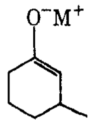
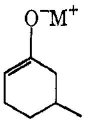
quenched. In the case of kinetic control, the trityllithium was about 20% in excess. The excess acetic anhydride was removed, the enol acetates were extracted with pentane, and the solution was distilled under vacuum. All the material which boiled below 150° at about 40 mm was collected and subjected to vapor phase chromatography. A 10 ft × $^3/_4$ in. copper tube packed with Carbowax on firebrick (9% Carbowax) was used. The column was operated at 150°. The two peaks due to the enol acetate of 3-methylcyclohexanone were collected and identified on the basis of their nmr spectra. In particular, the vinyl proton peak for the Δ^1 isomer was a doublet, and for the Δ^6 isomer it was a triplet.



Δ^1



Δ^6

The two vpc peaks are clearly separated, but are right next to each other. Retention times were not determined; however, a peak due to 3-methylcyclohexanone was identified from the vpc of the pure ketone, and the Δ^1 peak always appeared at 1.52 and the Δ^6 peak at 1.64, the time that the 3-methylcyclohexanone peak appeared. The areas under the two peaks were assumed to be proportional to the amounts of Δ^1 and Δ^6 isomers.

Tritylsodium and tritylpotassium were prepared directly from the metal and triphenylmethane, in the appropriate solvent, according to the method of House and Kramer.[8] Otherwise, the procedure was the same as that with trityllithium. Each experiment was performed in duplicate, and in no case was disagreement greater than 2%.

The solvents which were used were monoglyme (1,2-dimethoxyethane), diglyme [1,2-bis (2-methoxyethoxy)-ethane], triglyme [bis-2-(2-methoxyethoxy)ethyl ether], and tetrahydrofuran. Attempts to carry out the experiment in diethyl ether were unsuccessful. The enolization of 3-methylcyclohexanone in monoglyme, with trityllithium as the attacking agent, led to 18% Δ^1 isomer and 82% Δ^6 isomer under kinetic control, which is probably indicative of partial blockage by the methyl group of the approaching base. Equilibrium control was studied under a variety of conditions and the results are summarized in Table I.

TABLE I

Solvent	Cation	Δ^1, %	Δ^6, %
Monoglyme	Li^+	46	54
Monoglyme	Na^+	43	57
Monoglyme	K^+	48	52
Diglyme	Li^+	47	53
Diglyme	Na^+	26	74
Triglyme	Li^+	47	53
Tetrahydrofuran	Li^+	42	58

Under equilibrium conditions, the enolization of 3-methylcyclohexanone leads to a nearly 50:50 mixture of Δ^1 and Δ^6 isomers in all cases but one. In every case, the Δ^6 isomer is favored over the Δ^1 isomer.

As far as the lithium enolates are concerned, it apparently makes little or no difference whether the solvent is monoglyme, diglyme, or triglyme. On the other hand, there appears to be a significant difference for the sodium enolates. This may be a reflection of variations in cation–solvent interactions. The small lithium cation is perhaps equally as well solvated by any of the glymes. With tetrahydrofuran, for which the carbon chain is pulled out of the way of the oxygen, the equilibrium is shifted towards the Δ^6 isomer to a greater extent than with the glyme solvents. Indeed, in a situation in which the coordinating ability of the glyme molecule is eliminated, Agami and Prevost[9] have found that monoglyme is actually a better base than diglyme toward forming a hydrogen bond with chloroform. Zakharkin[10] and coworkers reported that Mg^{2+} is more strongly solvated by monoglyme than by diglyme. It should be pointed out, however, that other authors[11] have interpreted their results in terms of increased Li–glyme interaction in going up the glyme series. The nature of the anion may be significant. The studies reported in this paper involved an enolate anion which should bond to lithium *via* an oxygen, whereas the studies by Chan and Smid[11] involved the fluorenyl anion separated from the cation by a glyme molecule. With the larger sodium ion, it may be possible for the glyme molecule to wrap itself around the cation, and hence diglyme may interact to a considerably greater extent than monoglyme with Na^+. That is, the Na^+–diglyme system may involve solvent-separated ion pairs, whereas the other systems reported here may involve contact ion pairs. Perhaps, since the oxygen–sodium bond is weaker than the oxygen–lithium bond, the diglyme molecule is able to insert itself between cation and anion in the former case, but not in the latter. There is agreement among authors[11–13] that glyme–Na^+ interaction increases as the glyme series is ascended.

Registry No.—3-Methylcyclohexanone Δ^1-enol, 33521-81-2; 3-methylcyclohexanone Δ^6-enol, 33521-82-3.

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[8] H. O. House and V. Kramer, *J. Org. Chem.*, **27**, 4146 (1962).

[9] C. Agami and C. Prevost, *Bull. Soc. Chim. Fr.* 4467 (1968).

[10] L. J. Zakharin, O. Y. Okhlobystin, and K. Bilevich, *Tetrahedron*, **21**, 881 (1965).

[11] L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, **89**, 4547 (1967).

[12] R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967).

[13] M. Shinohara, J. Smid, and M. Szwarc, *ibid.*, **90**, 2175 (1968).

Mechanism of the Formation of 1,8,*exo*-9,11,11-Pentachloropentacyclo-[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-5-one in the Photolysis of Endrin

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Received August 27, 1971

Endrin (**1**) reportedly photolyzes to **2**[1,2] and two isomers, **3** and **4**.[3] Although proposed previously,[1] **2**

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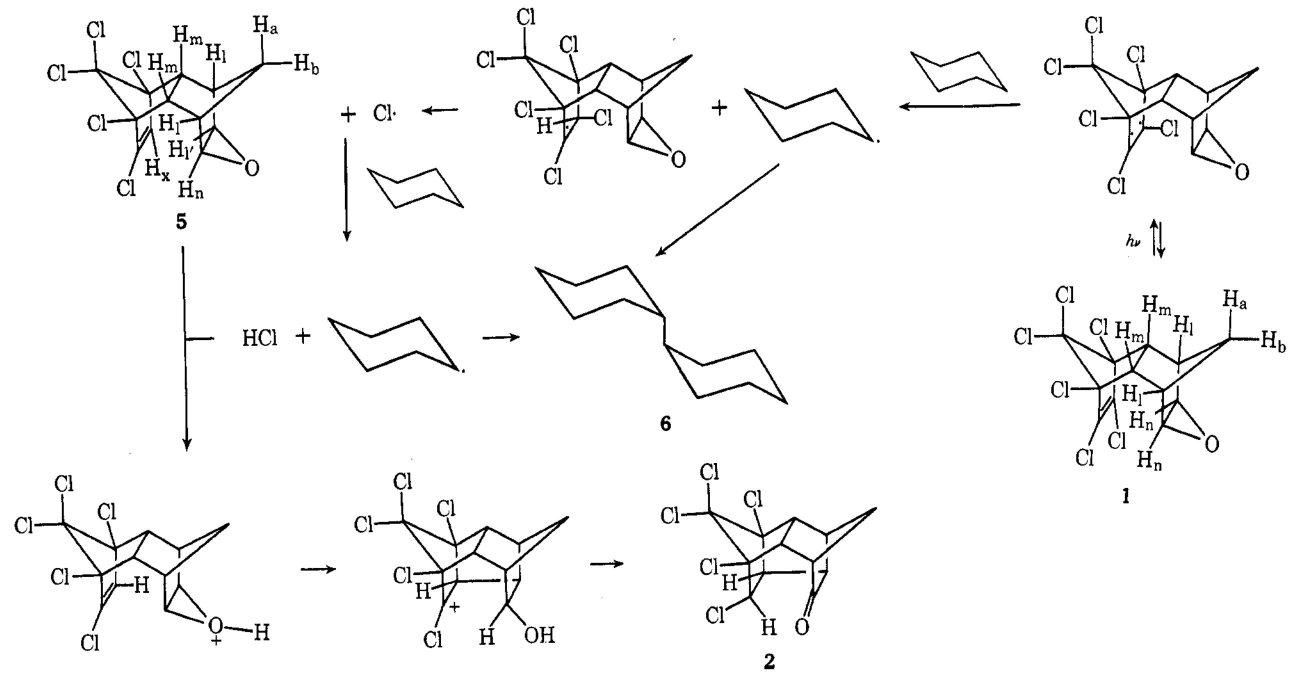
[1] M. Fujita, A. Ishii, and Y. Sakagami, *J. Hyg. Chem.*, **15**, 9 (1969).

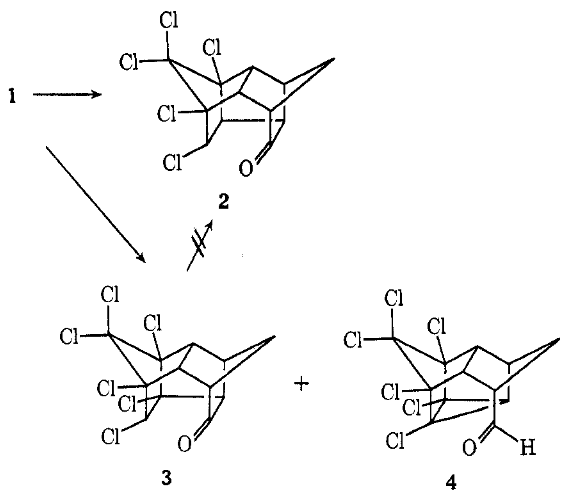
[2] M. J. Zabik, R. D Schuetz, W. L. Burton, and B. E. Pape, *J. Agr. Food Chem.*, **19**, 308 (1971).

[3] J. D. Rosen and D. J. Sutherland, *Bull Environ. Contam. Toxicol.*, **2**, 1 (1967).

SCHEME I



does not arise from **3**.[2] We now report experiments that bear on the mechanism of the conversion of **1** to **2**.



Isomer **3** is the major product of either thermal[4] or acid-catalyzed[5] rearrangement of **1**, but its formation could also be suitably explained photochemically *via* intramolecular H abstraction involving a six-membered transition state. However, since such an intramolecular H abstraction does not easily provide **2** from **1**, an alternate route involving the formation of an intermediate was explored. Base was added to take up the HCl produced in order to retard any effect of acid catalysis. When a heterogenous mixture of sodium hydroxide and **1** in cyclohexane was well stirred during the photolysis, only one photoproduct was formed as followed by nmr, ir, and tlc. No chemical shifts at δ 4.6 and 5.0, characteristic of compounds **2** and **3**, or any aldehydic resonances were observed in the nmr spectra. No hydroxyl or carbonyl bands were observed in the ir spectra. The photoproduct (**5**) was stable under the reaction conditions in the presence of **1**. The photolysis was followed for 16 hr with no appearance of compounds **2**, **3**, or **4**.

Bicyclohexyl (**6**) was found as a secondary product of the photolysis of **1** as identified by tlc, nmr, ir, and mass spectroscopy. Time studies using nmr as an analytical tool showed that bicyclohexyl was formed in a ratio of 1:1 with **5**.

Attempted separation of **5** from the concentrated reaction mixture by column chromatography through silica gel or Florisil gave over 90% rearrangement of **5** to **2**. A Florisil column prewashed with an alkaline solution still afforded 22% rearrangement of **5** to **2**. Heating **5** quickly to over 200° in a capillary tube gave nearly quantitative conversion to **2**; a trace component having an identical R_f value with that of 1,8,9,11,11-pentachlorohexacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]dodecan-5-ol was observed in the tlc.

On the basis of the data presented, it appears that the major route for the formation of **2** is *via* acid catalysis of **5**. The overall mechanism shown in Scheme I for the formation of **2** in the photolysis of **1** in cyclohexane is proposed.

Experimental Section[6]

Photolysis of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,-6,7,8,8a-octahydro-1,4-*endo*,*endo*-5,8-dimethanonaphthalene (1) (Endrin).—After stirring for 2 hr, a mixture of 25.0 g of Endrin and 2.65 g of NaOH pellets in 300 ml of pesticide grade cyclohexane[7] was irradiated in a distilled-water-cooled quartz immersion well (ambient temperature 29°) with a Hanovia 450-W mercury arc lamp equipped with a Vycor filter for 12 hr. Nmr

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[4] D. D. Phillips, G. E. Pollard, and S. B. Soloway, *J. Agr. Food Chem.*, **10**, 217 (1962).

[5] C. W Bird, R. C. Cookson, and E Crundwell, *J. Chem Soc.*, 4809 (1961).

[6] Infrared spectra were obtained with a Perkin-Elmer Model 21 double-beam recording spectrophotometer in CCl_4 solutions against a CCl_4 blank. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer using pesticide grade cyclohexane. Nmr spectra were determined on a Varian Associates Model A-60A spectrophotometer with tetramethylsilane as an internal standard. Mass spectral data were obtained using a Hitachi RMU-6 mass spectrometer at an ionization voltage of 70 eV Elemental analysis was determined by Dr. C. S. Yeh, Purdue University.

[7] Endrin, twice recrystallized from EtOH-H_2O gave uv max (cyclohexane) 222 nm (ϵ 4150).

analysis showed approximately 40% conversion of 1 to 5.[8] After concentration a representative sample, 0.200 g, was spotted on a Kontes K-416000 Chromaflex tlc plate coated with silica gel PF-254 and developed with a 4:1 solution of pentane–ethyl ether to yield three clear spots (1, 5, and 6) with R_f values of 0.54, 0.45, ad 0.81, respectively. Structures 1 and 6 were proved by isolation of these materials from the tlc plate and comparison (ir, nmr, tlc, and mass spectra) with authentic materials.

1,2,4,10,10-Pentachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (5).—This material, recovered from the tlc plate, slowly crystallized on standing to give mp 204-207° dec, sealed tube; uv max (cyclohexane) 219 nm (ϵ 2850); ir (CCl_4) 6.30 μ (ClC=CH), 11.73 μ (epoxide); nmr ($CDCl_3$) δ 6.04 (s, 1, H_x), 3.46 (m, 1, H_n), 3.13 (m, 2, H_m), 2.93 (m, 3, H_l), 1.81 (t of d, 1, J = 1.7, 10.0 Hz, H_b), and 0.99 (d, 1, J = 10.0 Hz, H_a); mass spectrum (70 eV), m/e (rel intensity) parent 344 (6.2) five chlorine pattern, P − Cl 309 (49.4) four chlorine pattern, base P − C_5H_6ClO 227 (78.0) four chlorine pattern, 82 (63.0), and 81 (75.2). The fragmentation pattern of photoproduct 5 is remarkably similar to that of 1 as seen by the alignment of their molecular ions.

Anal. Calcd for $C_{12}H_9Cl_5O$: C, 41.60; H, 2.62; Cl, 51.18. Found: C, 41.44; H, 2.89; Cl, 51.40.

Registry No.—1, 72-20-8; 2, 33487-97-7; 5, 33487-96-6.

Acknowledgment.—This investigation was supported in part by the Celanese Corp., Standard Oil of Ohio, and the Purdue Research Foundation, and by generous samples of Endrin from the Shell Development Co.

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[8] An initial solution containing 8.5 g of Endrin gave over 95% conversion of 1 to 5 in 4 hr.

Oxidation of Tetramethyl-1,3-cyclobutanedione under Baeyer–Villiger Conditions

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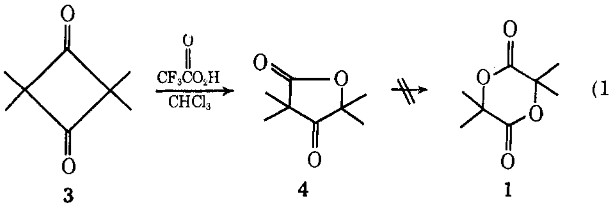
Received September 14, 1971

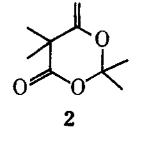
As part of a study on the acyloin reaction of lactones, we required large quantities of dilactones 1 and 2. A scan of the literature revealed only one laboratory synthesis of 1,[1] a vacuum pyrolysis of α-hydroxyisobutyric acid. The reported yield of 1 was 12% (10% in our hands).

It occurred to us that we might be able to synthesize 1 and/or 2 as a separable mixture by treating tetramethyl-1,3-cyclobutanedione (3) with 2 equiv of peracid (eq 1).



(1)

3 4 1

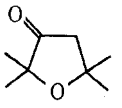


2

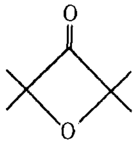
When this reaction was attempted using either monopermaleic acid[2a] or trifluoroperacetic acid[2b] in $CHCl_3$, only one product was formed. It was identified by its physical and spectral properties as 3,3,5,5-tetramethyl-2,4-furandione (4). When only 1 mol of peracid was used, 4 could be obtained in yields ranging from 95 to 75% depending on the scale of the reaction (0.1–to 1 mol).

Ketolactone 4 could not be further oxidized using either monopermaleic acid or trifluoroperacetic acid in chloroform even if the mixtures were heated for several days. In most cases good yields of 4 could be recovered. When the oxidation was run using monopermaleic acid in concentrated H_2SO_4–$CHCl_3$ (1:3), no oxidation products were observed but only 35% of 4 was recoverable. No attempt was made to isolate acidic products since if 1 were formed and subsequently hydrolyzed, α-hydroxyisobutyric acid would be formed and it, as noted, cannot be readily converted to 1.

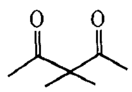
As part of the same project, we also found we were not able to oxidize 2,2,5,5-tetramethyl-3-furanone (5a)[3] by any of the above procedures.



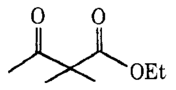
5a



5b



6



7

Boeseken and Jacobs[4] have shown that 2,2-dialkyl-1,3-dicarbonyl compounds 6 and 7 fail to undergo Baeyer–Villiger reaction. They speculated that the ketone carbonyls are too hindered to permit attack of the peracid. While this explanation might account for the lack of reaction of 4 and 5a, it does not account for the facile reaction of 3 or 5b[5] under similar conditions since their carbonyls are equally hindered to attack by the peracid. It seems apparent, however, that if the peracid can add to the carbonyl group of 3, relief of ring strain will be a driving force for product formation.

While we do not intend to pursue this approach to 1, the Baeyer–Villiger reaction on tetramethylcyclobutanedione appears to be an excellent and simple procedure for the synthesis of tetramethyltetronic acid (4), and probably of the other tetraalkylated derivatives of tetraonic acid, an important molecule in sugar chemistry.

Experimental Section

Melting points were taken on a Mel-temp apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrometer; nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard. Mass spectra were obtained on a Hitachi RMU6D mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

3,3,5,5-Tetramethyl-2,4-furandione (4) from 3.—Maleic anhydride (1.0 mol) is added carefully to a stirred mixture of 34 g of 98% hydrogen peroxide (1 mol + 10%) in 760 ml of $CHCl_3$. The mixture is warmed gently until the maleic anhydride is all

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[1] A. Golomb and P. D. Ritchie, *J. Chem. Soc.*, 838 (1962).

[2] (a) R. H. White and W. D. Emmons, *Tetrahedron*, **17**, 31 (1962); (b) W. F. Soger and A. Ruckworth, *J. Amer. Chem. Soc.*, **77**, 188 (1955).

[3] G. Dupont, *Ann. Chim Phys.*, **30**, 485 (1915).

[4] J. A. J. Boeseken and J. Jacobs, *Recl. Trav. Chim. Pays-Bas*, **55**, 804 (1936).

[5] J. K. Crandell and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966).