Reactions of Unsaturated Compounds. Part XI. The Oxidation of 2 : 3-Dimethylbut-2-ene by Chromic Acid.*

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2 : 3-Epoxy-2 : 3-dimethylbutane has been isolated after oxidation of dimethylbut-2-ene by chromic oxide in acetic anhydride. Indirect proof of its formation has been obtained by the formation of glycol esters when suitable carboxylic acids are added to the oxidation product.

2 : 3-Dimethylbut-2-ene and chromic acid in aqueous 50% sulphuric acid give notable amounts of 3 : 3-dimethylbutan-2-one. 2 : 3-Dimethylbutane-2 : 3-diol is rapidly oxidised to acetone under these conditions.

It has been shown (*J.*, 1948, 1334; 1951, 1600; 1953, 1906) that α- and β-di*iso*butylene, camphene, and 2 : 2 : 7 : 7-tetramethyloct-4-ene yield epoxides when oxidised by chromic oxide in acetic anhydride. Attempts to isolate the oxide from 2 : 3-dimethylbut-2-ene by the method then used were not successful, probably owing to the greater sensitivity of this oxide to the aqueous acetic acid used during working up. Indirect evidence of the formation of the epoxide was sought by adding acetic or formic acid to the product. Formic acid gave the monoformate of 2 : 3-dimethylbutane-2 : 3-diol with formic esters of glycol ether (I) and some 3 : 3-dimethylbutan-2-one. The products are qualitatively the same as those obtained by the action of formic acid on 2 : 3-epoxy-2 : 3-dimethylbutane and do not arise from the action of formic acid on the glycol. On oxidation of 2 : 3-dimethylbut-2-ene in a mixture of acetic anhydride and acetic acid the monoacetate of the glycol is the main product. If the oxidation mixture in acetic anhydride is diluted largely with water on completion of the reaction, 2 : 3-dimethylbutane-2 : 3-diol is obtained. These observations provide strong evidence for the existence of 2 : 3-epoxy-2 : 3-dimethylbutane in the oxidation mixture. Direct proof was obtained by distilling the volatile products of the oxidation in acetic anhydride at 20° under reduced pressure into cold traps: nearly pure 2 : 3-epoxy-2 : 3-dimethylbutane was isolated and it was recognised unambiguously by reduction to 2 : 3-dimethylbutan-2-ol, by hydration to 2 : 3-dimethylbutane-2 : 3-diol hydrate, and by isomerisation to 3 : 3-dimethylbutan-2-one.

(I) $(HO{\cdot}CMe_2{\cdot}CMe_2)_2O$ $\qquad$ $CMe_3{\cdot}CH_2{\cdot}CMe(CO_2H){\cdot}CMe_3$ (II)

The other product of the oxidation of 2 : 3-dimethylbut-2-ene under anhydrous conditions is 2 : 3-dimethylbut-2-enal derived from the olefin by attack of the oxidising agent at the α-methylenic position.

Oxidation of 2 : 3-dimethylbut-2-ene in aqueous sulphuric acid by chromic acid has also been examined. With low concentrations of sulphuric acid, oxidative fission to acetone is the main reaction; in aqueous sulphuric acid of strengths greater than 50% the product contains a considerable proportion of 3 : 3-dimethylbutan-2-one resulting from rearrangement. Butlerow (*J. Russ. Phys. Chem. Soc.*, 1879, **11**, 219) had reported the formation of αα-dimethylpropionic acid from 2 : 3-dimethylbut-2-ene by chromic acid in aqueous sulphuric acid of over 40% concentration, though below this concentration acetone was the main product. The differences between our results and those of Butlerow are indeed of little significance and due probably to differences in time of contact of the olefin with the oxidising solution and the ratio of olefin to chromic acid. Both sets of observations agree in the occurrence of rearrangement during the oxidation. Rearrangement during oxidation by chromic acid in aqueous sulphuric acid has been observed also with 2 : 4 : 4-trimethylpent-2-ene which gives some ααββ-tetramethylbutyric acid (Byers and Hickinbottom, *J.*, 1948, 1334). Technical tri*iso*butylene gives among other oxidation products α-*tert.*-butyl-αγγ-trimethylvaleric acid (II) (Conant and Wheland, *J. Amer. Chem. Soc.*, 1933, **55**, 2499; Whitmore and Wilson, *ibid.*, 1934, **56**, 1128), which can be formed only by an alteration of the carbon skeleton of any of the tri*iso*butylenes. Rearrange-

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* Part X, *J.*, 1953, 1906.

ment has also been observed during oxidation of 1 : 1 : 2-triphenylprop-1-ene by chromic acid in acetic acid (Schlenk and Bergmann, *Annalen*, 1930, **479**, 51). 9-Diphenylmethylenefluorene (Klinger and Lonnes, *Ber.*, 1876, **29**, 2152) and 2-methyl-1 : 1 : 3 : 3-diphenylpropene (Koelsch and White, *J. Amer. Chem. Soc.*, 1943, **65**, 1639) probably also behave similarly.

Such rearrangements on oxidation of an olefin can be explained simply by the initial formation of a glycol or epoxide or of some polar product easily convertible into glycol, epoxide, or rearrangement product (cf. Hickinbottom and Hogg, *J.*, 1954, 4200). From the present and previous work it would be not unreasonable to assume that formation of an epoxide from an olefin by oxidation under anhydrous conditions is a general reaction. The application of such a hypothesis to oxidation by chromic acid in aqueous sulphuric acid has obvious difficulties and the experimental examination must rely on indirect methods. It is possible, however, to reach a conclusion on the view that the glycol is responsible for rearrangement during the oxidation, by measuring the relative rates of rearrangement and oxidation. It is evident even from purely qualitative measurements that 2 : 3-dimethylbutane-2 : 3-diol could not be such an intermediate : the glycol is oxidised rapidly to acetone by aqueous sulphuric acid solutions of chromic acid of concentrations which easily yield 3 : 3-dimethylbutan-2-one from the olefin.

EXPERIMENTAL

Oxidation of 2 : 3-*Dimethylbut*-2-*ene by Chromic Acid in Aqueous Sulphuric Acid.*—The general procedure was to add a solution of chromic oxide (15 g.) in aqueous sulphuric acid (150 ml.) of the appropriate strength to 2 : 3-dimethylbut-2-ene (10 g.; b. p. 72·8°, n_D^{20} 1·4122) suspended in aqueous sulphuric acid (50 ml.) of the same strength, stirred vigorously. When reaction was complete, the mixture was almost neutralised with 10% aqueous sodium hydroxide and extracted with ether to remove 3 : 3-dimethylbutan-2-one and any αα-dimethylpropionic acid. The ketone was weighed as semicarbazone after crystallisation; the amount of the acid extracted from the ether was negligible. The aqueous solution remaining after ether-extraction was distilled and the acetone in the distillate determined by Messinger's method.

The speed of oxidation, as measured by discharge of the red colour of the solution, was markedly slower with more dilute acid. The concentration of acid is given by the weight of sulphuric acid in 100 g. of solution.

(*a*) Use of 20% sulphuric acid gave an inappreciable amount of ketone. The yield of acetone was 4·5 g.

(*b*) Use of 55% sulphuric acid gave acetone (0·7 g.) and 3 : 3-dimethylbutan-2-one semicarbazone (2·7 g.), m. p. and mixed m. p. 155° (corresponding to 1·47 g. of ketone).

(*c*) The olefin (10 g.) was oxidised by chromic oxide (7 g.) in 75% sulphuric acid (400 ml.). The yield of acetone was 0·4 g. and of 3 : 3-dimethylbutan-2-one 1·35 g. (calc. from semicarbazone).

Oxidation of 2 : 3-*Dimethylbut*-2-*ene by Chromic Oxide in Acetic Anhydride. Isolation of* 2 : 3-*Epoxy*-2 : 3-*dimethylbutane.*—A stirred solution of 2 : 3-dimethylbut-2-ene (80 g.) in acetic anhydride (100 ml.) was cooled in ice-salt and oxidised by chromic oxide (50 g.) in acetic anhydride (300 ml.), then allowed to warm to room temperature and distilled at 16 mm. into receivers cooled in acetone and solid carbon dioxide. The removal of volatile products was completed by warming gently to about 25° until acetic anhydride began to distil. The distillate was freed as far as possible from acetic anhydride by a preliminary distillation at 16 mm. at room temperature. Rapid fractionation of the distillate from a bath at 110° gave, in addition to unchanged olefin, a fraction (5·3 g.), b. p. 92—93·5°, n_D^{20} 1·4020—1·3969. Further distillation gave approximately pure 2 : 3-epoxy-2 : 3-dimethylbutane, b. p. 93°, n_D^{20} 1·3980 (lit., b. p. 90—93°, n_D^{20} 1·3981—1·3995) (Found: C, 71·0; H, 11·85. Calc. for $C_6H_{12}O$: C, 71·9; H, 12·1%). This and the neighbouring fractions gave 2 : 3-dimethylbutane-2 : 3-diol hydrate on treatment with 20% aqueous hydrochloric acid. The oxide gave no precipitate with a cold solution of 2 : 4-dinitrophenylhydrazine in 2% aqueous hydrochloric acid, but reacted immediately with 2 : 4-dinitrophenylhydrazine in warm 25% sulphuric acid to give 3 : 3-dimethylbutan-2-one dinitrophenylhydrazone, m. p. and mixed m. p. 126°. On reduction with lithium aluminium hydride in ether, 2 : 3-dimethylbutan-2-ol was formed (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 110—111°).

The glycol hydrate obtained in these hydrations and in other ways in this work was identified by comparison with an authentic specimen and by sublimation at 80° to give the anhydrous diol (mixed m. p.). It gave the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 126°, of 2 : 3-dimethylbut-3-en-2-ol on treatment with 3 : 5-dinitrobenzoyl chloride in hot pyridine–benzene. For comparison 2 : 3-dimethylbut-3-en-2-ol was prepared from methyl methylacrylate and methylmagnesium iodide. The alcohol, b. p. 117—119°, n_{D}^{20} 1·4030—1·4040, was characterised as its 3 : *5-dinitrobenzoate*, m. p. 126° (Found: C, 52·9; H, 4·6; N, 9·7. $C_{13}H_{14}O_6N_2$ requires C, 53·1; H, 4·8; N, 9·5%). Hydrogenation (platinic oxide–ethyl alcohol) gave 2 : 3-dimethylbutan-2-ol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 110—111°).

Oxidation of 2 : 3-*Dimethylbut*-2-*ene by Chromic Oxide in Acetic Acid. Formation of* 3-*Acetoxy*-2 : 3-*dimethylbutan*-2-*ol*.—A solution of chromic oxide (40 g.) in acetic anhydride (200 ml.) and acetic acid (650 g.) was added slowly to 2 : 3-dimethylbut-2-ene (96·7 g.; n_{D}^{20} 1·4120—1·4121) in acetic acid (100 ml.), at <10°. Stirring was continued for a further 12 hr., then the mixture was distilled at 25° (bath)/16—18 mm. into cold traps. The distillate consisted essentially of unchanged olefin and acetic acid, and the low-boiling products of the oxidation. The residue was diluted with water, neutralised with sodium carbonate, and extracted with ether. The following fractions were obtained on distillation of the washed and dried ether extract: (*a*) b. p. 28—36·5°/1·4 mm., n_{D}^{20} 1·4310 (2·5 g.); (*b*) b. p. 36—36·5°/1·25 mm., n_{D}^{20} 1·4323 (3·2 g.); (*c*) b. p. 35—36°/1 mm., n_{D}^{20} 1·4328 (2·6 g.); (*d*) b. p. 34—36°/0·8 mm., n_{D}^{20} 1·4333 (2·3 g.); (*e*) 32—34°/0·65 mm., n_{D}^{20} 1·4336 (3·5 g.); and (*f*) residue (1·0 g.). Fractions (*b*—*e*) on further distillation gave pure 3-acetoxy-2 : 3-dimethylbutan-2-ol, b. p. 40°/1 mm., n_{D}^{20} 1·4333 (Found: C, 60·0; H, 10·1; Ac, 25·5, 25·0. Calc. for $C_8H_{16}O_3$: C, 60·0; H, 10·1; Ac, 26·8%), which on alkaline hydrolysis yielded the glycol hexahydrate, m. p. and mixed m. p. 45—46°, and acetic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 84—85°).

Oxidation of 2 : 3-*Dimethylbut*-2-*ene in Acetic Anhydride with Subsequent Addition of Formic Acid. Formation of* 3-*Formyloxy*-2 : 3-*dimethylbutan*-2-*ol*.—2 : 3-Dimethylbut-2-ene (97 g.) in acetic anhydride (100 g.) was oxidised by chromic oxide (60 g.) in acetic anhydride (500 ml.). After 5 hr., when oxidation was substantially complete, anhydrous formic acid (500 g.) was added and the mixture kept for 3 days at room temperature. It was then diluted with water, neutralised with sodium carbonate, and extracted with ether. The total product, freed from solvent and unattacked olefin, amounted to 28·3 g. and was fractionated under reduced pressure. (*a*) Fractions boiling below 75°/11 mm. and the contents of the cold traps amounted to 12·1 g. The carbonyl material consisted mainly of 2 : 3-dimethylbut-2-enal (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 196°) with some 3 : 3-dimethylbutan-2-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°). The non-carbonyl product boiled at 54—59°/15 mm. (n_{D}^{20} 1·4210—1·4220) and was essentially 2 : 3-dimethylbut-3-en-2-ol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 126—127°). (*b*) The fractions of b. p. 75—77°/11—13 mm., n_{D}^{20} 1·4400—1·4412 (8 g.), were fractionated, to give 3-formyloxy-2 : 3-dimethylbutan-2-ol, b. p. 84—85°/18 mm., n_{D}^{20} 1·4409—1·4411 (Found: C, 57·2, 57·3; H, 9·3, 10·0; active H, 0·68, 0·65; H·CO, 18·7; 19·2. Calc. for $C_7H_{14}O_3$: C, 57·5; H, 9·7; active H, 0·68; H·CO, 19·8%), hydrolysed by 10% aqueous potassium hydroxide to 2 : 3-dimethylbutane-2 : 3-diol hydrate and formic acid (α-naphthalide, m. p. and mixed m. p. 136—137°). (*c*) Fractions of b. p. 93—144°/11 mm. (3·9 g.) contained only unidentified products.

Oxidation of 2 : 3-*Dimethylbut*-2-*ene by Chromic Oxide in Acetic Anhydride and Hydrolysis of the Mixture by Water*.—A stirred solution of the olefin (97 g.) in acetic anhydride (180 ml.) was cooled (ice–salt) and oxidised by chromic oxide (40 g.) in acetic anhydride (270 mg.) during 3 hr. Next morning the excess of anhydride was hydrolysed by ice-water, and the whole extracted with ether (A). The aqueous layer was distilled to half its bulk, the distillate containing acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°; 6 g. as determined by Messinger's method). The ethereal solution (A), freed from acetic acid and distilled to remove solvent and unchanged olefin, gave fractions: (*a*) b. p. 72—90°/75 mm., n_{D}^{20} 1·4275 (3 g.); (*b*) b. p. 90—101°/75 mm., n_{D}^{20} 1·4310 (1·6 g.); (*c*) b. p. 101—108°/75 mm., n_{D}^{20} 1·4321 (5·8 g.); (*d*) b. p. 80—90°/23 mm., n_{D}^{20} 1·4357 (1·0 g.); (*e*) b. p. 90—110°/23 mm., n_{D}^{20} 1·4377 (1·0 g.); and a residue (0·3 g.). Fractions (*a*—*c*) were unsaturated and restored the colour of Schiff's reagent. From them 2 : 3-dimethylbut-2-enal semicarbazone, m. p. and mixed m. p. 232—233°, and the 2 : 4-dinitrophenylhydrazone, m. p. mixed m. p. 195—196°, were obtained. The remainder of these fractions was combined with (*d*) and (*e*) and freed from carbonyl material by Girard T reagent in hot alcohol containing acetic acid. The non-carbonyl product thus obtained boiled at 70—86°/25 mm. (n_{D}^{20} 1·4177—1·4344) and from the fractions of higher b. p. 2 : 3-dimethylbutane-2 : 3-diol hexahydrate was obtained by crystallisation from water. The lower-boiling fractions gave further amounts of the glycol on addition of light petroleum.

2 : 3-*Dimethylbut*-2-*en*-1-*al*.—(*a*) Selenium dioxide (27 g.) was added to a stirred solution of 2 : 3-dimethylbut-2-ene (58 g.) in acetic anhydride (350 ml.) at 60° during 6 hr. Next morning the selenium was filtered off, the filtrate hydrolysed by water, and the volatile material distilled in steam. The product (39·9 g.) boiled over the range 44—150°/30 mm. It readily yielded 2 : 3-dimethylbut-2-en-1-al semicarbazone, m. p. 234° (Found : C, 53·9; H, 8·2; N, 27·0. Calc. for $C_7H_{13}ON_3$: C, 54·2; H, 8·4; N, 27·1%) {2 : 4-*dinitrophenylhydrazone*, red needles (from aqueous acetic acid), m. p. 198° [Found : C, 51·7; H, 5·1; N, 19·8%; *M* (Rast), 243. $C_{12}H_{14}O_4N_4$ requires C, 51·8; H, 5·1; N, 20·15%; *M*, 278]}. The non-carbonyl product consisted largely of an unsaturated ester, b. p. 78—82°/26 mm. (15 g.), still containing selenium. Hydrolysis gave 2 : 3-dimethylbut-2-en-1-ol (9 g.), b. p. 62—68°/25 mm., n_D^{20} 1·4600, containing selenium; it was identified by ozonolysis to acetone and hydrogenation (PtO_2) with difficulty to 2 : 3-dimethylbutan-1-ol (3 : 5-dinitrobenzoate, m. p. 52°). 2 : 3-Dimethylbut-2-en-1-ol was characterised as its 3 : 5-*dinitrobenzoate*, m. p. 107—108° (Found : C, 53·2; H, 4·6; $C_{13}H_{14}O_6N_2$ requires C, 53·1; H, 4·8%). (*b*) 2 : 3-Dimethylbut-2-en-1-ol (3·35 g.) in light petroleum (30 ml.) was added to *tert.*-butyl chromate [from chromic oxide (6·7 g.), *tert.*-butyl alcohol (14 g.), and light petroleum (b. p. 40—60°; 35 ml.)] and the mixture kept at room temperature for 24 hr., then shaken with water (50 ml.) with the addition of finely powered oxalic acid till the evolution of carbon dioxide ceased. The organic layer was separated, and washed with 10% sulphuric acid (3 × 100 g.) containing acetic acid (10 g.) and then with aqueous sodium carbonate till neutral. Distillation of the dry (Na_2SO_4) solution gave 2 : 3-dimethylbut-2-en-1-al (1 g.), b. p. 120—124°/128 mm., n_D^{20} 1·4165, yielding a semicarbazone, m. p. 234°, and a 2 : 4-dinitrophenylhydrazone, m. p. 198° not depressed on admixture with the derivatives from the selenium oxidation.

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