heated in a bath at a temperature which was raised slowly to 170°. After the reaction was completed (6 hr.) the volatile products were evaporated (18 mm.) at a temperature which was raised slowly to 200°. The fraction boiling at 203–209° (1 mm.) was collected and phenyl *p*-nitrophenyl phosphorochloridate was crystallized by cooling and scratching; yield 65%, m.p. 78–80°, fine needles. The infrared spectrum shows an absorption in the P→O (free) region at 7.65 μ. Chemically pure samples of the chloride are stable in refrigeration for more than 6 months.

Anal. Calcd. for $C_{12}H_9ClNO_5P$: C, 45.93; H, 2.87; N, 4.46; P, 9.88; labile Cl,[17] 2 H^+/mole. Found: C, 45.68; H, 2.58; N, 4.34; P, 9.57; labile Cl, 2.05 H^+/mole.

Phenyl, *p*-Nitrophenyl Hydrogen Phosphate.—To a solution of 4.25 g. (0.031 mole) of anhydrous potassium carbonate in 15 ml. of water, 9.4 g. (0.03 mole) of the above chloride was added in ten to fifteen portions, with vigorous stirring at a temperature not exceeding 75° (bath). An evolution of carbon dioxide gas was observed after a period of 30 min. The reaction mixture was cooled, acidified with sulfuric acid (1:2, pH 1), and then an oil precipitated which was extracted by ethyl ether. The ether layer was dried over potassium bromide and evaporated to a sirup. By treatment with hydrochloric acid a crystalline solid was obtained; yield 68%; m.p., after recrystallization from benzene, 101–102°.

Anal. Calcd. for $C_{12}H_{10}NO_6P$: N, 4.73; P, 10.5; neut. equiv. 1H^+/mole. Found: N, 4.92; P, 10.25; neut. equiv., 0.97 H^+/mole.

Phenyl *p*-Nitrophenyl Phosphamide.—3.1 g. (0.01 mole) of the chloride was treated with 5 ml. of ammonium hydroxide. A semisolid mass was precipitated which was crystallized by scratching; yield 70%; m.p., after recrystallization from ethanol, 167–168°.

Anal. Calcd. for $C_{12}H_{11}N_2O_5P$: N, 9.52; P, 10.51. Found: N, 9.63; P, 10.15.

Acknowledgment.—Our sincere thanks are due to Professor L. Zervas for many helpful and stimulating discussions. We wish to thank The Royal Hellenic Research Foundation for financial support.

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[17] For the titration precooled aqueous dioxane hydrolysate was used.

Thermal Decomposition of Dialkyl Oxalates

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Whereas dialkyl oxalates of tertiary alcohols thermally decomposed at about 140–160° to give good yields (80–100%) of olefins, those of primary and secondary alcohols resisted decomposition at least up to 325°. Dicyclohexyl, dibornyl, and diisobornyl oxalates, as well as oxalates of some cyclic tertiary alcohols, decomposed at higher temperatures, 200–300°, with decrease in olefin yield. Formate esters accompanied olefin formation whenever the decomposition temperature exceeded about 210°. With the exception of dibornyl and diisobornyl oxalates all other oxalates examined decomposed without skeletal rearrangements. The composition of the olefins obtained from the pyrolysis of dialkyl oxalates resembles those from acid and dimethyl sulfoxide dehydration of alcohols (Saytzeff-type elimination) rather than those from ester and xanthate pyrolysis (Hofmann-type elimination). An ion-pair mechanism is suggested for the reaction.

A wide variety of elimination reactions, whose mechanisms are fairly well understood, has been used for the preparation of olefins. The thermal decomposition of various esters, xanthates, amine oxides, halides, and related compounds involves cyclic concerted eliminations,[2] although in some cases of xanthate decomposition an ion-pair mechanism accommodates the results better.[3] The thermal decomposition of borate esters[4] and the dehydration of certain alcohols by dimethyl sulfoxide[5] have been interpreted in terms of ion-pair mechanisms.

We shall present the thermal decomposition of dialkyl oxalates as a convenient method for the dehydration of certain alcohols and briefly discuss the mechanism of the reaction.[6]

Results

Table I summarizes the results of the thermal decomposition of 22 dialkyl oxalates at atmospheric pressure. Olefin analysis was done by gas chromatography, n.m.r., and hydrogenation to saturated hydrocarbons. The n.m.r. analysis was facilitated by the differences in the chemical shifts of olefinic protons: terminal olefins ($CH_2=$) at τ *ca.* 5.4, nonterminal at 4.8–4.9, and endocyclic at 4.65 (cyclohexenes), 4.75 (cyclopentenes), and 4.38 (cyclobutenes). The gas chromatography and n.m.r. methods gave consistent results. At decomposition temperatures below about 160° the products are olefins and oxalic acid, whereas at higher temperatures the oxalic acid decomposes to water, carbon dioxide, and carbon monoxide.

Table II summarizes the results of the decomposition of dialkyl oxalates in quinoline solutions. In these reactions the oxalyl chloride was added to a solution of alcohol in quinoline and the oxalates were decomposed without prior isolation. The results are practically the same as those obtained from the decomposition of the pure oxalates.

In Table III the olefin composition is compared with those obtained from other elimination reactions. Table IV summarizes the *exo*/*endo* olefin ratios as functions of ring and alkyl group.

Dialkyl oxalates of primary and secondary acyclic alcohols, *e.g.*, neopentyl alcohol, 1-pentanol, 1-heptanol, 2-pentanol, and 3-pentanol, resisted decomposition up to 325°. Those of cyclohexanol, borneol, and isoborneol decomposed at higher temperatures than those of tertiary alcohols. Whenever the decomposition temperature exceeded 210° the olefins were accompanied by the formation of formates (eq. 1), whose identification was based on infrared (carbonyl stretch at 5.80 μ) and n.m.r. (formyl proton at τ 2.0) spectra. The

$$\text{ROCOCOOR} \longrightarrow \text{ROCHO} \qquad (1)$$

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[1] Fellow of the Alfred P. Sloan Foundation.

[2] For a review, see C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[3] (a) F. G. Bordwell and P. S. Landis, *J. Am. Chem. Soc.*, **80**, 6379 (1958); (b) D. G. Botteron and G. Shulman, *J. Org. Chem.*, **27**, 2007 (1962).

[4] O. L. Chapman and G. W. Borden, *ibid.*, **26**, 4193 (1961).

[5] V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *ibid.*, **27**, 2377 (1962).

[6] This project originated in the laboratories of Professor P. D. Bartlett whom we thank for his encouragement.

TABLE I

THERMAL DECOMPOSITION OF DIALKYL OXALATES

Oxalate	Decompn. temp., °C.	Olefin yield, %	Olefin compn. (mole %) Olefin	V.p.c.	N.m.r.	Hydrogenation product[a]
Di-*t*-butyl	147–150	82	Isobutylene	100		
Di-*t*-pentyl	141–142	90	2-Methyl-1-butene	31		2-Methylbutane
			2-Methyl-2-butene	69		
Di-(1,1-dimethylbutyl)	142–148	89	2-Methyl-1-pentene	35	42	2-Methylpentane
			2-Methyl-2-pentene	65	58	
Di-(1,1-dimethylpentyl)	144–147	84	2-Methyl-1-hexene	35	40	2-Methylhexane
			2-Methyl-2-hexene	65	60	
Di-(1,1-diethylpropyl)	142–148	90	3-Ethyl-2-pentene	100	100	3-Ethylpentane
Di-(1-ethyl-1-methylpropyl)	142	87	2-Ethyl-1-butene	6	8	3-Methylpentane
			trans-3-Methyl-2-pentene	27	92	
			cis-3-Methyl-2-pentene	67		
Di-(1-ethyl-1-methylbutyl)	147–150	100	2-Ethyl-1-pentene	20	15	3-Methylhexane
			cis- and *trans*-3-methyl-2-hexene	80	85	
			cis- and *trans*-3-methyl-3-hexene			
Di-(1-ethyl-1,2-dimethylpropyl)	140–144	73	2-Ethyl-3-methyl-1-butene	18	26	2,3-Dimethylpentane
			cis- and *trans*-3,4-dimethyl-2-pentene	51	53	
			2,3-Dimethyl-2-pentene	31	21	
Di-(1-cyclopentyl-1-methylethyl)	140–145	89	Isopropylidenecyclopentane	64	69	
			1-Isopropylcyclopentene	24	20	
			2-Cyclopentylpropene	12	11	
Di-(1-cyclohexyl-1-methylethyl)	135–140	87	Isopropylidenecyclohexane	17	17	
			1-Isopropylcyclohexene	83[b]	10	
			2-Cyclohexylpropene		73	
Di-(*trans*-1,2-dimethylcyclohexyl)	162–164	62	2-Methylmethylenecyclohexane	4	3	
			2,3-Dimethylcyclohexene	24	25	
			1,2-Dimethylcyclohexene	72	72	
Di-(1-methylcyclohexyl)	159–162	86	Methylenecyclohexane	6	7	Methylcycloyexane
			1-Methylcyclohexene	94	93	
Di-(1-ethylcyclohexyl)	156–165	73	Ethylidenecyclohexane	*b*	6	Ethylcyclohexane
			1-Ethylcyclohexene	*b*	94	
Di-(1-isopropylcyclohexyl)	250–280	50[c]	Isopropylidenecyclohexane	8		Isopropylcyclohexane
			1-Isopropylcyclohexene	92		
Di-(1-methylcyclopentyl)	134–138	91	Methylenecyclopentane	*d*	7	Methylcyclopentane
			1-Methylcyclopentene	*d*	93	
Di-(1-ethylcyclopentyl)	173–190	91	Ethylidenecyclopentane	24		Ethylcyclopentane
			1-Ethylcyclopentene	76		
Di-(1-isopropylcyclopentyl)	165–185	100	Isopropylidenecyclopentane	50	52	Isopropylcyclopentane
			1-Isopropylcyclopentene	50	48	
Di-(1-methylcyclobutyl)	220–250	39[e]	Methylenecyclobutane	52	51	
			1-Methylcyclobutene	48	49	
Di-(1-ethylcyclobutyl)	197–205	57	Ethylidenecyclobutane	75	77	
			1-Ethylcyclobutene	25	23	
Dicyclohexyl	245–250	81[f]	Cyclohexene	100		
Di-1-bornyl	300–310	88[g]	Bornylene	17		
			Tricyclene	47		
			Camphene	36		
Di-*dl*-isobornyl	250–280	54[h]	Bornylene	2		
			Tricyclene	4		
			Camphene	94		

[a] Product from the hydrogenation of the olefin mixture. [b] The two olefins could not be resolved by a didecyl phthalate or a silicone 550 oil column. [c] Contains 34% of the formate. [d] The olefins could not be resolved by a silicone 550 oil column. [e] Contains 41% of the formate. [f] Contains some formate. [g] Contains 40% of the formate. [h] Contains 5% of the formate.

infrared spectra of the formates isolated from the decomposition of dicyclohexyl, dibornyl, and diisobornyl oxalates matched those of authentic samples.

Dicyclopropylmethylcarbinol and tricyclopropylcarbinol did not react with oxalyl chloride. The reaction with dimethylcyclopropylcarbinol gave rearranged oxalates as evidenced from the loss of the cyclopropyl band at 9.8 μ and from the presence of vinyl protons in the n.m.r. spectrum.

Addition of oxalic acid to the dialkyl oxalates altered neither the decomposition temperature nor the % olefin composition. When refluxed for several hours with oxalic acid, a mixture of 2-cyclohexylpropene (73%), 1-isopropylcyclohexene (10%), and isopropylidenecyclohexane (17%) was changed to 2-cyclohexylpropene (24%), 1-isopropylcyclohexene (59%), and isopropylidenecyclohexane (17%). Methylenecyclohexane and 2-methyl-2-butene did not isomerize on distillation from pyridine–oxalic acid mixtures.

Discussion

Since any mechanistic conclusion from the available data must rely mainly on the olefinic composition, it is necessary to establish that olefin isomerization subsequent to olefin formation is mechanistically unimpor-

TABLE II

THERMAL DECOMPOSITION OF DIALKYL OXALATES FROM QUINOLINE SOLUTIONS

Oxalate	Decompn. temp., °C.	Olefin[a] yield, %	Olefin compn. (mole %)		
			Olefin	V.p.c.	N.m.r.
Di-*t*-pentyl	147–153	62	2-Methyl-1-butene	40	
			2-Methyl-2-butene	60	
Di-(1,1-diethylpropyl)	145–175	74	3-Ethyl-2-pentene	100	
Di-(1-ethyl-1-methylpropyl)	147–155	79	2-Ethyl-1-butene	12	
			trans-3-Methyl-2-pentene	23	
			cis-3-Methyl-2-pentene	65	
Di-(1-ethyl-1,2-dimethylpropyl)	160–170	66	2-Ethyl-3-methyl-1-butene	20	
			cis- and *trans*-3,4-dimethyl-2-pentene	48	
			2,3-Dimethyl-2-pentene	32	
Di-(1-methylcyclohexyl)	175–190	55	Methylenecyclohexane	6	
			1-Methylcyclohexene	94	
Di-(1-isopropylcyclohexyl)	204–207	40	Isopropylidenecyclohexane	8	
			1-Isopropylcyclohexene	92	
Di-(1-methylcyclopentyl)	130–145	74	Methylenecyclopentane		7
			1-Methylcyclopentene		93
Di-(1-ethylcyclopentyl)	165–185	86	Ethylidenecyclopentane	23	23
			1-Ethylcyclopentene	77	77
Di-(1-cyclopentyl-1-methylethyl)		73	Isopropylidenecyclopentane	66	72
			1-Isopropylcyclopentene	8	10
			2-Cyclopentylpropene	26	18
Di-(1-cyclohexyl-1-methylethyl)			Isopropylidenecyclohexane	33	35
			1-Isopropylcyclohexene	67[b]	9
			2-Cyclohexylpropene		56

[a] The yield is based on the amount of alcohol used. [b] The two olefins could not be resolved by v.p.c.

TABLE III

OLEFINIC COMPOSITIONS FROM ELIMINATION REACTIONS

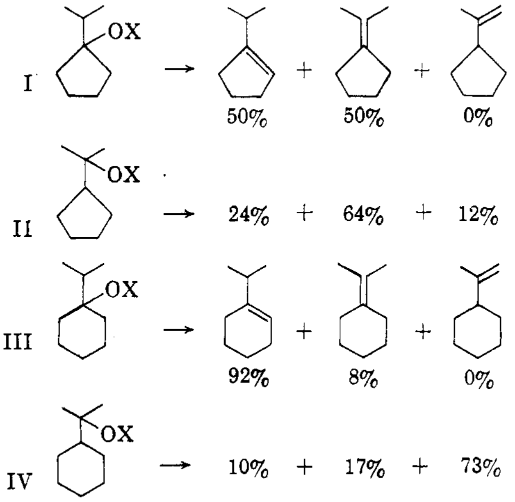
Alkyl group	Olefin	Mole %					
		Oxalate pyrolysis	Ester pyrolysis	Xanthate pyrolysis	Amine oxide pyrolysis	DMSO dehydration	Acid-catalyzed dehydration
1,1-Dimethylpropyl	2-Methyl-1-butene	31	70[a]			41[b]	22[c]
	2-Methyl-2-butene	69	30			59	78
1,1-Dimethylpentyl	2-Methyl-1-hexene	35				46[b]	55[c]
	2-Methyl-2-hexene	65				54	45
1,1-Diethylpropyl	3-Ethyl-2-pentene	100					100[c]
1-Methyl-1-ethylpropyl	2-Ethyl-1-butene	6					
	3-Methyl-2-pentene	94					~100[c]
1-Methylcyclobutyl	Methylenecyclobutane	52		15[d]			
	1-Methylcyclobutene	48		31			
	Isoprene	0		45			
1-Methylcyclopentyl	Methylenecyclopentane	7	16[e]		2.5[f]		
	1-Methylcyclopentene	93	84		97.5		
1-Ethylcyclopentyl	Ethylidenecyclopentane	24					12.5[g]
	1-Ethylcyclopentene	76					87.5
1-Methylcyclohexyl	Methylenecyclohexane	6	26[a]	21[h]	97.2[f]		
	1-Methylcyclohexene	94	74	79	2.8		
1-Ethylcyclohexyl	Ethylidenecyclohexane	6		12[h]			
	1-Ethylcyclohexene	94		88			
1-Isopropylcyclohexyl	Isopropylidenecyclohexane	8		22[h]			
	1-Isopropylcyclohexene	92		78			
trans-1,2-Dimethylcyclohexyl	2-Methylmethylenecyclohexane	4	55[i]				
	2,3-Dimethylcyclohexene	24	45				
	1,2-Dimethylcyclohexene	72	0				
Bornyl	Bornylene	17	24.5[j]	70[j]			
	Tricyclene	47	21.5	13.5			
	Camphene	36	54	16.5			Mainly[k]
Isobornyl	Bornylene	2	0[j]	38.5[j]			0[k]
	Tricyclene	4	13	0			0
	Camphene	94	87	61.5			100

[a] W. J. Bailey and W. F. Hale, *J. Am. Chem. Soc.*, **81**, 647 (1959). [b] Ref. 5. [c] J. M. Church, F. C. Whitmore, and R. V. McGrew, *J. Am. Chem. Soc.*, **56**, 176 (1934). [d] Ref. 9. [e] W. J. Bailey and W. F. Hale, *J. Am. Chem. Soc.*, **81**, 651 (1959). [f] A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957). [g] A. F. Plate and A. A. Mel'nikov, *Zh. Obshch. Chim.*, **29**, 1064 (1959); *Chem. Abstr.*, **54**, 1347 (1960). [h] R. A. Benkeser and J. J. Hazdra, *J. Am. Chem. Soc.*, **81**, 228 (1959). [i] D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *ibid.*, **81**, 643 (1959). [j] C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature*, **190**, 715 (1961). [k] V. N. Ipatieff and H. Pines, *J. Am. Chem. Soc.*, **66**, 1120 (1944).

TABLE IV
exo/endo OLEFIN RATIOS FROM THE PYROLYSIS OF DI-(1-ALKYLCYCLOALKYL) OXALATES

Cycloalkyl group	Alkyl group	*exo/endo* olefin ratio
Cyclohexyl	*trans*-1,2-Dimethyl	0.04
Cyclohexyl	Methyl	0.06
Cyclohexyl	Ethyl	0.06
Cyclohexyl	Isopropyl	0.09
Cyclopentyl	Methyl	0.08
Cyclopentyl	Ethyl	0.3
Cyclopentyl	Isopropyl	1.0
Cyclobutyl	Methyl	1.1
Cyclobutyl	Ethyl	3.0

tant. The following constitute cogent evidence that such isomerization is small and does not invalidate any mechanistic interpretation: constancy of olefin composition in the presence or absence of quinoline during the decomposition, constancy of decomposition temperature and olefin composition on addition of oxalic acid to dialkyl oxalates, failure of methylenecyclohexane and 2-methyl-2-butene to isomerize when distilled from quinoline–oxalic acid mixtures, significant differences in the composition of olefins obtained from bornyl or isobornyl oxalates, and differences in the composition of products obtained from I *vs.* II and III *vs.* IV.



From the similarity of the olefinic composition to those obtained from acid and dimethyl sulfoxide dehydration of alcohols rather than to those obtained from ester and xanthate pyrolysis, we suggest that dialkyl oxalate decomposition involves ion-pair formation rather than cyclic concerted elimination. In view of the experimental conditions—liquid instead of gas phase—and the greater acidity of oxalic acid, it is not surprising that dialkyl oxalate decomposition mechanistically differs from those of common ester pyrolysis.

The data do not permit a choice between a free-radical and an ionic mechanism for the formation of formates. If free radical, stretching of more than one bond must be involved in the transition state; *e.g.*, path 2 can be excluded in view of the stability of the dialkyl oxalates of primary and secondary alcohols at least up to 325°. The mechanism is under investigation.

$$\mathrm{ROCOCOOR} \longrightarrow 2\ \mathrm{ROCO}\cdot \qquad (2)$$

With the exception of the bornyl and isobornyl systems, all other systems examined eliminate without skeletal rearrangements. The lower temperature required for the decomposition of the isobornyl oxalate than that of bornyl oxalate is consistent with the higher ground-state energy of the isobornyl system and the possibility of anchimeric assistance in the transition state of this system. The high temperatures required for the decomposition of 1-alkylcyclobutyl oxalates result from the strain associated with the conversion of a tetrahedral cyclobutyl carbon to trigonal.

It has been observed with a variety of reactions that introduction of a double bond leads to higher *exo/endo* olefin ratios in five- than six-membered rings.[7] From the *exo/endo* olefin ratios summarized in Table IV it is apparent that this ratio is even higher when a four-membered ring is involved.[8] Alkyl substitution on the exocyclic double bond leads to pronounced increases of this ratio for a four-membered ring, less for a five-membered ring, and insignificant for a six-membered ring. It is of interest to note that, whereas the S-methyl xanthate of 1-methylcyclobutanol gives 45% isoprene,[9] the decomposition of the oxalate is unaccompanied by ring opening.

In view of its simplicity, low temperature of decomposition, and preferential dehydration of tertiary alcohols, dialkyl oxalate thermolysis compares favorably with other thermal decomposition methods. Its nonselectivity in the introduction of double bonds is an obvious disadvantage.

Experimental

Preparation of Dialkyl Oxalates.—The following is a typical procedure for the preparation of dialkyl oxalates. In a 500-ml., three-neck flask equipped with a dropping funnel, condenser, and mechanical stirrer were placed 11.1 g. (0.150 mole) of *t*-butyl alcohol, 13.0 g. (0.164 mole) of distilled pyridine, and 100 ml. of dry ether. To this 10.0 g. (0.079 mole) of oxalyl chloride in 50 ml. of dry ether was added dropwise during 35 min. The reaction mixture was stirred at room temperature for 12 hr. The slurry was then washed consecutively with cold water, cold 10% sulfuric acid, cold saturated sodium bicarbonate solution, and again with cold water. After the organic layer had been dried over magnesium sulfate, the ether was removed by distillation, yielding 11.5 g. (76%) of di-*t*-butyl oxalate, m.p. 69–70.5° (lit.[10] m.p. 71°).

Thermal decomposition of the oxalates was accomplished by two methods: (A) the esters were isolated and purified prior to decomposition and (B) the esters were prepared in the presence of a high-boiling base (quinoline) and thermally degraded *in situ*.

Method A.—To a 10-ml., round-bottom flask fitted with a 3.5-in. Vigreux column and a distillation head was added 2.50 g. (0.0097 mole) of di-(1,1-dimethylbutyl) oxalate. On heating in an oil bath, the ester decomposed at 142–148° to yield 1.45 g. (89%) of olefin.

Method B.—In a 500-ml., three-neck flask equipped with a reflux condenser, dropping funnel, and stirrer were placed 8.55 g. (0.075 mole) of 1-ethylcyclopentanol and 60 ml. of distilled quinoline. To the stirred solution was added dropwise 5.10 g. (0.040 mole) of oxalyl chloride. The mixture was allowed to react at room temperature for 3 hr. The condenser was then replaced by a 3.5-in. Vigreux column with distillation head, and the reaction mixture was heated at 165–185° for 90 min. while the ester decomposed, yielding 6.20 g. (86%) of olefin.

Hydrogenation of Olefins.—The following is a typical procedure. The olefin mixture, 0.5 ml., from the thermal decomposi-

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[7] For a review, see H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

[8] To avoid any misunderstanding it should be pointed out that these ratios are from kinetically controlled olefin formation. For *exo/endo* olefin ratios under equilibrium conditions, see, for five- and six-membered rings, R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958); for four-membered ring, E. Gil-Av and J. Herling, *Tetrahedron Letters*, **1**, 27 (1961).

[9] D. A. Semenov, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

[10] H. J. Backer and J. D. H. Homan, *Rec. trav. chim.*, **58**, 1048 (1939).

tion of di-(1,1-dimethylbutyl) oxalate was dissolved in 2.5 ml. of ethyl acetate and placed in a 50-ml. erlenmeyer flask with 0.05 g. of hydrogenation catalyst (10% Pd on charcoal). The flask was attached to a low pressure hydrogenation apparatus and the mixture was stirred magnetically overnight at room temperature under 1 atm. of hydrogen pressure. After filtering, the solution was submitted to gas chromatographic analysis. In addition to the solvent peak only one more peak was obtained which had identical retention time with that of authentic 2-methylpentane.

Gas chromatographic analyses were obtained from a Perkin-Elmer Model 154, an F and M Model 500, and a Beckman GC-2. All n.m.r. spectra were taken on an Varian A-60 n.m.r. spectrometer.

Acknowledgment.—One of us, J. M. Corbett, thanks the Dow Chemical Company, Midland, Michigan, for a leave of absence and generous support during the summer of 1962.

Organometallic Isocyanates and Isocyanurates of Groups IV and V[1]

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New synthetic methods are described for organotin, -antimony, and -arsenic isocyanates. They consist of fusing organometallic oxides with urea at 130°. Identical isocyanates were obtained by fusion of organometallic oxides with biuret at 170° and with isocyanic acid solutions at 70° and by metathetical reactions of organometallic halides with sodium cyanate. Organotin isocyanurates, a new class of compounds, were prepared by fusion of organotin oxides with cyanuric acid. They are remarkably thermostable.

Little is known about the synthesis and properties of organometallic isocyanates. The only organotin isocyanate described is triethyltin isocyanate,[2] prepared from triethyltin chloride and silver cyanate in alcohol. E. Krause[3] mentioned the preparation of triphenylantimony diisocyanate from triphenylantimony dichloride and silver cyanate. This paper is primarily concerned with new preparative methods for organometallic isocyanates of tin, antimony, and arsenic.

Urea Fusion.—In the course of an investigation into the preparation of N-organotin- and N-organoantimonyureas, the following discovery was made. When organotin oxides were fused with urea at 130°, ammonia was evolved and organotin isocyanates were obtained by the reactions shown below. Yields of 85–95% were achieved if dry nitrogen was bubbled through the melt at 130–140°, thereby removing ammonia and water from the reaction mixture.

$$R_3SnOH + (H_2N)_2CO \longrightarrow R_3Sn(NCO) + NH_3 + H_2O$$

$$(R_3Sn)_2O + 2(H_2N)_2CO \longrightarrow 2R_3Sn(NCO) + 2NH_3 + H_2O$$

$$\begin{gathered} \text{I, } R = n\text{-}C_4H_9 \\ \text{II, } R = i\text{-}C_4H_9 \\ \text{III, } R = C_2H_5 \end{gathered}$$

In analogous reactions trialkylantimony diisocyanates were obtained by fusion of trialkylantimony oxides (or bishydroxides) with urea. The reaction mixtures were quite viscous, and it became difficult to isolate trialkylantimony diisocyanates by distillation unless reduced pressure was applied during the fusion reaction for the removal of ammonia and water. Also triphenylarsenic diisocyanate was prepared by fusing triphenylarsenic oxide with urea.

$$R_3MO + 2(H_2N)_2CO \longrightarrow R_3M(NCO)_2 + 2NH_3 + H_2O$$

$$\begin{gathered} \text{V, } R = i\text{-}C_4H_9;\ M = Sb \\ \text{VI, } R = n\text{-}C_4H_9;\ M = Sb \\ \text{VII, } R = C_6H_5;\ M = As \end{gathered}$$

Fusion of polymeric dibutyltin oxide with urea resulted in evolution of ammonia and water, after which a clear melt was formed at 170–180°, which soon solidified at this temperature. Analyses of the wax-like reaction product (melting range 195–215°) indicated a conversion of the oxide to a polymeric isocyanate corresponding to the following complex structure.

$$[(C_4H_9)_2SnOSn(C_4H_9)_2(NCO)_2]_n$$

X

Fused urea also reacted with organotin and organoantimony chlorides. However, yields of isocyanates were only in the order of 20–30%, and the separation of the isocyanates from unreacted chlorides by fractional distillation was difficult.

The identity of isocyanates obtained by fusion with urea was confirmed by syntheses from organometallic chlorides and excess sodium cyanate. Excellent yields were obtained by refluxing the components in acetonitrile. Under these conditions, the sodium cyanate method appeared to be particularly suitable for organometallic diisocyanates.

Mechanism.—The formation of organotin isocyanates by fusion of organotin oxides with urea could conceivably proceed in different ways. Isocyanic acid, cyanuric acid, biuret, or organotinurea derivatives are possible reactive intermediates.

Triethyltin oxide is reported[2b] not to react with free isocyanic acid to form triethyltin isocyanate. Perhaps the reaction conditions in these attempts had been too mild. It has now been found that isocyanic acid reacts rapidly and almost quantitatively with organotin oxides at 70–80°. Refluxing benzene was found to be most suitable if the water of reaction was azeotropically removed into a Dean–Stark trap. Also trialkylantimony diisocyanates could be isolated by treating trialkylantimony oxides with isocyanic acid, which,

$$(R_3Sn)_2O + 2HNCO \longrightarrow 2R_3Sn(NCO) + H_2O$$

$$\begin{gathered} \text{I, } R = n\text{-}C_4H_9 \\ \text{III, } R = C_2H_5 \end{gathered}$$

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[1] After completion of this work, the synthesis of tributyltin isothiocyanate from thiourea was published by R. A. Cummins and P. Dunn [*Australian J. Chem.*, **17**, 411 (1964)]. Since their results are identical with observations in this work, reactions with thiourea have been eliminated from this paper.

[2] (a) P. Kulmiz, *J. prakt. Chem.*, **80**, 91 (1860); (b) H. H. Anderson and J. A. Vasta, *J. Org. Chem.*, **19**, 1300 (1954).

[3] E. Krause and W. v. Grosse, "Die Chemie der metall-organischen Verbindungen," Gebr. Borntraeger, Berlin, 1937, p. 631.