Oxidative Fission of Some α-Substituted β-Diketones by Selenium Dioxide

By R. Howe* and D. Johnson, Imperial Chemical Industries Ltd., Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire SK10 4TG

3-Acetyl-1,2,3,4-tetrahydroisoquinoline-1,4-dione (Ia), the β-diketone tautomer of 3-acetyl-1,2-dihydro-4-hydroxyisoquinolin-1-one (I), was oxidised to 1,2,3,4-tetrahydroisoquinoline-1,3,4-trione (VI) and acetic acid by selenium dioxide (1 mol). The proposed mechanism involves 1,2,3,4-tetrahydro-5'-hydroxy-5'-methylisoquinoline-3-spiro-4'-(1,3,2-dioxaselenolan)-1,4-dione (VIII). This β-diketone fission may be general, but not always recognised because of further oxidation of the characteristic products. 1,2,3-Triphenylpropane-1,3-dione (XV), in which ready oxidation of fission products is precluded, gave benzil and benzoic acid as the only products.

THE oxidation of 3-acetyl-1,2-dihydro-4-hydroxyisoquinolin-1-one (I) [1] by selenium dioxide was examined as a possible method for preparing the related glyoxal (II), which was required for other work. With selenium dioxide (1·04 mol. equiv.) in acetic acid solution, 1,2,3,4-tetrahydroisoquinoline-1,3,4-trione [2] (VI) was obtained in high yield (89%). There was no trace of any glyoxal (II). The high yield of the trione (VI) suggested that it was not formed *via* possible intermediates (II) ⟶ (V) or their tautomers, which would have required 3 equivalents of selenium dioxide. This suggestion was supported by the fact that no carbon dioxide was evolved during the reaction. A reasonable mechanism, which requires only 1 equivalent of selenium dioxide, involves the intermediacy of the selenium(II) ester (VII),[3] which is possibly stabilised against hydrolysis as the spirodioxaselenolan (VIII), which can form a hydrogen bond with the neighbouring carbonyl group. Collapse of the spiro-compound (VIII) could then give the isoquinolinetrione (VI), acetic acid, and selenium. The proposition that the trione (VI) arises by oxidation of the dione (V), itself formed from the dione (Ia) by base-catalysed fission,[4] is untenable, because (Ia) was unaffected by treatment with acetic acid–water (8 : 1) at 100° for 12 h.

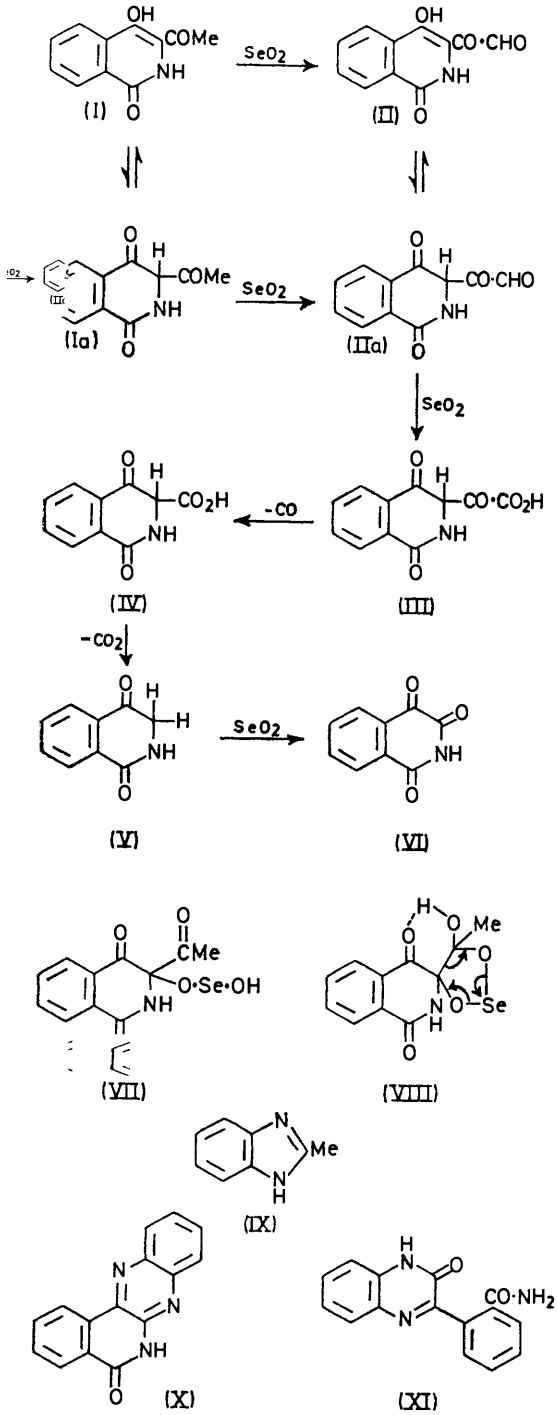
The conversion of the ketone (I) into the trione (VI) could be carried out less cleanly in aqueous dioxan (69% yield), which allowed the postulated formation of acetic acid to be verified. This was done by trapping it with *o*-phenylenediamine to form 2-methylbenzimidazole (IX). Quantitative isolation of the latter was not wholly satisfactory. The best yield [52%, based on 69% yield of (VI)], and the cleanest formation of (IX), was obtained by acidifying the total oxidation mixture and steam distilling the dioxan and acetic acid. After treatment of the distillate with sodium hydroxide and evaporation of the dioxan, the residual sodium acetate was heated under reflux with *o*-phenylenediamine in acid solution. The 2-methylbenzimidazole was isolated by preparative t.l.c. The isoquinolinetrione (VI) crystallised from the distillation-flask liquors.

It was not possible to trap the acetic acid cleanly by adding *o*-phenylenediamine directly to the total oxidation mixture. Under acid conditions, 2-methylbenzimidazole (IX) was formed, and the trione (VI) reacted with *o*-phenylenediamine to give the quinoxaline (X).[5] In another experiment, solid sodium carbonate was added to the oxidation mixture to neutralise the expected acetic acid. The dioxan was removed and then the residue was heated with *o*-phenylenediamine in acid solution. 2-Methylbenzimidazole was formed, along with the quinoxalin-2-one (XI). This was presumably formed by condensation of *o*-phenylenediamine with *o*-carbamoylphenylglyoxylic acid, produced by hydrolysis of (VI) under alkaline conditions.

In checking the scope and possible utility of this β-diketone fission it became clear that the isoquinolone (I) was a particularly suitable substrate because its fission product (VI) was not susceptible to further oxidation by selenium dioxide. In an experiment with the simple analogue 2-acetylcyclohexanone, which is not further reported, a complex mixture of products was obtained. According to the scheme proposed before, two fission pathways would be possible for the oxidation of 1-phenylbutane-1,3-dione (XII), (*a*) leading to benzoic acid and pyruvaldehyde and (*b*) leading to acetic acid and phenylglyoxal. Piutti [6] has reported that oxidation of 1-phenylbutane-1,3-dione by selenium dioxide in alcohol does not give 1-phenylbutane-1,2,3-trione. The acidic products identified by us were phenylglyoxylic acid and a trace of benzoic acid. Much starting material was recovered, and there was no trace of phenylglyoxal. It could be supposed at this stage that pathway (*b*) had predominated, and that initially formed phenylglyoxal had been further oxidised to phenylglyoxylic acid,[7] but alternative explanations are possible. 2-Methyl-1-phenylbutane-1,3-dione (XIII) also gave phenylglyoxylic acid and a trace of benzoic acid as the acidic products, but the neutral fraction contained 1-phenylpropane-1,2-dione (XIV) (16% yield on starting material), as well as starting material. 1-Phenylpropane-1,2-dione was converted in part into phenylglyoxylic acid and a trace of benzoic acid in a separate experiment. Thus, although the key product

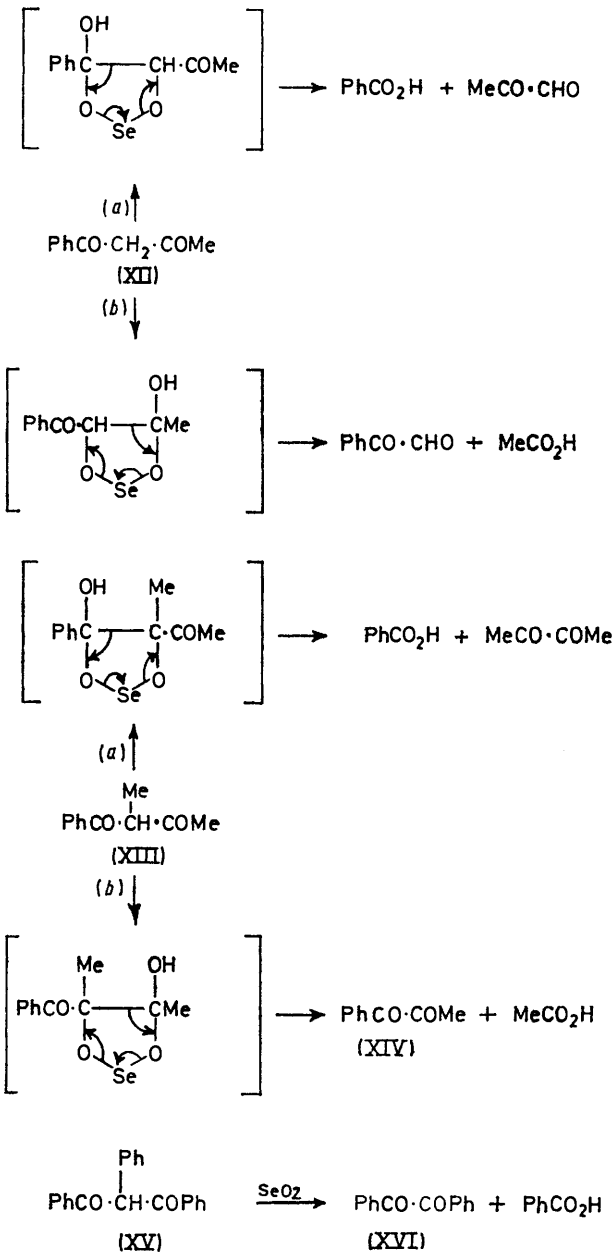
[1] S. Gabriel and J. Colman, *Ber.*, 1900, **33**, 2630.
[2] S. Gabriel and J. Colman, *Ber.*, 1902, **35**, 2421.
[3] E. J. Corey and J. P. Schaefer, *J. Amer. Chem. Soc.*, 1960, **82**, 918.
[4] R. G. Pearson and A. C. Sandy, *J. Amer. Chem. Soc.*, 1951, **73**, 931.
[5] S. Gabriel, *Ber.*, 1904, **37**, 4316.
[6] P. Piutti, *Gazzetta*, 1936, **66**, 276.
[7] R. Howe, B. S. Rao, and H. Heyneker, *J. Chem. Soc.* (*C*), 1967, 2510.

(XIV) was again susceptible to further oxidation, there was some support for the general nature of the fission. 1,2,3,-Triphenylpropane-1,3-dione (XV),[8] chosen so as to



preclude further oxidation of expected fission products, gave benzil (XVI) and benzoic acid as the only products. The reaction was conveniently short (6 h) in propionic acid at 139°, but in dioxan the reaction only proceeded to the extent of 50% during 3 days at 100°.

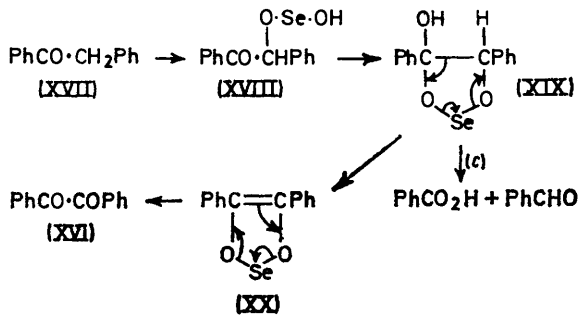
Cyclic selenium(II) ester hemiacetals could formally be involved in the oxidation of mono-ketones, *e.g.* deoxybenzoin (XVII), to α-diketones [3] and, in view of what has been shown above, fission (*c*) [arrows in (XIX)] might be expected to occur if there were no other over-riding factors. If all stages following the formation of the selenium(II) ester (XVIII) are fast, as Corey and Schaeffer [3] suggest, then there would be no contradiction of their kinetic data. We repeated the literature [3] oxidation of deoxybenzoin in acetic acid and confirmed



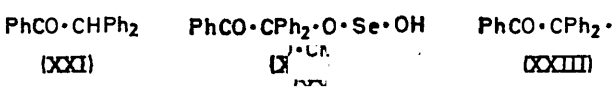
that benzil (XVI), the sole neutral product, is formed in excellent yield. The potassium carbonate wash used to remove the acetic acid was found to contain benzoic

[8] J. Marshall, *J. Chem. Soc.*, 1915, **107**, 509.

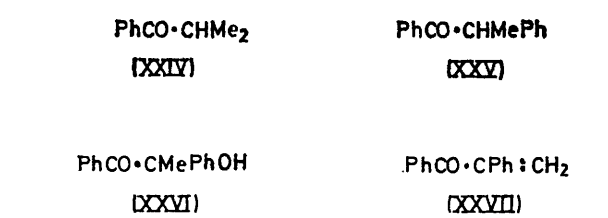
acid in *ca.* 1% yield. This did not provide any support for pathway (*c*), however, because when deoxybenzoin was heated in acetic acid in the absence of selenium dioxide, benzoic acid was obtained in *ca.* 3% yield. A



negligible amount of benzoic acid was formed when benzil was heated with selenium dioxide in acetic acid. We umed, therefore, that if the hemiacetal (XIX) were involved at all, then dehydration to the dioxaselenole (XX) leading to benzil (XVI) must be the preferred pathway. α-Phenyldeoxybenzoin [9] (XXI), in which the proposed dehydration step was precluded, gave α-phenylbenzoin [10] (XXIII) as the sole neutral product, and the predicted fission products, benzoic acid and benzophenone, were absent. It is possible that steric hindrance militated against formation of an intermediate



cyclic selenium(II) ester hemiacetal and that hydrolysis of the selenium(II) ester (XXII) was the preferred reaction. Under similar conditions, isopropyl phenyl ketone [11] (XXIV), which could have led to a less sterically hindered analogue of the ester (XXII), only reacted to



the extent of 10%, to give a mixture of products which was not further investigated. The lower reactivity of isopropyl phenyl ketone is reasonable because the C–H bond (*CH*Me$_2$) in (XXIV), which must be broken, does not have the benzylic character of the analogous bond in the α-phenyldeoxybenzoin (XXI). The final substrate, 1,2-diphenylpropan-1-one [12] (XXV), which does have a benzylic carbon atom, gave α-methylbenzoin [13] (XXVI) and 1,2-diphenylprop-2-en-1-one [14] (XXVII) as major products, and benzoic acid and phenylglyoxylic acid as minor products. Under the conditions of the experiment the hydroxy-ketone (XXVI) gave traces of benzoic acid and phenylglyoxylic acid but none of the unsaturated ketone (XXVII); starting material was largely recovered. Thus, the unsaturated ketone (XXVII) must arise directly from the ketone (XXV).

Thus, there is no evidence to suggest that monoketones with one or two substituents on the α-carbon atom can undergo oxidative fission of the type found for α-substituted β-diketones.

EXPERIMENTAL

T.l.c. was carried out using silica GF plates which were viewed under u.v. light.

Oxidation of 3-*Acetyl*-1,2-*dihydro*-4-*hydroxyisoquinolin*-1-*one* (I) *with Selenium Dioxide*.—(a) A solution of 3-acetyl-1,2-dihydro-4-hydroxyisoquinolin-1-one (2·03 g, 0·01 mol) and freshly sublimed selenium dioxide (1·15 g, 0·0104 mol) in glacial acetic acid (40 ml) and water (5 ml) was heated at 100° for 2 h. The mixture was filtered and the filtrate was evaporated to small volume. The solid 1,2,3,4-tetrahydroisoquinoline-1,3,4-trione which separated formed needles (1·55 g, 89%), m.p. 224—225° (from methanol) (lit.,[2] 224°) (Found: C, 61·7; H, 2·9; N, 8·0. Calc. for $C_9H_5NO_3$: C, 61·7; H, 2·9; N, 8·0%).

(b) In a separate experiment the apparatus was flushed with carbon dioxide-free nitrogen before and during the experiment. It was shown, by passing the outflowing gas through lime-water, that no carbon dioxide was evolved.

Isolation of Acetic Acid as 2-*Methylbenzimidazole* (IX).—A solution of 3-acetyl-1,2-dihydro-4-hydroxyisoquinolin-1-one (2·03 g, 0·01 mol) and selenium dioxide (1·17 g, 0·0106 mol) in dioxan (150 ml) and water (2 ml) was heated at 100° for 10 h. The mixture was acidified (pH 2) with sulphuric acid and then steam distilled to give 800 ml of distillate. Sodium hydroxide (800 mg) was added to the steam distillate and then the water and dioxan were evaporated. The residue was dissolved in water (5 ml), *o*-phenylenediamine (1·08 g, 0·01 mol) was added, and then the pH was adjusted to 2 with conc. hydrochloric acid. The mixture was heated under reflux for 30 min, cooled, made alkaline with ammonium hydroxide, and then extracted with ether. The extract (1·12 g) was shown by t.l.c. (methanol–ethyl acetate 1 : 9) to consist mainly of 2-methylbenzimidazole, R_F 0·2, and *o*-phenylenediamine, R_F 0·4. Preparative t.l.c. gave 2-methylbenzimidazole, m.p. and mixed m.p. 175—176° [0·48 g, 52% based on 69% yield of (VI)].

The residue after steam distillation was filtered to remove selenium and then concentrated to give, after purification, 1,2,3,4-tetrahydroisoquinoline-1,3,4-trione (VI) (1·2 g, 69%), m.p. 224°.

5,6-*Dihydroisoquino*[3,4-b]*quinoxalin*-5-*one* (X).—A solution of 3-acetyl-1,2-dihydro-4-hydroxyisoquinolin-1-one (2·03 g, 0·01 mol) and selenium dioxide (1·17 g, 0·0106 mol) in dioxan (80 ml) and water (2 ml) was heated at 100° for 10 h. *o*-Phenylenediamine (2·38 g, 0·022 mol) and water (100 ml) were added, and the pH was adjusted to 2 with conc. hydrochloric acid. The mixture was heated under reflux for 30 min, cooled, and filtered. The residual solid quinoxalinone (X) (1·8 g, 73%) formed needles, m.p. 274—276° (from methanol) (lit.,[5] 267—268° (Found: C, 72·8; H,

[9] H. Blitz, *Ber.*, 1893, **26**, 1952.
[10] S. F. Acree, *Ber.*, 1904, **37**, 2753.
[11] C. Schmidt, *Ber.*, 1889, **22**, 3249.
[12] V. Meyer and L. Oelkers, *Ber.*, 1888, **21**, 1295.
[13] R. Roger, *J. Chem. Soc.*, 1925, **127**, 518.
[14] H. Fiesselmann and J. Ribka, *Chem. Ber.*, 1956, **89**, 27.

3·7; N, 16·8. Calc. for $C_{15}H_9N_3O$: C, 72·85; H, 3·7; N, 17·0%), *m/e* 247. The filtrate was concentrated, made alkaline with ammonium hydroxide, and extracted with ether. T.l.c. examination of the extract (1·9 g) (methanol–ethyl acetate 1 : 9) showed that it contained 2-methylbenzimidazole, R_F 0·2, *o*-phenylenediamine, R_F 0·4, and the quinoxalinone (X), R_F 0·7, as major constituents, but no clean separation was obtained by column chromatography on alumina.

3-(2-*Carbamoylphenyl*)-1,2-*dihydroquinoxalin*-2-*one* (XI).—A solution of 3-acetyl-1,2-dihydro-4-hydroxyisoquinolin-1-one (2·03 g, 0·01 mol) and selenium dioxide (1·17 g, 0·0106 mol) in dioxan (250 ml) and water (2 ml) was heated at 100° for 20 h and then cooled. A solution of sodium carbonate (2·12 g, 0·02 mol) in water (5 ml) was added, and then the dioxan was removed *in vacuo*. *o*-Phenylenediamine (1·2 g, 0·011 mol) was added, the pH was adjusted to 2 with hydrochloric acid, and then the mixture was heated under reflux for 30 min. The mixture was made alkaline with ammonium hydroxide and shaken with chloroform. Filtration gave a solid (XI), of low solubility in chloroform and in aqueous ammonia, and separation gave a chloroform extract. 3-(2-*Carbamoylphenyl*)-1,2-*dihydroquinoxalin*-2-*one* (XI) formed needles (0·35 g), m.p. 245—247° (from methanol) (Found: C, 67·3; H, 4·3; N, 15·7. $C_{15}H_{11}N_3O_2$ requires C, 67·9; H, 4·2; N, 15·8%), $\nu_{max.}$ (Nujol) 1668 cm^{-1} (C=O of quinoxalin-2-one), and 1650 and 1615 cm^{-1} ($CO{\cdot}NH_2$), *m/e* 265 (*M*), 248 (*M* − NH_3), and 247 (*M* − H_2O). T.l.c. examination of the chloroform extract (methanol–ethyl acetate 1 : 9) showed the presence of the quinoxalin-2-one (XI), R_F 0·28, 2-methylbenzimidazole, R_F 0·35, and the isoquinolinetrione (VI), R_F 0·7, as major components, but no clean separation was obtained by column chromatography on alumina.

Selenium Dioxide Oxidation of 1-*Phenylbutane*-1,3-*dione* (XII).—A solution of 1-phenylbutane-1,3-dione [15] (0·4 g) and selenium dioxide (0·29 g, 1·05 mol. equiv.) in acetic acid (3 ml) and water (0·15 ml) was heated at 100° for 2 h and then cooled. Ether was added and the mixture was separated conventionally into an acid fraction, which was soluble in aqueous sodium hydrogen carbonate, and a neutral fraction. T.l.c. examination (ethyl acetate–formic acid 99 : 1) showed that the acid fraction (0·1 g) consisted of phenylglyoxylic acid, R_F 0·53 (yellow with 2,4-dinitrophenylhydrazine spray), and a trace of benzoic acid, R_F 0·73. The phenylglyoxylic acid had m.p. and mixed m.p. 62—63° (from carbon disulphide). T.l.c. examination showed that the neutral material (0·25 g, 62·5%) was starting material, R_F 0·82, and that it did not contain any phenylglyoxal, R_F 0·75. This was confirmed by g.l.c. (2½% SE-30 column at 120°): starting material, R_t 8 min, phenylglyoxal standard, 2·5 min.

Thallium Salt of 1-*Phenylbutane*-1,3-*dione*.—Ethoxythallium (1·2 g) was added to a solution of 1-phenylbutane-1,3-dione [15] in light petroleum (b.p. 60—80°; 30 ml). The yellow *thallium salt* formed needles, m.p. 106—107° (from ethanol) (Found: C, 32·8; H, 2·5. $C_{10}H_9O_2Tl$ requires C, 32·9; H, 2·5%).

2-*Methyl*-1-*phenylbutane*-1,3-*dione* (XIII).—The fo[illegible]ing thallium salt (0·7 g) and methyl iodide (5 ml) were heated under reflux for 3 h and then cooled. Ether (50 ml) was added, the mixture was filtered through Celite, and the ether was evaporated to give 2-methyl-1-phenylbutane-1,3-dione, a gum, pure by t.l.c. [ether–light petroleum (b.p. 60—80°) 7 : 13], R_F 0·27, and by g.l.c. (2½% SE-30 column at 120°), R_t 8·5 min, τ ($CDCl_3$) 1·9—2·6 (5H, m, ArH), 5·48 (1H, q, 2-H), 7·83 (3H, s, 4-H_3), and 8·55 (3H, d, 2-Me).

Selenium Dioxide Oxidation of 2-*Methyl*-1-*phenylbutane*-1,3-*dione* (XIII).—A solution of 2-methyl-1-phenylbutane-1,3-dione (0·27 g) and selenium dioxide (0·17 g, 1 mol. equiv.) in acetic acid (1 ml) and water (0·05 ml) was heated at 100° for 2 h, and then cooled. Ether was added and the mixture was separated conventionally into an acid fraction and a neutral fraction. T.l.c. examination (ethyl acetate–formic acid 99 : 1) showed that the acid fraction (0·14 g) consisted of phenylglyoxylic acid, R_F 0·53 (yellow with 2,4-dinitrophenylhydrazine spray), and a trace of benzoic acid, R_F 0·73. The neutral material (0·12 g) [ether–light petroleum (b.p. 60—80°) 7 : 13] consisted of starting material, R_F 0·27, and 1-phenylpropane-1,2-dione (XIV), R_F 0·48. This was confirmed by g.l.c. (2½ SE-30 column at 120°), which showed starting material, R_t 8·5 min, and 1-phenylpropane-1,2-dione, R_t 2·6 min (24 mg, 16% on starting material used) in the ratio 4 : 1.

Action of Selenium Dioxide on 1-*Phenylpropane*-1,2-*dione* (XIV).—A solution of 1-phenylpropane-1,2-dione (2·96 g) and selenium dioxide (2·22 g, 1 mol. equiv.) in acetic acid (13 ml) and water (0·65 ml) was heated at 100° for 2 h and then cooled. Selenium (0·63 g, 40%) was removed by filtration, ether was added to the filtrate, and the mixture was separated conventionally into an acid fraction and a neutral fraction. The acid fraction (0·4 g) consisted of phenylglyoxylic acid, R_F 0·53, together with some benzoic acid, R_F 0·73 (ethyl acetate–formic acid 99 : 1). The neutral fraction (2·11 g) was starting material, R_F 0·48, containing traces of polar materials, R_F 0·12 and 0·02 [ether–light petroleum (b.p. 60—80°) 7 : 13].

Oxidation of 1,2,3-*Triphenylpropane*-1,3-*dione* (XV).—A solution of 1,2,3-triphenylpropane-1,3-dione [8] (1·2 g) and selenium dioxide (0·489 g, 1·1 mol. equiv.) in propionic acid (15 ml) was heated under reflux for 6 h and then cooled. Selenium (0·316 g, 99%) was removed by filtration and then the propionic acid was evaporated under reduced pressure. The residue was shaken with aqueous sodium hydrogen carbonate and ether. The ether layer gave neutral material (0·9 g), shown by t.l.c. (benzene) to consist of benzil, R_F 0·49, and starting material, R_F 0·27. Chromatography on silica gel and elution with benzene gave benzil (0·725 g, 95% on starting material), m.p. and mixed m.p. 95°, and starting material (0·111 g, 9%). The aqueous hydrogen carbonate solution was acidified and extracted with ether. The extract consisted only of benzoic acid, R_F 0·62 (ethyl acetate–formic acid 99 : 1) (0·382 g, 86% on starting material), m.p. and mixed m.p. 121° (from aqueous ethanol).

Oxidation of Deoxybenzoin (XVII) *with Selenium Dioxide*.—A solution of deoxybenzoin (1·96 g) and selenium dioxide (1·22 g, 1·1 mol. equiv.) in acetic acid (70%, 30 ml) was heated at 88—90° for 12 h and then cooled. Selenium was removed by filtration and then the filtrate was poured into water and extracted with ether. The ether extract was washed with saturated potassium carbonate solution, water, and dried. The extract (2·0 g) consisted of benzil, R_F 0·45 (benzene), and a trace of deoxybenzoin, R_F 0·35. The potassium carbonate washing liquid was acidified and then extracted with ether. The extract was dried and evaporated to give benzoic acid (16 mg, 0·7—1·4%), m.p. and m[illegible] m.p. 121°.

Action of Selenium Dioxide on Benzil (XVI).—A solution

[15] L. Claisen, *Ber.*, 1905, **38**, 693.

of benzil (2·1 g) and selenium dioxide (1·22 g, 1·1 mol. equiv.) in acetic acid (70%, 30 ml) was heated at 88—90° for 12 h and then cooled. Selenium (10 mg) was removed by filtration. The residue was separated into a neutral and an acid fraction. The neutral fraction (2·08 g) consisted of benzil, R_F 0·25 (ether–light petroleum 1 : 9). The acid fraction (1 mg) consisted of benzoic acid, R_F 0·75 (ethyl acetate–formic acid 99 : 1).

Action of Acetic Acid on Deoxybenzoin (XVII).—A solution of deoxybenzoin (1·96 g) in acetic acid (70%, 30 ml) was heated at 88—90° for 12 h, cooled, poured into water, and the mixture was extracted with ether. The ether extract was washed with saturated potassium carbonate solution, water, and dried. The extract (1·9 g) consisted of deoxybenzoin. The potassium carbonate washing liquid yielded benzoic acid (55 mg, 2·3—4·6%), m.p. and mixed m.p. 121°.

Oxidation of α-Phenyldeoxybenzoin (XXI) *with Selenium Dioxide.*—A solution of α-phenyldeoxybenzoin (2·72 g) and selenium dioxide (1·22 g, 1·1 mol. equiv.) in propionic acid (30 ml) and water (4 ml) was heated under reflux for and then cooled. Selenium (0·68 g, 85%) was removed by filtration and then the propionic acid was evaporated under reduced pressure. The residue was shaken with aqueous sodium hydrogen carbonate and ether. The ether layer gave neutral material (0·27 g), shown by t.l.c. [ether–light petroleum (b.p. 60—80°) 1 : 9] to be almost entirely one product, R_F 0·13. Extraction with cold light petroleum (b.p. 60—80°) gave slightly impure α-phenylbenzoin (XXIII) (2·28 g, 80%), m.p. and mixed m.p. 83—84° (from light petroleum) (Found: C, 83·0; H, 5·6. Calc. for $C_{20}H_{16}O_2$: C, 83·3; H, 5·6%). The aqueous hydrogen carbonate solution was acidified and extracted with ether. The extract (20 mg) contained no benzoic acid by t.l.c.

Attempted Oxidation of Isopropyl Phenyl Ketone (XXIV) *with Selenium Dioxide.*—A solution of isopropyl phenyl ketone (1·48 g) and selenium dioxide (1·22 g, 1·1 mol. equiv.) in propionic acid (25 ml) and water (5 ml) was heated under reflux for 20 h and then cooled. Selenium (0·1 g, 13%) was removed by filtration and then the propionic acid was evaporated under reduced pressure. Work-up as before gave neutral material (1·4 g), which was largely starting material, R_F 0·7 (acetone–cyclohexane 2 : 3) contained traces of 4 more polar products, which were not further investigated. The acid fraction (5 mg) contained no benzoic acid by t.l.c.

Oxidation of 1,2-Diphenylpropan-1-one (XXV) *with Selenium Dioxide.*—A solution of 1,2-diphenylpropan-1-one (2 g) and selenium dioxide (1·165 g, 1·1 mol. equiv.) in propionic acid (30 ml) and water (4 ml) was heated under reflux for 66 h and then cooled. Selenium (520 mg, 69%) was removed by filtration (reflux for 17 h gave only 17% of selenium). The residue was separated as before. The neutral fraction (1·98 g) contained two major new products, R_F 0·33 and 0·1, in addition to starting material, R_F 0·4 (ether–light petroleum 1 : 9). Preparative t.l.c. gave 2-hydroxy-1,2-diphenylpropan-1-one (XXVI) (260 mg), m.p. and mixed m.p. 65—67° [from light petroleum (b.p. 60—80°)], R_F 0·1, and also 1,2-diphenylprop-2-en-1-one (XXVII) (630 mg), R_F 0·33, τ ($CDCl_3$) 2—2·3 (2H, m, ArH), 2·4—2·9 (8H, m, ArH), and 4·0 and 4·42 [2H, both s ($J < 1$ Hz), $C\dot{C}H_2$], *m/e* 208 and 105 ($PhC\equiv\overset{+}{O}$); 2,4-dinitrophenylhydrazone, orange rods, m.p. 231° (from ethyl acetate) (lit.,[14] 227°) (Found: C, 64·7; H, 4·2; N, 14·5. Calc. for $C_{21}H_{16}N_4O_4$: C, 64·9; H, 4·2; N, 14·4%). The acid fraction (10 mg) consisted of benzoic acid, R_F 0·75, and phenylglyoxylic acid, R_F 0·5 (ethyl acetate–formic acid 99 : 1).

Action of Selenium Dioxide on 2-Hydroxy-1,2-diphenylpropan-1-one (XXVI).—A solution of the ketone (226 mg) and selenium dioxide (108 mg, 1·1 mol. equiv.) in propionic acid (5 ml) and water (0·5 ml) was heated under reflux for 16 h and then cooled. Selenium (10 mg) was removed by filtration. The residue was separated into a neutral and an acidic fraction. The neutral fraction (200 mg) was starting material, R_F 0·1 (ether–light petroleum 1 : 9). The acid fraction (10 mg) consisted of benzoic acid, R_F 0·75, and phenylglyoxylic acid, R_F 0·45 (ethyl acetate–formic acid 99 : 1).

Samples of compounds (XXI), (XXIII), and (XXV) were kindly provided by our colleague Dr. D. N. Richardson.

[1/2099 *Received*, 10*th November*, 1971]