-1,4-naphthoquinone.

3-Alkyl Acenaphtho[1,2,*d*]-2-isoxazolines.—The following general procedure was followed: to 15 ml. of benzene were added 4.53 g. (0.038 mole) of phenyl isocyanate, 0.019 mole of 1-nitroalkane, 2.89 g. (0.019 mole) of acenaphthylene, and 2 drops of triethylamine. The reaction mixture was stirred for 1 hr. and refluxed for 1 hr. The solution was then cooled, filtered, and evaporated.

Methyl 3-Alkyl-2-isoxazoline-4-carboxylates.—The following general procedure was followed: to 75 ml. of benzene was added 35.7 g. (0.30 mole) of phenyl isocyanate, 0.15 mole of nitroalkane, 12.9 g. (0.15 mole) of methyl acrylate, and 3 drops of triethylamine. The reaction mixture was stirred for 1 hr., refluxed for 1 hr., cooled, and filtered. The solvent was removed and the residue was vacuum distilled to obtain the pure but oily product.

***Methyl 3-Methyl-2-isoxazoline-4-carboxylate* (Acetic Anhydride as the Dehydrating Agent).**—To 22.0 g. (0.216 mole) of acetic anhydride was added 16.2 g. (0.216 mole) of nitroethane, 18.6 g. (0.216 mole) of methyl acrylate, and 39.3 g. (0.49 mole) of pyridine. The reaction mixture was stirred for 1 hr. followed by 2 hr. of refluxing on a steam bath. The low boiling constituents were removed with a water aspirator. This material had a green color which turned orange on standing. The remainder of the reaction mixture was triply distilled under vacuum. A small amount, 2.79 g. (9.02% conversion), of the product, b.p. 78–79° (1 mm); $n^{26}\text{D}$, 1.4561, was obtained.

Anal. Calcd. for $C_6H_9NO_3$: C, 50.53; H, 6.34; N, 9.79. Found: C, 50.29; H, 6.54; N, 10.40.

3-Methylacenaphtho[1,2,*d*]-2-isoxazoline (Phosphorus Oxychloride as the Dehydrating Agent).—To 100 ml. of chloroform in a three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser fitted with a calcium chloride drying tube, and a dropping funnel was added 3.04 g. (0.02 mole) of acenaphthylene, 1.50 g. (0.02 mole) of nitroethane, and 9.07 g. (0.896 mole) of triethylamine. The solution was cooled to 0° in an ice bath and then 3.06 g. (0.02 mole) of phosphorus oxychloride was added dropwise over a 15-min. period. After the addition of phosphorus oxychloride was completed, the reaction mixture was stirred 30 min. at ice-bath temperatures. The ice bath was removed and the reaction mixture refluxed 30 min. The chloroform was evaporated leaving a solid which was washed with petroleum ether (30–60°) and then with water. The product was recrystallized from methanol, m.p. 129–131°, and 1.55 g. (37.07% conversion) was obtained.

Formation of 2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetrione from Dimethylketene and from Its Polymers

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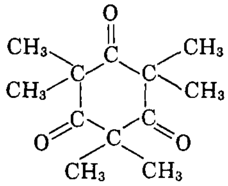
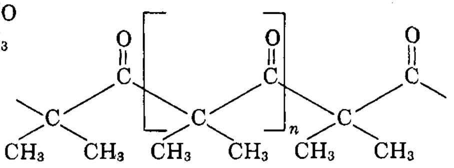
The dimerization reaction of dimethylketene forming tetramethyl-1,3-cyclobutanedione has been known for a long time, but recently[1,2] a cyclic trimer was obtained from dimethylketene. The structure of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione (I) was assigned to it.



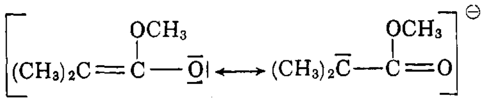
I



II

The reaction described by us[1] occurs readily in the presence of aluminum halides and, depending on the experimental conditions, the polymerization can stop after the addition of three monomeric units or can continue to the formation of linear macromolecules having structure II. Erickson and Kitchens[2] subsequently have obtained compound I in high yield by heating dimethylketene or tetramethyl-1,3-cyclobutanedione at 110° in the presence of sodium methoxide.

The mechanism of the reaction proposed by these authors involves the successive addition of two molecules of dimethylketene to carbanion III



$$\left[(CH_3)_2C{=}\overset{OCH_3}{\overset{|}{C}}{-}\overline{\underline{O}}| \longleftrightarrow (CH_3)_2\overline{C}{-}\overset{OCH_3}{\overset{|}{C}}{=}O\right]^{\ominus}$$

III

such that the polymerization stops with removal of the methoxyl anion. A mechanism of this type is similar to that indicated by Shashoua and co-workers for the polymerization of isocyanic compounds.[3]

The interpretation of the formation of hexamethyl-1,3,5-cyclohexanetrione, according to Erickson, does not agree with what we observed for the low-temperature polymerization of dimethylketene in the presence of basic substances. In fact, with organometallic compounds of the first three groups of the periodic table as catalysts, dimethylketene reacts rapidly,[4] yielding,

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(1) G. F. Pregaglia, G. Mazzanti, and M. Binaghi, *Makromol. Chem.*, **48**, 234 (1961).

(2) J. L. E. Erickson and C. Kitchens, *J. Org. Chem.*, **27**, 460 (1962).

(3) V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 867 (1960).

(4) G. Natta, G. Mazzanti, G. F. Pregaglia, and M. Binaghi, *Makromol. Chem.*, **44**, 537 (1961).

Table I

The Synthesis of 2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetrione from Dimethylketene and from Its Polymers

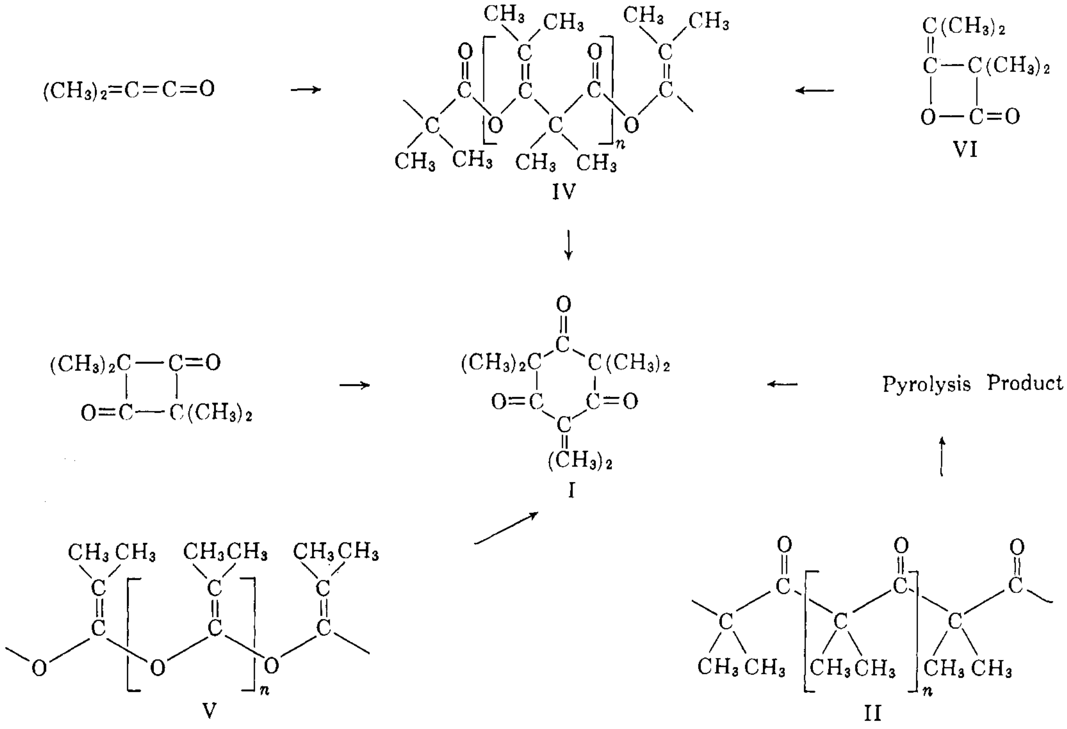


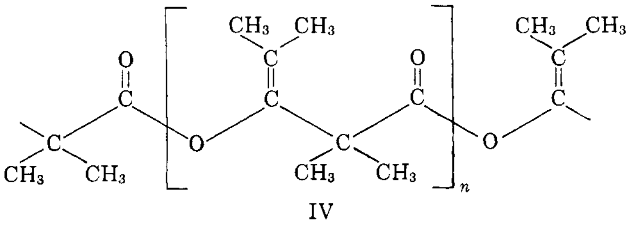
Table II

Formation of Hexamethyl-1,3,5-cyclohexanetrione (HCH) at 110° from Dimethylketene and from Its Derivatives

Starting material	Catalyst	Monomer units, moles / Catalyst, moles	Time	HCH yields, %	DMK high polymer yields, %[b]
DMK[a]	$NaOCH_3$	19.1	10 min.	57	40
DMK	$NaOCH_3$	43.5	2 min.	..	90
DMK	$NaOCH_3$	43.5	0.5 hr.	..	70
β-Lactone dimer (VI)	Na	6.6	16 hrs.	58	..
β-Lactone dimer (VI)	$NaOCH_3$	10.8	2 hrs.	80	..
β-Lactone dimer (VI)	$NaNH_2$[c]	5.1	6 hrs.	4	..
β-Lactone dimer (VI)	NaH	8.6	5 hrs.	..	70
Tetramethyl-1,3-cyclobutanedione	$LiOCH_3$	6	8 hrs.	80	..
Poly DMK (V)	$NaOCH_3$	8.7	20 hrs.	78	..
Poly DMK (IV)	$NaOCH_3$	4.35	20 hrs.	80	..
Poly DMK (II) (pyrolysis product)	$NaOCH_3$	10.8	0.5 hr.	80	..

[a] DMK = dimethylketene. [b] Methanol insoluble fraction. [c] One sixth of the catalyst was added at the start of the reaction and the remainder after 4 hours.

under suitable conditions, macromolecular compounds in which the structure of the polyester type IV is predominant.



IV

The same product was also obtained by Hasek,[5] by polymerizing dimethylketene in boiling ether solution with sodium methoxide as catalyst.

We have found that all the dimethylketene oligomers, or polymers with a high degree of polymerization, so far obtained, can be transformed almost quantitatively into the cyclic trimer by basic catalysts, such as sodium alkoxides, particularly when the reaction is carried out in solution (Table I). Moreover, if the dimethylketene monomer is employed as reagent, it does not cyclize directly, as reported by Erickson and Kitchens, but the hexamethylcyclohexanetrione is the final product of a more complex reaction, in which polymer IV is an intermediate. If dimethylketene is added to boiling toluene in the presence of catalytic amounts of sodium or lithium methoxide, and the reaction is stopped by an excess of methanol, a polymer with polyester IV structure is isolated in almost quantitative yield. The degree of polymerization of the macromolecules is obviously lower than that of polydimethylketene obtained at lower temperatures and, in some cases, oily

(5) R. H. Hasek, R. Donald Clark, E. V. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).

fractions can be isolated; however, the formation of the cyclic trimer was not observed. With an increase in the initial ratio of catalyst to monomer, the amount of macromolecular products decreases, and increasing amounts of cyclohexanetrione are formed. Finally, by the technique described by Erickson, if the reaction is started with catalytic amounts of sodium alcoholate and if after about half an hour a subsequent addition of catalyst is made, two steps of the process can be clearly distinguished; the first consists of the formation of linear macromolecules with a polyester structure, the second of degradation to form hexamethylcyclohexanetrione. The basic character of the catalyst seems to have a marked influence on the behavior of the reaction; for example, in the presence of sodium hydride or of sodium amide, dimethylketene at 110° polymerizes to a polyester and, even after several hours, the yield of hexamethyl-1,3,5-cyclohexanetrione is low. These results will be discussed in more detail in a subsequent paper.

In addition the dimethylketene dimer, 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (VI) is rapidly transformed at 110° into the cyclic trimer (I) by alkaline catalysts. If the reaction is stopped after a few minutes, it is possible to separate polyester IV in high yields, but high yields of hexamethylcyclohexanetrione are formed (Table II) in the presence of a sufficient amount of alcoholate or metallic sodium.

We have also observed that dimethylketene polymers having a polyacetalic (V) or polyketonic (II) structure can be transformed into the cyclic trimer rather slowly by sodium alcoholate. In the case of II, the conversion is low when molten polymer or a toluene suspension of polymer react directly; on the other hand, as was previously described,[4] the low solubility in nonpolar solvents and, perhaps, the chemical structure of polyketone make the chemical attack difficult in some cases. However, if the polymer is pyrolyzed at 300° and the viscous liquid thus formed reacts with sodium alcoholate, hexamethyl-1,3,5-cyclohexanetrione is isolated in high yield (80%).

The degradation of the dimethylketene polymers to cyclic trimer is only formally similar to that observed by Shashoua and co-workers for polyisocyanates.[3] While the trisubstituted cyanuric acid is formed by heating the linear polymer (together with the monomer), the conversion of dimethylketene polymers to cyclohexanetrione occurs only in the presence of a catalyst. In fact, the thermal degradation of polyketone II gives oily products which are apparently linear oligomers of dimethylketene, polyester IV is converted into β-lactone dimer[5] and polyacetal V partly cross-links and partly decomposes into the original monomer. In these three cases, the presence of the cyclic trimer was not observed. The mechanism of the reactions described will be discussed in a subsequent paper.

Experimental

Hexamethyl-1,3,5-cyclohexanetrione (I) from Dimethylketene.—Anhydrous toluene (50 ml.) and 0.5 g. of sodium methoxide were introduced under a nitrogen atmosphere into a flask immersed in an oil bath at 110°. The flask was equipped with a stirrer, a reflux condenser, and a jacketed dropping funnel cooled to −78°. During a period of 10 min., 22 ml. of dimethylketene was added to the stirred suspension. After the addition, the mixture was quickly cooled to room temperature, treated with an excess of ether, and then filtered. Distillation of the solution removed the ether and toluene leaving 10 g. of a white solid which, after crystallization from petroleum ether (b.p. 40–70°), melted at 80°. A mixed melting point with a sample of hexamethyl-1,3,5-cyclohexanetrione was undepressed.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.83; H, 8.83; mol. wt., 210.3. Found: C, 68.54; H, 8.83; mol. wt. (by cryoscopy in benzene), 207.

The precipitate which resulted by treating the reaction mixture with excess ether was washed with ether and dried *in vacuo* to give 8 g. of a solid. This product was soluble in boiling ether to the extent of 16.2% and on the basis of its infrared spectrum was polydimethylketene with a regular polyester structure (IV).

Polymerization of Dimethylketene without Formation of I.—Toluene (30 ml.) and 0.1 g. of sodium methoxide were introduced under a nitrogen atmosphere into a flask immersed in an oil bath at 110°. The flask was equipped with a stirrer, a reflux condenser, and a jacketed dropping funnel cooled to −78°. During a period of 2 min., 10 ml. of dimethylketene was added; after the addition, the contents of the flask were quickly cooled to room temperature and a large quantity of ethyl ether was added. The polymer formed was separated by filtration, and the ethereal filtrate was dried over anhydrous sodium sulfate. Evaporation left a few drops of oily residue. The polymer, washed with methanol and dried *in vacuo,* weighed 7.3 g. and was soluble in boiling ethyl ether to the extent of 5%. On the basis of its infrared spectrum it had a regular polyester structure.

Hexamethyl-1,3,5-cyclohexanetrione from 3-Hydroxy-2,2,4-trimethyl-3-pentenoic Acid β-Lactone (VI).—Sodium methoxide (0.5 g.) was added to 10 g. of VI in 30 ml. of toluene and the reaction flask was immersed in an oil bath at 150° for 2 hr. with frequent shaking. Toluene and unconverted β-lactone were distilled under slightly reduced pressure. Ether was added to the residue and the catalyst removed by filtration. The solvent then was evaporated to leave 8.0 g. of cyclohexanetrione residue (m.p. 78–80°, crystallized from petroleum ether).

Hexamethyl-1,3,5-cyclohexanetrione (I) from Polydimethylketene with a Polyketonic (II) Structure.—Eight grams of polydimethylketene with a polyketonic structure was introduced into a glass flask equipped with a distillation head. The flask was immersed in a bath of Wood's metal at 300°, and when the polymer was completely molten, 0.5 g. of sodium methoxide was rapidly introduced. Soon afterwards a yellow oily liquid began to distil. Six grams of liquid was collected in 1 hr., and about 0.1 g. of hexamethyl-1,3,5-cyclohexanetrione crystallized in the distillation head and in the condenser. Two grams of the pyrolysis product, dissolved in 10 ml. of toluene, was refluxed for 15 min., in the presence of 0.1 g. of sodium methoxide, and finally 1.6 g. of cyclic trimer of dimethylketene was isolated.

Hexamethylcyclohexanetrione from Polydimethylketene with a Polyacetalic Structure (V).—Four grams of polydimethylketene having a polyacetalic structure, 30 ml. of anhydrous toluene, and 0.5 g. of sodium methoxide were introduced in a flask equipped with a reflux condenser. The flask was immersed in an oil bath heated to 150° and the mixture was refluxed for 20 hr. A distillation head was then connected to the flask and toluene and any volatile products were removed by distillation (initially at atmospheric pressure and then under reduced pressure). The distillation residue was extracted by petroleum ether (b.p. 40–70°) and after filtration and subsequent evaporation the ether solution yielded 3.1 g. of a crystalline product (m.p. 78–80°). No depression was observed in a mixed melting point determination with hexamethylhexanetrione.

Reaction of 1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene with Alkoxide Ion; Evidence for the S_N2' Mechanism

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Previous work in this laboratory[1] showed that 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (I) reacts

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(1) J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am. Chem. Soc.* **72**, 2342 (1951).