425. *The Bismuth-catalysed Air-oxidation of Acyloins.*

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A procedure has been developed for the preparation of 1 : 2-diketones from acyloins by oxidation with air in the presence of acetic acid and catalytic amounts of bismuth compounds.

It has been noted (Rigby, *J.*, 1951, 793) that the finely divided metallic bismuth produced during the oxidation of acyloins by bismuth acetate is very susceptible to air-oxidation; indeed, bismuth filtered off after an oxidation conducted in acetic acid becomes warm and white almost as soon as the liquid has drained off. It seemed that a little bismuth oxide might suffice to oxidise a large quantity of an acyloin if the metal were allowed to oxidise again as fast as it was formed : the process would complement the well-known oxidation of acyloins by air in *alkaline* solution.

The first attempts to apply the principle, by stirring an acetic acid solution of benzoin with oxygen in the presence of a few per cent. of bismuth oxide, were disappointing : there was initially a rapid uptake of oxygen but the rate soon fell off because the metal coalesced into flocks; addition of dispersing agents such as kieselguhr effected no notable improvement. However, when bismuth carbonate was substituted for the oxide reaction was smooth, the particles of carbonate were apparently only superficially reduced, and the metal remained dispersed on them. Air was found superior to oxygen in this oxidation, as use of the latter led to more discoloration and a higher proportion of by-products whilst not greatly increasing the rate of oxidation.

When a hot acetic acid solution of an acyloin is stirred with air—or especially oxygen—in the absence of bismuth compounds, oxidation takes place and some diketone is produced, but fission also occurs with formation of acids. The extent of the undesired fission appears to vary with the acyloin, benzoin being more susceptible than some of its derivatives. On using one-sixtieth to one-fifteenth mol. of bismuth carbonate per mol. of acyloin, yields obtained were : benzil, 70% ; anisil, 74·5% ; 4-methoxybenzil, 70% ; furil, 68%. As is to be expected, these yields are lower than those for the corresponding bismuth acetate (non-catalytic) oxidation (96, 95, 85, and 92% resectively) ; but as the main losses are caused by direct action of oxygen to give acids, and as this attack is much slower than the oxidation with bismuth acetate, a reasonable increase in the amount of catalyst used might minimise the side-reaction and a satisfactory compromise should be possible in any particular case. As was found with the simple oxidations with bismuth acetate, dilution of the acetic acid with technical 2-ethoxyethanol is usually advantageous.

The oxidation of 4-methoxybenzoin with bismuth acetate is described, and a new melting point of 58° is found for 4-methoxybenzil.

Experimental.

Bismuth Carbonate.—The usual basic carbonate was used: it lost 9·5% of its weight on ignition. Of two samples, the one with the greater particle size appeared to be the more efficient—presumably owing to the complete dissolution of the finest particles of carbonate and the consequent loss of so much dispersing agent. When the carbonate (1 g.) was shaken in a test-tube with water (20 ml.) and set aside for a minute or two, the solid rapidly settled leaving, in the case of the better samples, a clear supernatant liquor containing only a few discrete particles suspended on air bubbles: in the case of the less satisfactory samples the liquor was strongly opalescent and was not clear even after a day. The better material consisted largely of particles with diameter of 3—4 μ., but the other contained large quantites of particles apparently 1—2 μ. in diameter, which showed active Brownian movement when mounted in water.

4-*Methoxybenzoin.*—The procedure of "Organic Reactions," Vol. IV, p. 280 was modified in that the first crude crystal magma was spread on a previously chilled porous plate and left for a day in the ice-chest before recrystallisation. Without this preliminary treatment, enormous losses were encountered in the crystallisation, which was more satisfactory from methyl alcohol.

Benzil.—Benzoin (53 g.), acetic acid (135 ml.), technical 2-ethoxyethanol (15 ml.), and bismuth carbonate (2 g.) were briskly stirred in a 1-l. 3-necked flask which was heated over a gauze while a filter-pump drew air in down the stirrer-guide and out from the top of an efficient reflux condenser which contained a loose plug of glass-wool to trap mist; the stirring was of a type to facilitate contact between the liquid and the air. When the temperature reached 95°, the suspension rapidly blackened; the air stream was adjusted so that the suspension again became white and remained so while the temperature of the liquid was raised to 100°. The reaction was allowed to continue at 100° until a test sample, after dilution with an equal volume of acetic acid, no longer brought about reduction when boiled for a minute with a little bismuth oxide (spuriously negative results may be obtained when solutions rich in 2-ethoxyethanol and containing only a low concentration of an acyloin are boiled with bismuth oxide), this requiring up to 2½ hours. A thin film of metallic bismuth which formed on the walls of the flask early in the experiment persisted almost to the end and served as a useful rough indicator. After addition of water (25 ml.) the solution was heated to boiling and filtered; the filtrate deposited virtually pure benzil, and crystallisation was completed by the further addition of water (75 ml.) and cooling to room temperature. The yield was 38 g. (72%) and the m. p. 95°. Benzoic acid, m. p. 122°, was the main by-product of the reaction, and the mother-liquors were slightly discoloured by an impurity which became deep brown in alkali. Results for the use of different solvents were: acetic acid, 2·5 hours, 36 g.; 25% of 2-ethoxyethanol in acetic acid, 5·5 hours, 37 g.; 10% of water in acetic acid, 24 g. of benzil and 8 g. of benzoin after 3 hours; 25% of water in acetic acid, very little oxidation in 2·25 hours. In a blank experiment without the bismuth carbonate, the m. p. of the material obtained by precipitation with water had only been reduced from 130° (benzoin) to 125—128° even after 6 hours' passage of air.

Anisil.—Anisoin (25 g.) with acetic acid (90 ml.), technical 2-ethoxyethanol (10 ml.), and bismuth carbonate (3 g.), at 95° rising to 110° when the air stream could cope with the re-oxidation of the bismuth at the higher temperature, was similarly oxidised within 2 hours. Filtration and cooling without dilution gave anisil, m. p. 134° (18·6 g., 74·5%). With 1 g. of catalyst in acetic acid, the reaction required 4·5 hours (71% yield), but when 1 g. of the inferior catalyst was similarly used it was dissolved within 1 hour; 2 g. of the inferior catalyst gave a 71% yield within 3 hours.

4-*Methoxybenzil.*—(a) *Oxidation with bismuth acetate.* 4-Methoxybenzoin (4·03 g.), acetic acid (8 ml.), technical 2-ethoxyethanol (16 ml.), and bismuth oxide (3·1 g.) were stirred together at 108° (bath-temp.) for 1½ hours. After cooling, the solution was filtered and the residue was washed with 2-ethoxyethanol and then with benzene. The solvent was removed under reduced pressure and bismuth compounds were eliminated by filtering a solution of the product in benzene (25 ml.) through alumina (2 g.); after removal of the benzene, crystallisation in the ice-chest from methyl alcohol with the addition of a little light petroleum gave 4-methoxybenzil (3·4 g.) as almost colourless prisms, m. p. (soft- or hard-glass capillary) 58°, which was unchanged by recrystallisation from cineole–light petroleum or from 80% alcohol (Found: C, 74·9; H, 5·05. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%). 4-Methoxybenzil has been described as being bright yellow and having m. p. of 62—63° (Kinney, *J. Amer. Chem. Soc.*, 1929, **51**, 1596).

(b) *Catalytic oxidation.* 4-Methoxybenzoin (15 g.) with acetic acid (54 ml.), technical 2-ethoxyethanol (6 ml.), and bismuth carbonate (2 g.) was oxidised at 107° by air, as described for benzil, within 2½ hours. On cooling, the filtered solution deposited 4-methoxybenzil, m. p. 58° (7·4 g.), and a further 3 g. were obtained by working up the mother-liquors as described in the case of the oxidation with bismuth acetate. The yield was 70%.

Furil.—Furoin (20 g.) with acetic acid (90 ml.), technical 2-ethoxyethanol (40 ml.), and bismuth carbonate (3 g.) at 100° in a rapid air-stream was similarly oxidised within 1¾ hours. The brown mixture was filtered hot through a few mm. of alumina covered by activated charcoal (20 g.) which, in turn, was overlaid by a filter paper in a 3″ funnel. This is a most effective way of removing the brown contaminant from discoloured furil; there is practically no loss of furil on the adsorbents. The orange-coloured filtrate deposited pure furil, m. p. 165—166° (12·5 g.), on cooling, and a further 1·2 g. were obtained from the mother-liquors.

Experiments with Bismuth Oxide and with Oxygen.—Use of oxygen in an apparatus for catalytic hydrogenation, with benzoin (0·25 mol.), bismuth oxide (0·004 mol.), and acetic acid (100 ml.), at 100°, led to an initial absorption at 200 ml. per minute, but the rate rapidly decreased owing to the cohering of the bismuth into heavy flocks, and uptake of the theoretical amount of oxygen required 0·75 hour; the benzil isolated was contaminated with benzoin. The time required was almost halved when arrangement was made for the oxygen to be passed over the stirred mixture by a system of aspirators. In a blank experiment, carried out similarly but without the bismuth oxide, the oxygen was absorbed in 200 minutes, but there was considerable discoloration, production of much benzoic acid, and at least 20% of the benzoin remained unattacked.

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