

## A Comparison of Decomposition and Solvolysis Reactions of 1-Adamantyl Chloroglyoxylate and 1-Adamantyl Chloroformate

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Decomposition of 1-adamantyl chloroglyoxylate (I) in nitrobenzene at 105° is about 40,000 times slower than the analogous decomposition of 1-adamantyl chloroformate (II). In benzene at 105°, the ester (I) forms appreciable amounts of 1-phenyladamantane. Unlike the heterolytic reactions of ester (II), decomposition reactions of ester (I) may well be homolytic in nature. In contrast to the fragmentation observed during solvolysis-decomposition of ester (II), ester (I) undergoes a rapid methanolysis to give the mixed oxalate ester. However, ester (II) will give mixed carbonate esters in the presence of alkoxide or upon extensive dilution of the alcohol with benzene.

THE recently reported preparations of 1-adamantyl hydrogen oxalate and 1-adamantyl oxamate *via* 1-adamantyl chloroglyoxylate, which was isolated as an oil and used immediately,<sup>1</sup> prompts us to report a brief study we have made of this chloroglyoxylate. It is

extremely moisture sensitive, but, in the absence of moisture, of moderate stability. It was prepared from adamantan-1-ol and oxalyl chloride<sup>1-3</sup> in dry hexane under nitrogen.

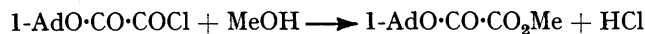
<sup>2</sup> G. V. Frank and W. Caro, *Ber.*, 1930, **63**, 1532.

<sup>3</sup> M. S. Simon and H. Mc. C. Seyferth, *J. Org. Chem.*, 1958, **23**, 1078.

<sup>1</sup> K. Bartel, A. Goosen, and A. Scheffer, *J. Chem. Soc. (C)*, 1971, 3766.

When the solid had been stored at room temperature for 2 months, 1-adamantyl chloride (80% yield) and traces of hexane-insoluble tar were isolated. In nitrobenzene, decomposition again gave 1-adamantyl chloride and traces of tar; this decomposition was appreciably slower than the analogous decomposition of 1-adamantyl chloroformate.<sup>4</sup> By use of the same analytical technique as previously employed for 1-adamantyl chloroformate,<sup>4</sup> a specific decomposition rate in nitrobenzene of  $1.7 (\pm 0.2) \times 10^{-5} \text{ s}^{-1}$  at  $105^\circ$  was observed; by extrapolation of the previously reported data,<sup>4</sup> it can be shown that 1-adamantyl chloroformate would decompose about 40,000 times faster under these conditions. Also, thermal reactions appeared to be of similar rate in both benzene and decane. From a reaction in benzene, a 13% yield of 1-phenyladamantane was isolated (with some tar). In decane, whether or not the reaction was protected from light, large amounts of tar were produced, in addition to unidentified carbonyl-group containing compounds. It has previously been suggested<sup>5</sup> that thermal reactions of  $\alpha$ -phenylethyl chloroglyoxylate in nitrobenzene and tetralin can be considered as  $S_N1$  decompositions incorporating, in the transition state, very little charge development. The complex behaviour of 1-adamantyl chloroglyoxylate in benzene and decane shows, at least for this substrate, the need to consider other reaction pathways; free-radical pathways, similar to those previously observed in photochemical reactions of chloroglyoxylates<sup>6,7</sup>, may well be implicated.

Addition of methanol to 1-adamantyl chloroglyoxylate leads rapidly to the mixed oxalate ester:



This behaviour differs from that of 1-adamantyl chloroformate, where loss of carbon dioxide is followed by formation of a mixture of 1-adamantyl chloride and 1-adamantyl methyl ether.<sup>8</sup> Several other reactions are known in which chloroglyoxylates retain the  $-\text{O}\cdot\text{CO}\cdot\text{CO}-$  unit under conditions where chloroformates eject their  $-\text{O}\cdot\text{CO}-$  unit as carbon dioxide. Friedel-Crafts reactions of alkyl derivatives are probably the best documented.<sup>9</sup>

In the solvolysis-decomposition of 1-adamantyl chloroformate in alcohols,<sup>8</sup> a delicate balance between attack at the acyl carbon atom and ionization was indicated by the introduction of a pronounced bimolecular component to the reaction upon addition of sodium alkoxide, with production of the 1-adamantyl alkyl carbonate. It was predicted<sup>8</sup> that alcoholysis of bridgehead chloroformates, which on ionization would lead to carbonium ions of energy appreciably greater than that of 1-adamantyl, would yield disubstituted carbonate esters and not ether and chloride. The 9-triptycyl carbonium ion is of this

type, and methanolysis of 9-triptycyl iodoformate does indeed lead to high yields of methyl 9-triptycyl carbonate.<sup>1</sup> Incidentally, this iodoformate appears to be the first ever to be prepared and characterized.<sup>10</sup>

In addition to the technique of enhancing nucleophilic attack at the acyl carbon atom by addition of sodium alkoxide, a method for the conversion of 1-adamantyl chloroformate into 1-adamantyl alkyl carbonates has been developed in which the ionization leading to carbon dioxide loss is inhibited by extensive dilution of the alcohol with low polarity benzene. Four 1-adamantyl alkyl carbonates have been prepared by one or both of these procedures.

#### EXPERIMENTAL

M.p.s were taken for samples in sealed capillary tubes by use of calibrated Anschutz thermometers and a Buchi apparatus. I.r. spectra were obtained with a Beckman IR-8 instrument and <sup>1</sup>H n.m.r. spectra with a Varian A-60A spectrometer. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

*Reagents.*—Solvents were purified and 1-adamantyl chloroformate was prepared as described previously.<sup>4,11</sup>

*1-Adamantyl Chloroglyoxylate.*—Adamantan-1-ol (2.0 g) was added to a solution of oxalyl chloride (10 g) in hexane (25 ml) under dry nitrogen. The mixture was stirred until all the adamantan-1-ol had dissolved (5–6 h), then evaporated to dryness. The residue was dissolved in the minimum amount of hexane. Cooling to  $-15^\circ$  precipitated a crop of impure solid which was recrystallized three times from hexane and dried under vacuum, to give a white solid (2.2 g, 70%), m.p.  $64-66^\circ$ ;  $\lambda_{\text{max}}$  (CCl<sub>4</sub>) 5.65 (C=O), 5.77 (C=O), 8.00 (C-O), 9.64, and 10.34  $\mu\text{m}$  (Found: C, 58.95; H, 6.35; Cl, 14.7. C<sub>12</sub>H<sub>15</sub>ClO<sub>3</sub> requires C, 59.4; H, 6.25; Cl, 14.6%).

*1-Adamantyl Methyl Oxalate.*—A suspension of adamantan-1-ol (1.0 g) in a solution of oxalyl chloride (5.0 g) in hexane (20 ml) was stirred under nitrogen until the adamantan-1-ol had dissolved. The solution was evaporated to dryness and methanol (25 ml) was drawn onto the residue. After 15 min, the excess of methanol was removed under reduced pressure and the oily residue was dissolved in the minimum amount of boiling hexane. The solution was cooled to  $0^\circ$  and the precipitate, containing adamantan-1-ol, filtered off. The filtrate was reduced in volume and cooled to  $-15^\circ$ , to give a white precipitate (0.99 g, 63%), m.p.  $42-44^\circ$ ;  $\lambda_{\text{max}}$  (KBr) 5.78 (C=O), 7.58, 8.38 (C-O), and 8.63 (C-O)  $\mu\text{m}$ ;  $\tau$  (CDCl<sub>3</sub>) 8.30 (6H, s), 7.80 (9H, s), and 6.15 (3H, s, Me) (Found: C, 65.45; H, 7.6. C<sub>13</sub>H<sub>18</sub>O<sub>4</sub> requires C, 65.5; H, 7.6%).

*Additional Reactions of 1-Adamantyl Chloroglyoxylate.*—(A) *Decomposition.* 1-Adamantyl chloroglyoxylate (4.0 g) was left in a stoppered Pyrex flask at room temperature for 2 months. The residue was dissolved in hot hexane and a small amount of insoluble tar was filtered off. Recrystallization of the hexane-soluble fraction from methanol gave

<sup>4</sup> D. N. Kevill and F. L. Weitzl, *J. Amer. Chem. Soc.*, 1968, **90**, 6416.

<sup>5</sup> S. J. Rhoads and R. E. Michel, *J. Amer. Chem. Soc.*, 1963, **85**, 585.

<sup>6</sup> C. Pac and S. Tsutsumi, *Tetrahedron Letters*, 1965, 2341.

<sup>7</sup> C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1966, **39**, 1926.

<sup>8</sup> D. N. Kevill and F. L. Weitzl, *Tetrahedron Letters*, 1971, 707.

<sup>9</sup> For chloroformates, see N. P. Buu-Hoi and J. Janicaud, *Bull. Soc. chim. France*, 1945, **12**, 640; for chloroglyoxylates, see L. Bert, *ibid.*, 1925, **37**, 1397, and R. G. Micetich, *Organic Preparations and Procedures*, 1970, **2**, 249.

<sup>10</sup> D. N. Kevill, in 'The Chemistry of Carbonyl Halides,' ed. S. Patai, Wiley-Interscience, New York, 1972.

<sup>11</sup> D. N. Kevill, K. C. Kolwyck, and F. L. Weitzl, *J. Amer. Chem. Soc.*, 1970, **92**, 7300.

1-adamantyl chloride (2.2 g, 80%), m.p. 164—165° (lit.,<sup>12</sup> 165°). A 0.054M-solution in nitrobenzene at 95° developed only traces of acid and tar after 3 days and the carbonyl group i.r. absorption disappeared. Presumably, a decomposition to 1-adamantyl chloride was the dominant reaction.

(B) *Reaction with benzene.* A sealed tube containing substrate (2.0 g) in benzene (10 ml) was maintained at 105—115° for 14 days. The solution yellowed and a small amount of brown tar separated. The solution was evaporated to dryness and several recrystallizations of the crude product from methanol gave 1-phenyladamantane (0.23 g, 13%), m.p. 77—80° (lit.,<sup>13</sup> 82°); i.r. and n.m.r. spectra consistent with the proposed structure.

(C) *Reaction with decane.* A 0.113M-solution of the substrate in decane was heated for several days at 95°. The inside of the Pyrex vessel became completely covered with black tar (even when wrapped in aluminium foil). In addition, carbonyl group i.r. absorption at 5.98  $\mu\text{m}$  (not due to unchanged chloroglyoxylate ester) developed within the solution.

*1-Adamantyl Methyl Carbonate.—Procedure A.* To 1-adamantyl chloroformate (1.0 g) in benzene (25 ml) was added, during ca. 2 h, a solution of methanol (0.5 g) and pyridine (2.0 g) in benzene (25 ml). The mixture was stirred overnight at room temperature, then washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to leave a crude, white solid which was recrystallized from hexane; yield 0.65 g (66.5%); m.p. 99—101°;  $\lambda_{\text{max}}$  (KBr) 3.44, 3.50, 5.79, 6.99, 8.02, 9.62, and 11.22  $\mu\text{m}$ ;  $\tau$  8.33 (6H, s), 7.88 (9H, s), and 6.32 (3H, s, Me) (Found: C, 68.55; H, 8.75.  $\text{C}_{12}\text{H}_{18}\text{O}_3$  requires C, 68.5; H, 8.65%).

*Procedure B.* To methanolic 0.5M-sodium methoxide (5 ml), 1-adamantyl chloroformate (0.5 g) was added. An immediate exothermic reaction was accompanied by sodium chloride precipitation. Evaporation under reduced pressure was followed by hexane extraction. Evaporation of the hexane left a white solid (0.40 g, 82%), m.p. 99—100°;  $\lambda_{\text{max}}$  (KBr) 5.79 (C=O) and 8.02 (C-O)  $\mu\text{m}$ .

*1-Adamantyl Ethyl Carbonate.—Procedure A.* This reaction was carried out as for the methyl derivative but with ethanol (0.8 g) substituted for the methanol and with an

\* Celite supplied by the Johns-Manville International Corp., New York.

extraction with 0.05M-hydrochloric acid preceding the wash with water. Evaporation yielded a liquid residue (0.95 g, 91%). A portion (0.25 g) was eluted from a silicic acid-Celite\* column with first hexane and then benzene. The benzene fraction yielded a colourless liquid (0.20 g, 73%), m.p. 13.5—15.5°;  $\lambda_{\text{max}}$  (hexane) 5.80, 8.11, 9.64, 11.50, 12.70, and 14.90  $\mu\text{m}$ ;  $\tau$  5.87 (2H, m, *J* 7 Hz,  $\text{CH}_2\text{-CH}_3$ ), 7.85 (9H, s), 8.32 (6H, s), and 8.70 (3H, t, *J* 7 Hz,  $\text{CH}_2\text{-CH}_3$ ) (Found: C, 69.35; H, 9.25.  $\text{C}_{13}\text{H}_{20}\text{O}_3$  requires C, 69.65; H, 9.0%).

*1-Adamantyl Isopropyl Carbonate.—Procedure A.* This was carried out as for the ethyl derivative but with propan-2-ol (1.0 g) substituted for the ethanol. Evaporation yielded a white solid (0.93 g), m.p. 57—67°. This material was eluted from a silicic acid-Celite column with first hexane and then benzene. The benzene fraction gave a white, crystalline solid (0.58 g, 52%), m.p. 69—70°;  $\lambda_{\text{max}}$  (KBr) 3.45, 5.86, 8.10, 9.68, and 11.19  $\mu\text{m}$ ;  $\tau$  5.22 (1H, m, *J* 6 Hz,  $\text{Me}_2\text{CH}$ ), 7.87 (9H, s), 8.33 (6H, s), and 8.75 (6H, d, *J* 6 Hz,  $\text{Me}_2\text{CH}$ ) (Found: C, 71.0; H, 9.45.  $\text{C}_{14}\text{H}_{22}\text{O}_3$  requires C, 70.55; H, 9.3%).

*1-Adamantyl t-Butyl Carbonate.—Procedure B.* To a solution of 1-adamantyl chloroformate (1.1 g) in t-butyl alcohol (20 ml) at room temperature was added 0.2M-sodium t-butoxide in t-butyl alcohol (25 ml). The solution was set aside overnight, then sodium chloride was filtered off. The filtrate was evaporated and the residue extracted with benzene. Celite was added to the benzene solution, which was then filtered. Evaporation of the benzene from the filtrate gave the crude product (1.1 g). A portion (0.58 g) was eluted from a silicic acid-Celite column with first hexane and then benzene. The benzene fraction gave a white, crystalline solid (0.32 g, 45%), m.p. 83—85°;  $\lambda_{\text{max}}$  (KBr) 3.44, 5.83, 8.00, 8.68, 9.63, and 11.62  $\mu\text{m}$ ;  $\tau$  7.87 (9H, s), 8.34 (6H, s), and 8.54 (9H, s,  $\text{Bu}^t$ ) (Found: C, 71.45; H, 9.65.  $\text{C}_{15}\text{H}_{24}\text{O}_3$  requires C, 71.4; H, 9.6%).

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<sup>12</sup> H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.

<sup>13</sup> S. Landa and S. Hala, *Chem. listy*, 1957, **51**, 2325.