389. *Oxidations with Sodium Bismuthate: Glycol Fission and Related Reactions.*

By W. Rigby.

Sodium bismuthate in an acid medium smoothly and selectively effects oxidations similar to those brought about by lead tetra-acetate and periodic acid; αβ-glycols undergo fission to aldehydes or ketones, acyloins to the derived carbonyl compound and carboxylic acid, and α-hydroxy-acids to the lower aldehyde or ketone, all in good yield. Aldehydes are not further oxidised.

Of the relatively small number of reagents which effect the scission of αβ-glycols, converting the >C(OH)·C(OH)< group into >CO and OC<, only two—periodic acid (Malaprade, *Bull. Soc. chim.*, 1928, **43**, 683; *Compt. rend.*, 1931, **186**, 382) and lead tetra-acetate (Criegee, *Ber.*, 1931, **64**, 260)—have found wide application. Closely related reactions—scission of >C(OH)·CO– to >CO + HO·CO–, degradation of α-hydroxy-acids to the corresponding carbonyl compound, and some ammono-analogues of these reactions—are also brought about, the differences between the two reagents in this respect being of degree rather than of kind, and the reagents are reasonably specific for these types of oxidation. In practice, periodate and lead tetra-acetate are more or less complementary, the former having perhaps its greatest value in quantitative applications and in reactions requiring the use of aqueous media, while the latter is not so well suited for quantitative work and is typically used in non-aqueous media for preparative purposes. Other reagents capable of effecting selective oxidative glycol cleavage are known (cf. Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159) but have been less investigated or have been shown to be less convenient for general use; some of the more familiar oxidising agents can also be shown to be capable of producing the typical "glycol fission" products, but they either lack selectivity or bring about the result by a more or less minor side reaction; Slack and Waters (*J.*, 1949, 594) have shown that the same cleavage products represent a stage in the oxidation of αβ-glycols by chromyl chloride.

Compounds of bismuth have been but little investigated as oxidising agents for organic compounds, but from the broad analogies subsisting between lead and bismuth, and especially from the occurrence in both of valency states of high oxidising potential two units above the common state, oxidations by quinquevalent bismuth might be expected to be analogous to those by quadrivalent lead. Experiment confirmed this, as was announced in a preliminary note (Rigby, *Nature*, 1949, **164**, 185). Sodium bismuthate is available commercially, is quite stable, can be used directly, and in an acid medium at or about room temperature rapidly effects typical glycol fissions. The course of the reaction is readily followed visually, the carbonyl compounds are produced in good yield, and there appears to be no tendency for aldehydes to be oxidised further. The rates of reaction are comparable with those of the corresponding periodate and lead tetra-acetate oxidations. The oxidation can be carried out in water, an organic solvent, or mixtures of the two, bismuthate having the advantage over lead tetra-acetate in this respect (Criegee and Büchner, *Ber.*, 1940, **73**, 563). Like lead tetra-acetate, and unlike periodate, sodium bismuthate rapidly and smoothly oxidises α-hydroxy-acids to the lower aldehyde or ketone. Methyl and ethyl alcohols are only slowly oxidised, even when present in high concentration but, in contrast with Malaprade's reagent, bismuthate rapidly oxidises formic acid and, less rapidly, oxalic acid. While aldehydes in general are unattacked, a 10% aqueous solution of technical glyoxal was rapidly oxidised. With the only pair of *cis–trans*-glycols tried, the *cyclo*hexane-1 : 2-diols, no notable difference in rate of reaction with bismuthate was observed.

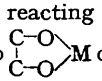
Two general experimental procedures have been used. In the first, the sodium bismuthate (usually the theoretical amount) is stirred or shaken with a solution of the glycol in glacial acetic acid at, or slightly above, room temperature until the reddish-brown, finely suspended bismuth pentoxide disappears and a clear colourless solution results (this requires a few minutes to several hours); if desired, the bismuth can be completely removed from the resulting solution by precipitation as phosphate. The marked change in appearance during reaction makes this procedure a convenient qualitative test for the classes of substances oxidised by the reagent. In the second procedure, the reaction is similarly carried out in water or aqueous dioxan in the presence of a slight excess of phosphoric acid. The initial bright orange-yellow suspension (presumably some compound of bismuth pentoxide and phosphoric acid) is ultimately replaced by pure white bismuth phosphate, again making it easy to follow the reaction visually. When the reaction products are isolated by ether-extraction, there is usually no need to filter off the bismuth phosphate, as it does not interfere or cause emulsification.

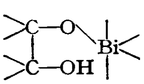
On a 1/50—1/200-mol. scale, the expected products (given in parentheses) were isolated as derivatives from the following: ethylene glycol (formaldehyde); glycerol 1-benzyl ether (benzyloxyacetaldehyde); ethyl tartrate (ethyl glyoxylate); *cis*- and *trans-cyclo*hexane-1 : 2-diol (adipdialdehyde); *trans*-tetralin-1 : 2-diol (*o*-2-formylethylbenzaldehyde); *threo*-9 : 10-dihydroxystearic acid (pelargonaldehyde and azelaic acid-aldehyde); hydrobenzoin (benzaldehyde); pinacol hydrate (acetone); glycerol (formaldehyde and glycollaldehyde); benzoin (benzaldehyde and benzoic acid); 4-methoxybenzoin (benzaldehyde and *p*-anisic acid); lactic acid (acetaldehyde); mandelic acid (benzaldehyde); α-hydroxy*iso*butyric acid (acetone); and benzilic acid (benzophenone).

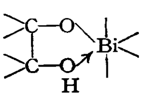
Moderate-scale preparations have been developed for: ethyl glyoxylate alcoholate (51%); adipdialdehyde (49% from *trans-cyclo*hexane-1 : 2-diol; cf. Criegee, *loc. cit.*, 67% from the *cis*-diol, and English and Barber, *J. Amer. Chem. Soc.*, 1949, **71**, 3310, 68% from mixed *cis-trans*-diols, both by means of lead tetra-acetate), and its cyclic monoacetal with *cis-cyclo*hexane-1 : 2-diol (33% from *cis-cyclo*hexane-1 : 2-diol); benzyloxyacetaldehyde (68%), pelargonaldehyde [53%; isolation of azelaic acid-aldehyde in a pure state from the same reaction being unsatisfactory (17%)].

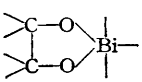
Glycollaldehyde and formaldehyde (formed together by the oxidation of glycerol) are readily separated as dimedon derivatives by making use of the solubility of the formaldehyde–dimedon compound in benzene and that of the glycollaldehyde derivative in 60% alcohol. The product from glycollaldehyde is an anhydro-compound; whether it has a xanthan structure has not been determined.

Simple methods have been evolved for the preparation of *cis*- (*ca.* 36% yield), and *trans-cyclo*hexane-1 : 2-diol (*ca.* 50% yield).

The mechanism of the reaction of bismuthate with glycols is presumably essentially similar to those of oxidation with lead tetra-acetate of periodic acid, concerning which however there is still controversy. Many examples are known or organic compounds which contain adjacent hydroxyl groups reacting readily with metal hydroxides to produce substances considered to contain the group  M or R–O–M, hydroxides of copper, iron, aluminium, bismuth^{III}, boron, etc., being typical. Criegee and Büchner (*loc. cit.*) considered that $Pb(OAc)_2(OH)_2$ must react with glycols in this sort of way more readily than does the tetra-acetate in order to account for the catalytic effect of water on the lead tetra-acetate oxidation. The metals and their valency states are diverse enough to make it reasonable to suppose that formation of such metal derivatives is a general property, and that the specific nature and valency of the metal are of secondary importance—with the obvious reservation that they should not favour ionic structures to the exclusion of covalent ones. If so, hydrated bismuth pentoxide might be expected to combine with a suitable polyhydroxy-compound in an analogous manner, at least as a primary act, and a theory of the mechanism of the oxidation reaction would then concern itself with transformations of the primary compound which would contain some such structure as



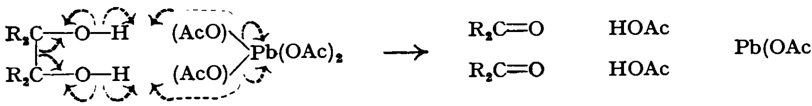




(I.)

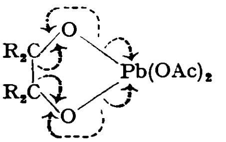
The bismuth in such a compound is apparently able to withdraw permanently two electrons from the organic moiety and fission of a C–C bond results. Such a cyclic intermediate compound as (I) would be analogous to the lead compound (V) formerly postulated by Criegee (*loc. cit.*) as the immediate precursor of the fission reaction; an analogous stage has been assumed to account for the Malaprade reaction.

Dewar ("The Electronic Theory of Organic Chemistry," Oxford, 1949, pp. 276—277) formulates the lead tetra-acetate reaction as

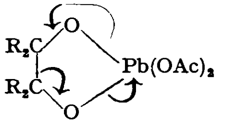


and, from considerations of the bond-energies involved, gives a satisfying explanation of the resistance of ordinary alcohols to the reagent; he maintains that "The essential feature of the two reagents [Criegee's and Malaprade's] is their ability to accept simultaneously the two H atoms from the glycol."

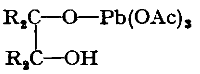
A formulation analogous to Dewar's would be better applied to Criegee's postulated cyclic intermediate; this would be (II), where also the passage of the two "reducing" electrons to the inner shell of the lead atom would be facilitated by the *simultaneous* withdrawal of the electrons from the C–C link. This is the essential feature of the process: the cyclic compound is a mechanism which allows the energy necessary to break the C–C bond to be, in part, provided by



(II.)

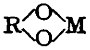


(III.)

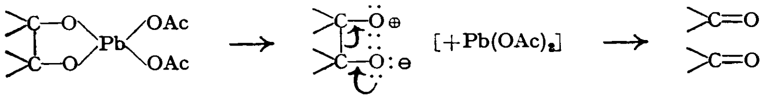


$$\begin{array}{l} R_2C\text{—O—}Pb(OAc)_3 \\ \;| \\ R_2C\text{—OH} \end{array}$$

(IV.)

that liberated on the formation of other bonds. Formally, the bond fissions need not be written as homolytic, formulation (III) giving the same result. Such a scheme would give a plausible indication why a few reagents—periodate, quadrivalent lead, and quinquevalent bismuth—should specifically effect glycol fissions smoothly and with remarkable freedom from side reactions: they all concern elements which (*a*) can reasonably be envisaged as capable of forming a preliminary compound  with the glycol, and (*b*) exist in two stable oxidation states which are two valency units apart, the lower representing a substance which is not an oxidising agent under ordinary conditions (Pb^{II} or Bi^{III}) or which no longer fulfils condition (*a*) (the IO_3' ion).

This proposed formulation seems preferable to that of Criegee (*Annalen*, 1948, **560**, 132—133) which involves a zwitterion (VI), this being essentially a polar form of an olefin peroxide (moloxide) since from the moment of its formation it will presumably have a *cis*-configuration; the relationship of (VI) to (III) is obvious. Criegee's mechanism puts the glycol-fission reaction

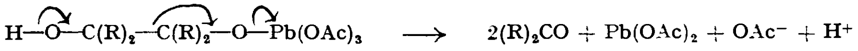


(V.) (VI.)

in line with certain others formulated by him as involving oxygen carrying a sextet of electrons and with reactions of C^+. In his discussion of the formation of ozonides, Criegee (*loc. cit.*, p. 131) points out that his proposed mechanism does not satisfactorily explain why the action of ozone on certain olefins does not lead to the formation of keto-hydroperoxides. Application of the same principles to a zwitterion (VI) derived from a non-tertiary glycol would similarly lead to the expectation of its transformation into an acyloin as an alternative to the observed "glycol-fission" products.

That a cyclic intermediate is an essential step in the lead tetra-acetate reaction has been demonstrated by Criegee: the specific effect of acetic acid in retarding the lead tetra-acetate oxidation is reasonably interpreted by him as being due to the primary formation of an open-chain compound (IV) which is stable to fission but cyclises to (V), and this then decomposes;

such an effect would not perhaps be explained so simply by using Dewar's bimolecular formulation. Further, the difference in reactivity of *cis*- and *trans*-glycols (Criegee, *loc. cit.*; Criegee, Büchner, and Walther, *Ber.*, 1940, **73**, 571) would be difficult to account for if the oxidation process occurred in an open-chain compound such as (IV). Mechanisms such as:



$$H—O—C(R)_2—C(R)_2—O—Pb(OAc)_3 \longrightarrow 2(R)_2CO + Pb(OAc)_2 + OAc^- + H^+$$

are therefore excluded. As soon, however, as the second hydroxyl group of the glycol became associated with the lead atom, the way would be open for the appropriate electron transfers to take place, and it is conceivable that they might occur practically simultaneously with ring closure and elimination of acetic acid.

As an explanation of any of these reactions, the two-stage free-radical mechanism proposed by Waters (*Trans. Faraday Soc.*, 1946, **42**, 184) seems less probable; Criegee and Büchner (*loc. cit.*, p. 566) have pointed out that the initial reaction with quadrivalent lead compounds cannot be a simple dehydrogenation, and Dewar (*loc. cit.*) has brought forward criticisms of Waters's mechanism for the lead tetra-acetate reaction which seem irrefutable. The difference in reactivity of *cis*- and *trans*-compounds is also a difficulty.

While the mechanism outlined here is suggested as being applicable in the cases defined, there is no reason to suppose that there can be only one path for the transition glycol ⟶ fission products, independently of the oxidising agent used, and it is reasonable to conclude with Waters (*Nature*, 1946, **158**, 380) that reaction of Fenton's reagent with pinacol to produce acetone involves free radicals.

EXPERIMENTAL.

Sodium Bismuthate.—Technical or laboratory grades of sodium bismuthate were used in the earlier experiments; different batches varied in colour from pale buff to pink and reddish-brown; dark grades appeared to be rather less reactive than the lighter ones. Only two samples failed to give a pure white bismuth phosphate after reduction, the product being grey in these cases. It was later found that the analytical-reagent grade offered definite practical advantages: its bulk density is about half that of the ordinary grade and it is free from grittiness. Although it is claimed (Scholder and Stobbe, *Z. anorg. Chem.*, 1941, **247**, 392) that it is possible to prepare sodium bismuthate of virtually 100% purity, commercially available material has an oxidising capacity equivalent to about 82—85% of $NaBiO_3$; very old samples which had suffered much exposure were no worse, and AnalaR samples had a titre of about 85%. The relatively few published methods for analysis of sodium bismuthate for available oxygen are not entirely satisfactory. A convenient method involves oxidation of Fe^{++}; this gives consistent results and is preferred for routine analysis; the results are reasonably close to those obtained gravimetrically by a process involving the oxidation of ethylene glycol to formaldehyde and weighing this as its dimedon derivative. Somewhat higher (2%) figures were obtained by a commercially-used iodometric assay, but, as no reasonable explanation offered itself for spuriously *low* results being obtained by the iron method, the fault probably lies with the iodometric method.

Analysis.—(*a*) *Preferred method.* The sample (0·45 g.) was swirled with ferrous sulphate solution (25 ml.; 0·125N. in 4N-sulphuric acid) and a dozen ¼″ glass beads until dissolved, the beads breaking up any gritty particles. After addition of phosphoric acid (5—10 ml. of 85%) the solution was titrated with 0·1N-potassium dichromate (freshly prepared diphenylamine indicator). A blank determination was carried out.

(*b*) *Gravimetric method.* The sample (0·3—0·5 g.), in a 100-ml. graduated flask, was swirled with water (20 ml.), phosphoric acid (1 ml. of 3⅓M.), and ethylene glycol (0·04 mol.) until the solid became completely white (*ca.* 5—15 minutes), a known volume of glass beads being added if necessary. The mixture was diluted to volume and allowed to settle. Portions (25 ml.) of the filtered supernatant liquid were diluted to 50 ml., adjusted to pH *ca.* 4·5 with sodium acetate–acetic acid, and heated in the steam-bath for ¼ hour with dimedon (0·2—0·3 g.) in alcohol (2 ml.). The precipitate was dried at 60° and weighed. The small correction was applied for the volume of bismuth phosphate produced.

Typical results, obtained with a sample of AnalaR sodium bismuthate, were (*a*) 85·1; (*b*) 86·1% of $NaBiO_3$. Bell (*J.*, 1948, 994) pointed out that certain grades of dimedon are liable to give high results in (semimicro-)formaldehyde determinations; no correction was applied in these bismuthate assays. A third analytical procedure, favoured by a commercial supplier of sodium bismuthate, involving liberation of iodine from potassium iodide in hydrochloric acid solution was found to give still higher results (*ca.* 87% of $NaBiO_3$ for the same sample).

Dioxan.—Technical material was purified (cf. Eigenberger, *J. prakt. Chem.*, 1931, [ii], **130**, 75) by being boiled for 7 hours with 10% of N-hydrochloric acid while acetaldehyde was removed by an air-stream; the product was dried (KOH) and distilled over sodium. Such material was inert to sodium bismuthate; technical dioxan reduced sodium bismuthate under the usual experimental conditions, giving rise to formaldehyde.

cis-cyclo*Hexane*-1 : 2-*diol.*—*cyclo*Hexene (41 g.) was vigorously stirred under a reflux condenser with osmium tetroxide solution (5 ml. of 1%), and 100-volume hydrogen peroxide (60—65 ml.) was added very slowly (1 drop per 5 seconds) at 67°. After a short initial period when mixing was poor, the two phases formed a uniform emulsion under the vigorous stirring and the heat of reaction maintained the temperature; in some experiments a small amount of *cyclo*hexene remained undissolved at the end. Water was removed at reduced pressure and the residue distilled from an oil-bath. The material

(22 g.) distilling at 130°/25 mm. to 160°/4 mm. (mainly 130—140°/25 mm.) solidified, and on crystallisation from ethyl acetate or benzene gave the *cis*-diol, m. p. 97·5—99°.

trans-cyclo*Hexane*-1 : 2-*diol* (cf. Boeseken and Elsen, *Rec. Trav. chim.*, 1929, **48**, 369).—A solution of peracetic acid (*ca.* 1·3 mols.), made by heating acetic acid (480 ml.) and 100-volume hydrogen peroxide (150 g.) at 80—85° for 1 hour (Scanlan and Swern, *J. Amer. Chem. Soc.*, 1940, **62**, 2305), was added in 100-ml. portions to *cyclo*hexene (82 g.) stirred with occasional cooling as needed to keep the temperature at 45°. The addition required ¾ hour, the *cyclo*hexene finally dissolving. After a further ¼ hour at 45° the solution was heated in a boiling water-bath with a little spent palladium–charcoal catalyst until the perchromic acid test became negative. Water was distilled off, finally at 15—20 mm., alcohol (200 ml.) and hydrogen chloride (1—2 g.) or acetyl chloride (2—3 ml.) were added, and ethyl acetate and alcohol were slowly removed through a Vigreux column (b. p. *ca.* 74°). On distillation of the almost black crystalline residue, the fraction of b. p. 134—180°/15 mm. (mainly *ca.* 143°) was almost pure *trans*-diol. Recrystallisation from benzene or methyl ethyl ketone gave the pure material, m. p. 104·5—105·5° (63 and 37% in 2 experiments). The distillation residue yielded a *substance*, $C_{18}H_{28}O_4$, m. p. 193°, colourless prisms from technical 2-ethoxyethanol [Found : C, 70·0; H, 8·9%; *M*(Rast), 320. $C_{18}H_{28}O_4$ requires C, 70·1; H, 9·15%; *M*, 304).

trans-*Tetralin*-1 : 2-*diol*.—Crude dihydronaphthalene, b. p. 210·5—211·5°, prepared by reduction of naphthalene with sodium and alcohol, was oxidised with peracetic acid by a procedure analogous to that used in the case of *cyclo*hexene. After destruction of excess of peroxide by palladium–charcoal and removal of excess of acetic acid, the residue was heated for 1 hour with a slight excess of sodium hydroxide solution, to hydrolyse the ester, and the glycol was then extracted with ether. Removal of the ether and extraction of the residue with boiling water yielded almost pure *trans*-diol, which formed colourless needles, m. p. 112·5—113°, from water or ethyl acetate.

Oxidations.

Small-scale Experiments.—The glycol (0·01 mol.), AnalaR sodium bismuthate (0·01 mol. as determined by titration), 3⅓M-phosphoric acid (6—7 ml.), and water or dioxan (or both) (*ca.* 10—20 ml.) were shaken in 100-ml. stoppered bottles on a reciprocating machine until the bismuth compound was completely reduced (disappearance of the orange-yellow colour). If required, the bottles could be covered with layers of asbestos paper and heated to about 50° by radiation from an electric fire supported above the machine. The bismuth phosphate was removed by filtration, washed with water or alcohol, and, by treatment with the appropriate reagent, the carbonyl compound was isolated from the filtrate as a derivative which was recrystallised if necessary. In the following list, in parentheses after the name of the glycol, the solvent, the time for complete reduction, and the temperature are given.

Ethylene glycol [water (15 ml.), ¾ hour, room temperature] gave formaldehyde *p*-nitrophenylhydrazone, m. p. 178—179° (>90%), or the dimedon derivative, m. p. 189—190° after sintering at 185° (~100%). Glycerol 1-benzyl ether, b. p. 157·5°/3 mm. [water (15 ml.), ¾ hour, 20°], gave, after the oily aldehyde had been extracted with ether, *benzyloxyacetaldoxime* as colourless tablets (from light petroleum), m. p. 64—65° (Found : C, 65·4; H, 6·7; N, 8·65. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·7; N, 8·5%). Ethyl tartrate [water (10 ml.), 3½ hours, 17—18°] gave glycollaldehyde phenylhydrazone, m. p. 128—129° (94%) (m. p. 131·5° after recrystallisation from methyl alcohol). *cis*- or *trans-cyclo*Hexane-1 : 2-diol [water (3 ml.) and purified dioxan (10 ml.), 2—3 hours at 30—40°, or 6 hours at 20—30°] gave adipic dialdehyde dioxime, m. p. 177—178° (70%). *trans*-Tetralin-1 : 2-diol, m. p. 113° [dioxan (15 ml.), 6 hours, 40°], gave o-2-*formylethylbenzaldehyde bis*-2 : 4-*dinitrophenylhydrazone*, small red lozenge-shaped crystals, m. p. 253° (decomp.) (unchanged on recrystallisation from cresol) (77%) (Found : C, 50·6; H, 3·8; N, 20·8. $C_{22}H_{18}N_8O_8$ requires C, 50·5; H, 3·5; N, 21·45); alternatively it gave the corresponding *bisphenylhydrazone*, m. p. 111°, pale buff prisms from alcohol (Found : C, 76·2; H, 5·9; N, 17·7. $C_{22}H_{22}N_4$ requires C, 77·1; H, 6·5; N, 16·4%). Pinacol hydrate [water (15 ml.), 3 hours, 30—40°] gave acetone 2 : 4-dinitrophenylhydrazone, m. p. 123—124° (99%), after separation of aqueous acetone from the reaction mixture by distillation. Hydrobenzoin, m. p. 138° [purified dioxan (15 ml.), 5½ hours, 40—50°], gave benzaldehyde phenylhydrazone, m. p. 158° (75%). Mandelic acid [water (25 ml.), 3½ hours, room temperature] gave benzaldehyde phenylhydrazone, m. p. 158° (64%). α-Hydroxy*iso*butyric acid [water (25 ml.), ¼—½ hour, room temperature] gave acetone 2 : 4-dinitrophenylhydrazone, m. p. 124—125° (82%), after separation of aqueous acetone from the reaction mixture by distillation. Benzilic acid [acetic acid (15 ml.) (phosphoric acid being omitted), 1½ hours, 50—60%] gave benzophenone, m. p. 49° (99%), isolated by ether extraction after addition of phosphoric acid (5 ml. of 3⅓M.).

A similar series of experiments was carried out by shaking the glycols (0·01 mol.) with sodium bismuthate (0·01 mol.) in glacial acetic acid (usually 15 ml.) until the reddish-brown suspension of bismuth pentoxide dissolved to give a clear solution; the bismuth was removed by precipitation with 5—6 ml. of 3⅓M-phosphoric acid, and the carbonyl compound isolated as a derivative. The results were similar to those recorded above.

Lactic acid (0·05 mol.) in water (25 ml.) with sodium bismuthate (0·01 mol.) and phosphoric acid (6 ml. of 3⅓M.) was rapidly oxidised, the mixture becoming warm. The evolved gases were led into a solution of 2 : 4-dinitrophenylhydrazine (0·01 mol.) in sulphuric acid (2 ml.) and alcohol (15 ml.), and when the reaction slackened the remainder of the aldehyde was driven over by warming while passing a stream of nitrogen, yielding acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 148° (1·8 g., 72% calc. on the sodium bismuthate). By use of equivalent amounts of freshly diluted lactic acid and sodium bismuthate, the reaction virtually stopped when about two-thirds of the oxidising agent had been used up, all the free lactic acid presumably having been consumed.

threo-9 : 10-Dihydroxystearic acid, m. p. 95—96° (0·01 mol.), prepared by the method of Scanlan and Swern (*loc. cit.*), in glacial acetic acid (15 ml.) was shaken at 40—45° with sodium bismuthate (0·01 mol.) until the latter was reduced (5½ hours). The product was transferred to a separator with water (40 ml.) and extracted with benzene (100-, 20-, and 20-ml. portions). To the water-washed extract was added a solution of 2 : 4-dinitrophenylhydrazine in the minimum of warm (purified) dioxan, and the mixture was refluxed for 10 minutes and cooled. After some hours, excess of reagent (*ca.* 1 g.) was filtered off and the solution was distilled to dryness on the water-bath. The residue, dissolved in warm methyl alcohol (25 ml.), was warmed gently with potassium hydrogen carbonate (2 g.) in water (10 ml.), and water (150 ml.) was added. The precipitate (2·0 g., 62%) was recrystallised from methyl alcohol or technical 2-ethoxyethanol to give pelargonaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 196°, as yellow needles. Acidification of the alkaline filtrate with hydrochloric acid, and recrystallisation from alcohol gave *azelaic aldehyde-acid* 2 : *4-dinitrophenylhydrazone* (1·7 g., 48%) as golden-yellow crystals, m. p. 122—122·5° (Found : C, 51·8; H, 5·7; N, 15·3. $C_{15}H_{20}O_6N_4$ requires C, 51·1; H, 5·7; N, 15·9%).

Benzoin (0·01 mol.), sodium bismuthate (0·01 mol), glacial acetic acid (12 ml.), and phosphoric acid (6 ml. of 3⅓M.) were shaken at 40—50°, reaction requiring 2 hours. After filtration, the mixture was steam-distilled. The distillate (250 ml.) yielded benzaldehyde phenylhydrazone (79%). The residue from the distillation yielded benzoic acid (0·25 g., 22%) and unchanged benzoin (0·1 g.). Analogous experiments, in which phosphoric acid was omitted or dioxan–aqueous phosphoric acid was used, gave similar results, as did working up by solvent extraction. 4-Methoxybenzoin similarly gave benzaldehyde phenylhydrazone, m. p. 157° (1·25 g., 64%), *p*-anisic acid, m. p. 184° (0·85 g., 56%), and unchanged 4-methoxybenzoin (0·6 g.).

Glycerol (0·03 mol.) in water (25 ml.) with phosphoric acid (6 ml. of 3⅓M.) reduced sodium bismuthate (0·01 mol.) within 2 or 3 minutes at room temperature. The bismuth phosphate was filtered off and washed with water. Half of the filtrate (25 ml.) was heated on the water-bath for 10 minutes with dimedon (0·005 mol., 2·8 g.) in alcohol (10 ml.) and then cooled, and the crystals (*A*) filtered off; the filtrate similarly treated with a further 0·005 mol. of dimedon gave a further crop of crystals (*B*). (*A*), m. p. *ca.* 180°, consisted mainly of the formaldehyde derivative; (*B*), m. p. 200—215°, mainly of the glycollaldehyde derivative. Heating (*A*) with 65% alcohol (15 ml.) and filtering hot left the formaldehyde compound, m. p. 189—190° (2·1 g.), and similar treatment of (*B*) with 70% alcohol (20 ml.) left a residue of 0·4 g. of the same (total yield 86%). The alcoholic extracts on cooling deposited respectively 0·5 and 1·4 g. of fairly pure glycollaldehyde derivative, m. p. 215—220°, and a further small amount was obtained from the mother-liquors; this crude material on digestion with hot benzene (5 ml.) gave a pure *anhydride* (1·75 g., 54%), glistening scales (from 70% alcohol), m. p. 228—229° (Found : C, 71·5; H, 8·0. $C_{18}H_{24}O_4$ requires C, 71·0; H, 7·95%), derived from 2 : 2-di-(2 : 6-diketo-4 : 4-dimethyl*cyclo*hexyl)ethanol. Since the formaldehyde–dimedon compound is readily soluble, and the glycollaldehyde derivative is only sparingly soluble in warm benzene, and the reverse is the case with warm 70% alcohol, the two-stage formation of the derivatives was probably unnecessary.

Benzyloxyacetaldehyde.—Carefully fractionated glycerol 1-benzyl ether (b. p. 157·5°/3 mm.; Fairbourne, Gibson, and Stephens, *J.*, 1931, 456, give b. p. 164—166°/2 mm.) (60·7 g., ⅓ mol.) was stirred with water (250 ml.) and sodium bismuthate (⅓ mol.) while a solution of phosphoric acid (110 g. of 85%) in water (20 ml.) was added gradually during ½ hour, the temperature being kept at 17—18° by a good cooling-bath. The bath was then removed and stirring continued until the suspension was white, requiring a further ¼ hour, during which the temperature rose to 21°. The mixture was extracted with ether (500 ml.) without removal of the bismuth phosphate. The ethereal solution was washed with, successively, water, potassium hydrogen carbonate solution, and water, and evaporated. Water was removed by distillation with benzene, and the residue was fractionally distilled through a 14-cm. Fenske column, yielding benzyloxyacetaldehyde, b. p. 121°/15 mm., 112°/10 mm. (34 g., 68%) (Palfray and Sabetay, *Bull. Soc. chim.*, 1937, **4**, 950, give b. p. 115°/15 mm.) [Found : equiv. (hydroxylamine hydrochloride titration), 151·4. Calc. for $C_9H_{10}O_2$: equiv., 150], and materials, b. p. 112°/10 mm. to 170°/5 mm. (1·7 g.), and 170°/5 mm., presumably unchanged glycerol benzyl ether (7·5 g.). The aldehyde gave an oxime, tablets, m. p. 64—65°.

Ethyl Glyoxylate Alcoholate.—Redistilled ethyl tartrate, b. p. 156·5°/12 mm. (51·5 g., 0·25 mol.), was stirred with water (120 ml.) and sodium bismuthate (0·25 mol.), and a solution of phosphoric acid (80 g. of 85%) in water (20 ml.) was added gradually during ½ hour, the temperature being kept at 35—40°, and then the reaction was completed by stirring for a further ½ hour at 35°. The bismuth phosphate was filtered off and washed with alcohol, the filtrate treated with calcium carbonate (30 g.) and again filtered, the cake being washed with alcohol. The filtrate (540 g.) was concentrated by distillation, finally at *ca.* 30°/20—30 mm., through a Vigreux column. After addition of alcohol (100 ml.) and excess of benzene the solution was decanted from salts. Water and alcohol were removed azeotropically through a 28-cm. Fenske column, and the product was distilled under reduced pressure. The fraction of b. p. *ca* . 79°/30 mm. was redistilled at atmospheric pressure through a small Fenske column, giving ethyl glyoxylate alcoholate, b. p. 137·5° (lit., 136—138°) (37·5 g., 51%). Fractionation was very sharp when excess of benzene was used in the azeotropic distillation, but much less so if excess of alcohol was present.

Adipic Dialdehyde and its Cyclic Monoacetal with cis-cyclo*Hexanediol.*—A solution of *trans-cyclo*hexane-1 : 2-diol, m. p. 105° (29 g., 0·25 mol.) in a mixture of water (75 ml.) and phosphoric acid (100 ml. of 3⅓M.) was covered with sodium-dried ether (125 ml.), and sodium bismuthate (0·125 mol.) was added in 2 portions with stirring, the temperature being kept at 30°. When reduction was almost complete, a further 50 ml. of 3⅓M-phosphoric acid was added and then the remaining sodium bismuthate (0·125 mol.) in 2 portions, and stirring was continued at 30° until the reaction was ended (*ca.* 1 hour). Without filtration, the mixture was transferred to a separator with water, the ethereal layer separated, and the aqueous phase extracted with ether (2 × 100 ml.). The ethereal extract was washed with a little water, dried (Na_2SO_4), and evaporated, and the product distilled under reduced pressure through a 14-cm. Fenske column, giving adipic dialdehyde, b. p. 97·5°/12 mm. (14 g., 49%) (oxime m. p. 177—178°), and a resinous residue. The mobile aldehyde became viscous on storage.

In a similar experiment with the *cis*-diol, m. p. 97·5—99° (29 g.), the bismuthate was not completely reduced even after 2 hours and the action seemed to have stopped. On working up, the products (yield 55%) consisted of adipic dialdehyde, b. p. 97·5°/12 mm. (23%), and cis-1 : 2-(5-*formyl*-1 : 2-*pentylidenedioxy*)cyclo*hexane*, b. p. 130°/1 mm. (33%), there was practically no resinous residue from the distillation, and the adipic dialdehyde did not become viscous on storage for some weeks. The cyclic acetal was a colourless, mobile liquid, lacking the characteristic odour of adipic aldehyde (Found : C, 67·6; H, 9·4. $C_{12}H_{20}O_3$ requires C, 67·8; H, 9·5%). Addition of the acetal-aldehyde (0·006 mol.) to a solution of 2 : 4-dinitrophenylhydrazine (0·005 mol.) in purified dioxan (10 ml.), concentration, and addition of a little cineole to induce crystallisation gave the corresponding 2 : 4-*dinitrophenylhydrazone*, as small bright orange crystals, m. p. 100—101·5°; a small amount of impurity was readily removed by running the solution in benzene containing 1·5% of ethyl alcohol through an alumina column, the hydrazone travelling as a dark brown band. The pure material crystallised as golden plates, m. p. 102—103° (Found : C, 54·7; H, 6·2; N, 14·0. $C_{18}H_{24}O_6N_4$ requires C, 55·1; H, 6·2; N, 14·3%). Warming the acetal-aldehyde in aqueous alcohol with hydroxylamine hydrochloride and neutralisation with sodium hydroxide gave adipic dialdehyde dioxime (white crystals from technical 2-ethoxyethanol), m. p. 177—178° (Found : C, 50·2; H, 8·4; N, 17·7. Calc. for $C_6H_{12}O_2N_2$: C, 50·0; H, 8·4; N, 19·4%).

Pelargonaldehyde and Azelaic Aldehyde-acid.—To *threo*-9 : 10-dihydroxystearic acid, m. p. 95—96° (31 g., 0·1 mol.), in acetic acid (150—200 ml.) sodium bismuthate (0·105 mol.) was added in (four) half-hourly portions, with stirring at 55°, and the mixture was stirred at this temperature until a clear solution resulted (2½ hours) (reaction time *ca.* 5½ hours at 45°, 2 hours at 55—60°). After dilution with water (200 ml.) the reaction products were extracted with benzene (30, 25, and 20 ml.), the benzene solution depositing *ca.* 1 g. of unchanged acid when kept at 0°; ether-extraction, as used by Scanlan and Swern (*loc. cit.*) at an analogous stage, is much less suitable owing to the unfavourable partition coefficient of acetic acid between ether and water. The benzene solution was steam-distilled, about 400 ml. of distillate being collected. The separated benzene layer yielded on evaporation and distillation, pelargonaldehyde, b. p. 95°/23 mm. (7·5 g., 53%), which gave a 2 : 4-dinitrophenylhydrazone, m. p. 106°, and an oxime, m. p. 62—63°. Evaporation of a benzene extract of the residue from the steam-distillation yielded a yellow oil (16·5 g.), crude azelaic aldehyde-acid, which formed a crystal magma on storage. Vacuum-distillation of this material yielded only 3 g. of azelaic aldehyde-acid (b. p. *ca.* 145°/3 mm., m. p. *ca.* 35°), which gave a 2 : 4-dinitrophenylhydrazone, m. p. 122—122·5°. The residue contained considerable amounts of azelaic acid. Alternatively, the initial benzene extract was directly vacuum-distilled through a 14-cm. Fenske column, yielding successively pelargonaldehyde (44%), pelargonic acid (8%), and azelaic aldehyde-acid (15%). While pelargonaldehyde isolated by the steam-distillation procedure remained unchanged on storage, that obtained by direct fractionation of the oxidation products soon set to a mass of needles of the trimer, m. p. 34° (lit., m. p. 28°), which readily recrystallised from alcohol (Found : C, 75·9; H, 12·6. Calc. for $C_{27}H_{54}O_3$: C, 76·0; H, 12·8%).

The author thanks Miss A. R. Cumming for assistance in the preparation of some of the glycols.

BIRKBECK COLLEGE, LONDON, E.C.4.

[*Received, December 22nd,* 1949.]