841. *Reactions of Unsaturated Compounds. Part XIII.* The Oxidation of* 1 : 1-*Diarylolefins by Chromic Oxide.*

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The oxidation of 2-methyl-1 : 1-diphenylprop-1-ene by chromic oxide in acetic anhydride gives 1 : 2-epoxy-2-methyl-1 : 1-diphenylpropane with small amounts of fission products. 2-Methyl-1 : 1-di-*p*-tolyl-, 1 : 1-di-*p*-chlorophenyl-2-methyl-, and 1 : 1-di-*p*-bromophenyl-2-methyl-prop-1-ene yield crystalline epoxides in satisfactory yield under similar conditions. 2 : 3-Dimethyl-1 : 1-diphenylbut-1-ene is similarly oxidised. The epoxides are relatively stable towards aqueous sulphuric acid.

Chromic acid in aqueous sulphuric acid brings about oxidative fission of the double bond without any rearrangement.

The significance of these results is discussed.

In earlier papers it has been shown that many alkyl-substituted olefins are oxidised by chromic oxide in acetic anhydride to the corresponding epoxides, in yields depending on the structure of the olefin. This paper reports an extension of the investigation to some diarylolefins. Epoxide was the major product from all the olefins examined, but fission products were also obtained. One of the olefins, 2 : 3-dimethyl-1 : 1-diphenylbut-1-ene also gave a small amount of an unsaturated aldehyde as the result of oxidation of a α-methylene group. The results are summarised in the Table, together with the effect of chromic acid in aqueous sulphuric acid.

	Product of the action of	
	CrO_3–Ac_2O	CrO_3–aq. H_2SO_4
$CMe_2{=}CPh_2$	Epoxide 88%; acetone; benzophenone	Benzophenone; acetone
$CMe_2{=}C(C_6H_4Me\text{-}p)_2$	Epoxide 60%; acetone; di-*p*-tolyl ketone	Di-*p*-tolyl ketone; acetone
$CMe_2{=}C(C_6H_4Br\text{-}p)_2$	Epoxide 64%; acetone; di-*p*-bromobenzophenone	Di-*p*-bromobenzophenone; acetone
$CMe_2{=}C(C_6H_4Cl\text{-}p)_2$	Epoxide 30%; acetone; di-*p*-chlorobenzophenone	Di-*p*-chlorobenzophenone; acetone
$Pr^iMeC{=}CPh_2$	Epoxide; acetone; benzophenone; *iso*butyric acid; 3 : 3-diphenyl-2-*iso*propylprop-2-enal	Benzophenone; *iso*butyric acid; acetone; a keto-acid

The epoxides obtained in the chromic oxidation are crystalline and were identified by comparison with those obtained by the action of perbenzoic acid. They are relatively stable to aqueous sulphuric acid: those from 2-methyl-1 : 1-diphenyl- and -1 : 1-di-*p*-tolyl-prop-1-ene are slowly converted into the corresponding glycols by agitation with cold 43% sulphuric acid. The epoxides from the other olefins are not appreciably attacked by acid of this concentration even after 3 days. Acid of this concentration was used as the medium for chromic acid oxidation, so epoxides can no longer be considered as the true intermediates. The simplest and, at present, most satisfactory view of the course of the oxidation is to assume some intermediate formed by addition of chromic acid or chromic oxide to the double bond. It is only by such an assumption that the rearrangements observed in aqueous sulphuric can be correlated with the formation of epoxides in acetic anhydride. The intermediate in anhydrous solvents can split out CrO_2 to give an epoxide; in aqueous sulphuric acid, either hydrolysis and oxidation or rearrangement may occur according to the concentration of sulphuric acid. Such intermediates may well result by electrophilic addition of chromic oxide (Hickinbottom and Peters[1]) or from cyclic compounds of the type postulated by Zeiss and Zwanzig.[2]

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* Part XII, *J.*, 1955, 1360.

[1] Hickinbottom and Peters, *J.*, 1955, 1360.

[2] Zeiss and Zwanzig, *Chem. and Ind.*, 1956, 545; *J. Amer. Chem. Soc.*, 1957, **79**, 1733.

EXPERIMENTAL

Concentrations of sulphuric acid are expressed in g. of acid per 100 g. of solution.

*2-Methyl-*1 : 1-*diphenylprop-*1-*ene.*—2-Methyl-1 : 1-diphenylpropan-1-ol was dehydrated by heating it with phthalic anhydride (50% yield) or with acetic anhydride (60% yield); but the most satisfactory conditions consisted in keeping the alcohol (40 g.), pyridine (50 g.), and phosphorus oxychloride (42 g.) at room temperature for several days. The olefin was isolated by pouring the mixture on ice, extracting it with ether, washing the ether solution with sodium carbonate solution and dilute hydrochloric acid, then drying and distilling it. Refluxing with sodium for 6 hr. then gave a product of b. p. 114°/1·6 mm., $n_D^{23.5}$ 1·586 (Found: C, 92·5; H, 7·6. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%). Sabatier and Murat[3] give b. p. 293°, n_D^{16} 1·596.

Oxidation by chromic oxide. Chromic oxide (15 g.) in acetic anhydride (80 c.c.) was added during 0·5 hr. to a stirred, cooled solution of 2-methyl-1 : 1-diphenylprop-1-ene (20 g.) in acetic anhydride (100 c.c.). Stirring was then continued for 3 hr. The mixture was then poured into ice-water (1·5 l.), and the product isolated by ether. Drying and distillation of the ether solution, after it had been washed with aqueous sodium carbonate, gave the main product, b. p. 102—112°/0·7 mm. (14·4 g.). This solidified, and consisted essentially of 1 : 2-epoxy-2-methyl-1 : 1-diphenylpropane. Purified by trituration with alcohol and crystallisation from the same solvent, it had m. p. 64° (Found: C, 85·6; H, 7·1. Calc. for $C_{16}H_{16}O$: C, 85·7; H, 7·1%). Ramart-Lucas[3] gives m. p. 61—62°.

From the alcoholic liquors benzophenone was isolated as 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 242—243°. Acetone was identified in the aqueous washings of the crude ether extract.

For comparison, 1 : 2-epoxy-2-methyl-1 : 1-diphenylpropane was prepared by reaction of the olefin with benzoyl peroxide, then having b. p. 88°/0·25 mm., m. p. and mixed m. p. 64°.

The epoxide (0·2 g.) was shaken in suspension in aqueous sulphuric acid (5 c.c.; 43%) for several days. The diol, crystallised from light petroleum (b. p. <40°), had m. p. 94—95° (Ramart-Lucas[4] gives m. p. 91°); benzophenone was obtained by oxidation with aqueous periodic acid.

Oxidation by chromic acid in aqueous sulphuric acid. To a stirred suspension of 2-methyl-1 : 1-diphenylprop-1-ene (20 g.) in aqueous sulphuric acid (110 c.c.; 65%), chromic oxide (30 g.) in water (46 c.c.) was added continuously during 15 min. The ensuing vigorous reaction was controlled by cooling the flask with alcohol–solid carbon dioxide. Stirring was continued for 3 hr. after all the oxidising agent had been added. Next morning the mixture was diluted with water and extracted with ether. From the ether extract, washed with aqueous sodium carbonate, benzophenone (11·5 g.), m. p. and mixed m. p. 49° (from alcohol), was obtained. Steam-distillation of the alkaline washings of the ether extract gave acetone (1·2 g., estimated by Messinger's method).

*2-Methyl-*1 : 1-*di-*p-*tolylprop-*1-*ene.*—2-Methyl-1 : 1-di-*p*-tolylpropan-1-ol, m. p. 95°, was prepared as described by Schlenk and Bergmann[5] who give m. p. 99°. It was dehydrated to 2-methyl-1 : 1-di-*p*-tolylprop-1-ene by saturating it with hydrogen chloride in ethereal solution, and treating the resulting chloro-compound with pyridine. The olefin, crystallised from methyl alcohol, melts at 50° (Schlenk and Bergmann[5] give m. p. 50°) (Found: C, 91·2; H, 8·4. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%).

Oxidation by chromic oxide in acetic anhydride. The olefin (20 g.) in acetic anhydride (100 c.c.) was oxidised by chromic oxide (11 g.) in acetic anhydride (120 c.c.) as above except that the addition of the oxidising agent required 80 min. and the mixture was kept overnight. Distillation of the neutral product gave 1 : 2-epoxy-2-methyl-1 : 1-di-*p*-tolylpropane (13 g.), b. p. 139—142°/1·5—1·7 mm., m. p. and mixed m. p. 58—59° (from alcohol), and a fraction (1 g.), b. p. 142/1·5 mm., containing di-*p*-tolyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229°). The aqueous washings of the crude product contained acetone.

The *epoxide* was also prepared from the olefin and perbenzoic acid in chloroform; crystallised from alcohol it melted at 58—59° (Found: C, 85·6; H, 8·0. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

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[3] Sabatier and Murat, *Compt. rend.*, 1913, **156**, 1433.

[4] Ramart-Lucas, *Bull. Soc. chim. France*, 1929, **45**, 718.

[5] Schlenk and Bergmann, *Annalen*, 1930, **479**, 49.

It is hydrated by cold 43% sulphuric acid to give a glycol, identified by oxidation with periodic acid to di-*p*-tolyl ketone, m. p. and mixed m. p. 94—95° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229°).

Oxidation by chromic acid in aqueous sulphuric acid. 2-Methyl-1 : 1-di-*p*-tolylprop-1-ene (4 g.), suspended in 65% sulphuric acid (22 c.c.) and oxidised by chromic oxide (2·6 g.) in water (9·2 c.c.), gave di-*p*-tolyl ketone, m. p. and mixed m. p. 94—95° (3 g.), and acetone (0·29 g.).

1 : 1-*Di*-p-*bromophenyl*-2-*methylprop*-1-*ene*.—1 : 1-Di-*p*-bromophenyl-2-methylpropan-1-ol was obtained by reaction of ethyl *iso*butyrate (110 g.) with the Grignard reagent from *p*-dibromobenzene (500 g.) and magnesium (60 g.). The crude alcohol, distilled under reduced pressure, gave 1 : 1-di-*p*-bromophenyl-2-methylprop-1-ene (52 g.), b. p. 174°/0·7 mm., m. p. 97° (from alcohol) (Ashley *et al.*[6] give m. p. 96°). A sticky polymer remained as residue.

Oxidation by chromic oxide. The olefin (15 g.) in acetic anhydride (150 c.c.) was oxidised by chromic oxide (5·2 g.) in acetic anhydride (80 c.c.). The ether solution of the neutral products deposited 4 : 4 -dibromobenzophenone (3 g.), m. p. and mixed m. p. 176°, on concentration. The remainder of the neutral product was distilled, to give 1 : 1-di-*p*-bromophenyl-1 : 2-epoxy-2-methylpropane (10 g.), b. p. 177—178°/1·2 mm., m. p. 94—95° (from alcohol). Distillation of the aqueous-alkaline washings of the crude product gave acetone. No acidic products were recognised.

The *epoxide* was also prepared from the olefin and perbenzoic acid. After crystallisation from alcohol it had m. p. and mixed m. p. 94° (Found: C, 50·6; H, 3·6; Br, 41·3. $C_{16}H_{14}OBr_2$ requires C, 50·3; H, 3·7; Br, 41·8%).

Oxidation by chromic acid in aqueous sulphuric acid. The olefin (10 g.) in 65% sulphuric acid (55 c.c.), oxidised by chromic oxide (4·2 g.) in water (23 c.c.) at room temperature for 4 days, gave 4 : 4′-dibromobenzophenone (8·5 g.), m. p. and mixed m. p. 176° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 263—265°). Acetone (0·29 g.) was identified in the aqueous-alkaline washings.

1 : 1-*Di*-p-*chlorophenyl*-2-*methylprop*-1-*ene*.—1 : 1-Di-*p*-chlorophenyl-2-methylpropan-1-ol (290 g.), m. p. 115° (Skerrett and Woodcock [7] record m. p. 115—116°), was prepared from ethyl *iso*butyrate (135 g.), *p*-bromochlorobenzene (500 g.), and magnesium (70 g.). It was converted, as described for 2-methyl-1 : 1-di-*p*-tolylpropan-1-ol, into 1 : 1-di-*p*-chlorophenyl-2-methylprop-1-ene (125 g.), b. p. 132°/0·2 mm., m. p. 71—72° (Found: C, 69·6; H, 4·9; Cl, 25·4. Calc. for $C_{16}H_{14}Cl_2$: C, 69·3; H, 5·1; Cl, 25·6%). Skerrett and Woodcock [7] give m. p. 69—70°.

Oxidation with chromic oxide. The olefin (20 g.) with chromic oxide (9·1 g.) in acetic anhydride gave 4 : 4′-dichlorobenzophenone (3 g.), m. p. and mixed m. p. 238—240°, acetone (0·27 g.), and 1 : 1-di-*p*-chlorophenyl-1 : 2-epoxy-2-methylpropane (6 g.), m. p. and mixed m. p. 57—58°, b. p. 148—150°/0·65 mm.

The *epoxide*, prepared by perbenzoic acid, had m. p. and mixed m. p. 57—58° (Found: C, 65·4; H, 4·9; Cl, 23·5. $C_{16}H_{14}OCl_2$ requires C, 65·5; H, 4·8; Cl, 24·2%).

Oxidation by chromic acid in aqueous sulphuric acid. The olefin (15 g.), 65% sulphuric acid (82·5 c.c.), chromic oxide (8·5 g.), and water (34·5 c.c.) gave 4 : 4′-dichlorobenzophenone (3·7 g.), m. p. and mixed m. p. 145° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 238—240°), acetone (0·3 g.), and some unchanged olefin.

2 : 3-*Dimethyl*-1 : 1-*diphenylbut*-1-*ene*.—Refluxing 2 : 3-dimethyl-1 : 1-diphenylbutan-1-ol (205 g.) with phthalic anhydride (600 g.) for several hours gave 2 : 3-*dimethyl*-1 : 1-*diphenylbut*-1-*ene*, b. p. 168—170/15 mm., n_D^{15} 1·5740 (94·4 g.) (Found: C, 91·2; H, 8·4. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

The *alcohol* (240 g.), b. p. 198—200/15 mm., n_D^{17} 1·564, was obtained from ethyl αβ-dimethylbutyrate (147·5 g.) and phenylmagnesium bromide (from bromobenzene, 490 g., and magnesium, 75 g.) (Found: C, 84·85; H, 8·7. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%).

αβ-Dimethylbutyric acid, b. p. 188°, n_D^{19} 1·4120, was prepared from ethyl methyl*iso*propylmalonate, b. p. 142—146°, n_D^{20} 1·4023.

Oxidation by chromic oxide. The olefin (10 g.) in acetic anhydride (50 c.c.) was oxidised by chromic oxide (5·2 g.) in acetic anhydride (50 c.c.). Distillation of the neutral product gave main fractions: (*a*) b. p. 164—170°/11—13 mm.; (*b*) 170—172°/12 mm.; (*c*) 180—190°/12 mm.; (*d*) 190—212°/11—12 mm. Fractions (*a*) and (*b*), triturated with alcohol, gave 1 : 2-epoxy-2 : 3-dimethyl-1 : 1-diphenylbutane, m. p. 93°. A further small amount of the epoxide was

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[6] Ashley, Grove, and Henshall, *J.*, 1948, 261.

[7] Skerrett and Woodcock, *J.*, 1950, 2718.

obtained from (*c*). From the alcoholic solutions remaining after these crystallisations, benzophenone was isolated as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 242°. Fraction (*d*) reduced permanganate and gave a red 2 : 4-dinitrophenylhydrazone, m. p. 186—187° (from alcohol–ethyl acetate) (Found: C, 66·4; H, 4·95; N, 13·1. $C_{24}H_{22}O_4N_4$ requires C, 67·0; H, 5·1; N, 13·0%). The colour and the analysis suggest that this is the 2 : *4-dinitrophenylhydrazone* of 3 : 3-diphenyl-2-*iso*propylprop-2-enal. From the alkaline washings of the crude oxidation product, acetone and *iso*butyric acid (*S*-benzylthiuronium salt, m. p. and mixed m. p. 143°) were obtained.

The *epoxide*, b. p. 172—174°/12 mm., was also prepared by perbenzoic acid. Crystallised from ethyl alcohol, it had m. p. and mixed m. p. 93° (Found: C, 85·8; H, 8·0. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

Oxidation by chromic acid in aqueous sulphuric acid. The olefin (10 g.) in 65% sulphuric acid (55 c.c.) was oxidised by chromic oxide (6·4 g.) in water (23 c.c.). The neutral product consisted of benzophenone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 242°). The alkaline aqueous washings of the crude product contained acetone, *iso*butyric acid, and a small amount of a *keto-acid,* m. p. 199—200° (Found: C, 76·0; H, 6·1. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%) (2 : 4-dinitrophenylhydrazone, m. p. 115—117°).

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