

Thermal Decomposition of Oxalate Diesters in the Presence of Iodine

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Dialkyl oxalates decomposed in the presence of iodine at temperatures at which the pure diesters were stable. Dioctadecanyl, dicyclohexyl, and di-1-adamantyl oxalate gave the corresponding iodides, whereas dibenzyl oxalate gave diphenylmethane. The mechanism of the iodine-induced decomposition of dialkyl oxalates is discussed.

THE photolysis of 1,2-dicarbonyl compounds has been suggested to lead to fission of the carbonyl-carbonyl bond.¹ Abstraction reactions which occur during photolysis of alkyl phenyl glyoxylates have been cited as evidence for the initial excitation of the carbonyl group to form an alkoxyl radical.² In order to account for the

products obtained in the photolysis of diethyl oxalate, Odaira and co-workers³ postulated alkoxy-carbonyl bond fission. These workers suggested that different initial fission processes of oxalyl chloride to produce chloro-oxalyl or chlorocarbonyl radicals occur with light of different wavelength.

The thermal decomposition of dialkyl oxalates has

¹ (a) P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Amer. Chem. Soc.*, **1964**, **86**, 1768; (b) N. C. Yang and A. Morduchowitz, *J. Org. Chem.*, **1964**, **29**, 1654; (c) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **1961**, **83**, 2395.

² E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, **1964**, **29**, 276.

³ Y. Odaira, T. Shimodaira, T. Tominaga, Y. Shigemitsu, and S. Tsutsumi, *Technol. Reports Osaka Univ.*, **1966**, **16**, 221.

recently been studied,⁴ and the thermal process has been suggested^{4a} to occur through concerted alkyl-oxygen and carbonyl-carbonyl bond cleavage.

In our study⁵ of the photochemical decomposition of alkyl hydrogen oxalates in the presence of mercury(II) oxide and iodine, it was shown that, apart from the 1-apocamphyl system, all systems gave appreciable yields of dialkyl oxalates and in most cases negligible yields of alkyl iodides. Treatment of 1-apocamphyl hydrogen oxalate with mercury(II) oxide and bromine in the dark resulted in the spontaneous evolution of carbon dioxide and the formation of 1-bromoapocamphane.⁶ The photolysis of 9-triptycyl hydrogen oxalate in the presence of mercury(II) oxide and iodine yielded 9-triptycyl iodoformate. This iodoformate was stable at room temperature and was decomposed to 9-iodotriptycene at 260°. The isolation of the iodoformate (in addition to other observations) was presented as evidence for the stability of the alkoxy carbonyl radical (I), in contrast to the instability of acyloxy radicals.⁷

In view of the thermal instability of 9-triptycyl iodoformate, it was envisaged that the thermal decomposition of dialkyl oxalates in the presence of iodine would lead to the formation of alkyl iodides and carbon dioxide. The results of these experiments are given in the Table.

Products of the thermal decomposition of oxalate diesters (RO·CO·CO·OR) in the presence of iodine.

R	Solvent	T/°C	t/h	Products	Yield (%)
Octadecanyle	Toluene	110	21	Diocadecanyle oxalate ^{a,b}	> 95
Octadecanyle	Xylene	140	21	Diocadecanyle oxalate ^{a,b}	> 95
Octadecanyle	Diphenyle ether	260	21	Diocadecanyle oxalate ^{a,b}	> 95
Octadecanyle		260	2	Octadecane ^{a-c}	79
Octadecanyle		140	2	1-Iodo-octadecane ^{a-c}	60
Cyclohexyle		110	2	Iodocyclohexane ^{a,b}	42
t-Butyle		80	2	Hydrocarbons ^{a-c}	
Benzyle		110	2	Diphenylmethane ^{a-c}	1.8
1-Adamantyle		140	2	1-Iodo-adamantane ^{a-d}	13
1-Adamantyle		140	0.75	1-Iodo-adamantane ^{a-d}	27
Phenyle		140	2	Diphenyle oxalate ^{a,b}	> 95
Phenyle		300	3	Unidentified tars	

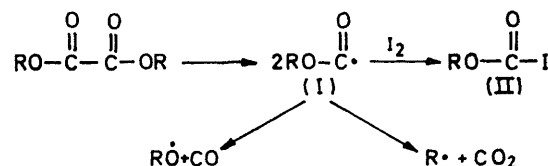
^a Identified by i.r. spectroscopy. ^b Identified by n.m.r. spectroscopy. ^c Identified by mass spectroscopy. ^d Found: C, 46.0; H, 5.8. Calc. for C₁₀H₁₅I: C, 45.8; H, 5.8%.

Although neat diocadecanyle oxalate could be heated at 260° for 2 h with negligible decomposition, a mixture of iodine and diocadecanyle oxalate decomposed at 140° in 2 h to 1-iodo-octadecane (60%). At higher temperatures (260°) the iodide was reduced to the alkane. When

⁴ (a) W. S. Trahanovsky, J. A. Lawson, and D. E. Zabel, *J. Org. Chem.*, 1967, **32**, 2287; (b) W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Amer. Chem. Soc.*, 1968, **90**, 2839; (c) W. S. Trahanovsky and C. C. Ong, *Tetrahedron Letters*, 1968, 3627; (d) W. S. Trahanovsky and C. C. Ong, *J. Amer. Chem. Soc.*, 1970, **92**, 7174; (e) W. S. Trahanovsky and P. W. Mullen, *Chem. Comm.*, 1971, 102; (f) D. G. L. James and S. M. Kambanis, *Trans. Faraday Soc.*, 1969, **65**, 1350.

diocadecanyle oxalate and iodine were refluxed in toluene (b.p. 110°), xylene (b.p. 140°), or diphenyle ether (b.p. 260°), the diester was recovered almost quantitatively after prolonged heating (21 h). The investigation of the reaction was extended to other primary, secondary, tertiary, and bridgehead systems. Diethyl, dicyclohexyle, and di-1-adamantyle oxalates gave the corresponding iodides when heated with iodine to temperatures below those at which the pure diesters were stable. Di-t-butyle oxalate gave polymeric hydrocarbons, which were probably formed from isobutene by polymerisation. The thermal decomposition of di-t-butyle oxalate has been shown⁸ to give a nearly quantitative yield of isobutene. Dibenzyle oxalate gave diphenylmethane, which was found to be readily formed when benzyle iodide was heated with iodine at the same temperature (110°). Other workers^{9,10} have obtained diphenylmethane from toluene, and suggested⁹ that it arose from reaction with benzene which was present as an impurity. Diphenyle oxalate in the presence of iodine was stable at 140°, but decomposed at 300° to give a complex mixture of tars which could not be resolved. Pure diphenyle oxalate is stable at temperatures as high as 350°.^{4a} It has been reported^{4a} that primary and secondary dialkyl oxalates are stable up to 325°, whereas tertiary dialkyl oxalates are decomposed at 140–160° to give olefins.⁸

The results indicate that iodine initiates the decomposition of oxalate diesters at temperatures at which they are normally stable. The primary process is probably fission of the central bond between the two carbonyl groups to form the intermediate alkoxy carbonyl radical (I). The effect of iodine in facilitating decomposition



could be due to its complexation with the carbonyl oxygen atoms, leading to an increase in the partial positive charge on the carbonyl carbon atoms. The partial positive charge on the carbonyl carbon atoms has been suggested¹¹ to account for the weakness of the carbonyl-carbonyl bond. Another mechanism by which iodine could initiate the fission of the central bond is the attack by iodine radicals on a carbonyl carbon atom to produce the iodoformate (II) and alkoxy carbonyl radical (I).

The intermediate radical (I) can decompose either to

⁵ K. Bartel, A. Goosen, and A. Scheffer, *J. Chem. Soc. (C)*, 1971, 3766.

⁶ A. Goosen and A. Scheffer, *J. S. African Chem. Inst.*, in the press.

⁷ (a) D. H. R. Barton, H. P. Faro, E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 1965, 2438; (b) J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 2500.

⁸ G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, 1965, **30**, 689.

⁹ R. D. Abell, *J. Chem. Soc.*, 1951, 1379.

¹⁰ L. A. Errede and J. P. Cassidy, *J. Org. Chem.*, 1959, **24**, 1890.

¹¹ P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *J. Amer. Chem. Soc.*, 1962, **84**, 3101.

the alkyl radical and carbon dioxide or the alkoxy radical and carbon monoxide. Prior to decomposition, radical (I) could be trapped by iodine to form the iodoformate (II), which would subsequently decompose. It has been shown that halogenoformates can be decomposed to give alkyl halides.^{5,12} Evidence that alkoxy-carbonyl radicals (I) can decompose to alkoxy radicals has been presented by us,⁵ and this is confirmed by the formation of ethylene carbonate in the pyrolysis of ethylene oxalate.¹³ The formation of esters^{4a} or iodides in the thermal decomposition of dialkyl oxalates in the absence and presence of iodine, respectively, is confirmation that the alkyl radicals are formed.

Evidence has been presented by Rüchardt¹⁴ that the stability of alkyl radicals is not the major influence in their formation, except when the radical is stabilised by delocalisation. The formation of tarry products, and the absence of iodobenzene or biphenyl in the reaction mixture obtained when diphenyl oxalate was decomposed in the presence of iodine, is best explained by the formation of phenoxy radicals and carbon monoxide from the intermediate phenoxy-carbonyl radical or iodoformate.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. N.m.r. spectra were run on a Perkin-Elmer R12A 60 MHz spectrometer. Light petroleum is the fraction of b.p. 40–60°.

General Preparation of Oxalate Diesters.—The alcohol in ether was treated with oxalyl chloride (0.5 equiv.) and refluxed for 14 h. The mixture was washed (aq. Na₂CO₃), dried (Na₂SO₄), concentrated, and purified by either crystallisation or vacuum distillation. Dibenzyl oxalate had m.p. 77° (lit.,^{4c} 78°) (from light petroleum). *Diocetadecanyl oxalate* had m.p. 129–133° (from methanol) (Found: C, 76.6; H, 12.4. C₃₈H₇₄O₄ requires C, 76.7; H, 12.6%). Dicyclohexyl oxalate had b.p. 200° at 3–5 mmHg (lit.,¹⁵ 190° at 73 mmHg), m.p. 44° (lit.,¹⁵ 45°) (Found: C, 66.4; H, 8.7. Calc. for C₁₄H₂₂O₄: C, 66.1; H, 8.7%). Di-*t*-butyl oxalate had m.p. 71–72° (lit.,⁸ 69–70.5°) (from methanol–water) (Found: C, 59.1; H, 8.7. Calc. for C₁₀H₁₈O₄: C, 59.4; H, 9.0%).

1-Adamantyl Hydrogen Oxalate.—Adamantan-1-ol (5 g) in ether (200 ml) was refluxed with excess of oxalyl chloride (20 ml) for 14 h. The mixture was concentrated to an oil, which was taken up in ether. The solution was washed with distilled water until the washings were chloride-free, and extracted with a stoichiometric amount of *N*-ammonium hydroxide. The cooled alkaline extract was acidified with a stoichiometric amount of ice-cold *N*-hydrochloric acid and extracted with ether. The extract which was washed with water, dried (Na₂SO₄), and concentrated to leave a solid, which crystallised from light petroleum as

prisms of 1-adamantyl hydrogen oxalate, m.p. 68° (Found: C, 61.8, 62.0; H, 7.3, 7.5. C₁₂H₁₆O₄·0.5H₂O requires C, 61.8; H, 7.35%).

Di-1-adamantyl Oxalate.—1-Adamantyl hydrogen oxalate (8.36 g, 0.016 mol) in dry chloroform (200 ml) was treated with iodine (66 g, 0.26 mol) and yellow mercury(II) oxide (25 g, 0.12 mol) and stirred in a stream of nitrogen which was subsequently bubbled through a barium hydroxide trap. The mixture was stirred for 15 min and then irradiated at room temperature, with a 1000 W tungsten lamp, placed under the flask, until the formation of barium carbonate in the trap ceased. The mixture was filtered, washed (aq. Na₂S₂O₃; aq. Na₂CO₃), dried (Na₂SO₄), and concentrated. The residue (9 g) was chromatographed on silica gel (400 g). Elution with benzene gave *di*-1-adamantyl oxalate (3.5 g), m.p. 146.5° (from methanol) (Found: C, 73.6; H, 8.5. C₂₂H₃₀O₄ requires C, 73.7; H, 8.4%).

Attempted Thermal Decomposition of Dioctadecanyl Oxalate.—Dioctadecanyl oxalate (0.298 g) in a sealed tube was heated at 260° for 2 h. T.l.c. and i.r. and n.m.r. spectra showed that no change took place.

Thermal Decomposition of Oxalate Diesters in the Presence of Iodine.—(a) *Diethyl oxalate.* A mixture of diethyl oxalate (25 ml) and iodine (25.4 g, 0.1 mol) was refluxed for 40 h. G.l.c. analysis showed the presence of ethyl iodide (56% yield). Distillation of the mixture through a fractionating column gave a fraction of b.p. 70–85° which was dissolved in carbon tetrachloride and washed with conc. ammonium hydroxide (to remove diethyl oxalate), dilute hydrochloric acid, and water, and dried (Na₂SO₄). The i.r. and n.m.r. spectra of this solution were identical with those of authentic ethyl iodide.

(b) *Solid oxalate diesters.* An equimolar mixture of the oxalate diester and iodine was either heated in a sealed glass tube or refluxed in a solvent (volume adjusted to give 0.05M-ester solution). The crude product was washed (aq. Na₂S₂O₃ and H₂O) and dried (Na₂SO₄). Products were identified by g.l.c. and spectroscopic (i.r. and n.m.r.) comparison with authentic samples and, in certain cases, by elemental analysis and mass spectrometry. The results are summarised in the Table.

Thermal Decomposition of Benzyl Iodide in the Presence of Iodine.—Benzyl iodide (1.09 g, 0.005 mol) was heated at 110° for 2 h with iodine (1.27 g, 0.005 mol) in a sealed tube. The product in chloroform (100 ml) was washed (aq. Na₂S₂O₃), dried (Na₂SO₄), and concentrated. The residue (0.4 g) was chromatographed on silica gel preparative t.l.c. plates (developed in light petroleum). The major product (0.08 g) was identical (i.r., n.m.r., and mass spectra) with authentic diphenylmethane.

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¹³ M. D. Tilcheev, *Ber.*, 1923, **56**, 2218.

¹⁴ C. Rüchardt, *Angew. Chem. Internat. Edn.*, 1970, **9**, 830.

¹⁵ 'Handbook of Chemistry and Physics,' The Chemical Rubber Company, 1969–1970.