653. *Autoxidation in Basic Media. Part IV.* Hydrocarbon Autoxidation*

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The autoxidation of 1- and of 3-arylpropenes has been induced with the dimethyl sulphoxide–t-butyl alcohol solvent system containing potassium t-butoxide. Reasonable yields of cleavage products have been obtained.

The mechanism of alkaline autoxidation has been discussed, and evidence obtained in support of the theory that carbanions react with oxygen to furnish radicals and $\cdot O_2^-$ as the first step in the reaction sequence. In a suitable system partial capture of radicals by other than oxygen has been demonstrated.

The discovery that autoxidation of limonin in t-butyl alcohol containing potassium t-butoxide affords a good yield of the derived diosphenol [1] reawakened interest in the synthetic possibilities of this autoxidation system. Besides diosphenol formation the autoxidation of steroidal 20-ketones [2] give, in some cases, synthetically useful yields of 17α-hydroperoxides from which 17α-hydroxy-compounds can be obtained on reduction.

In principle if the anions of hydrocarbons could be prepared their autoxidation should prove a process of synthetic interest. Recent work [3] has shown that the solvent dimethyl sulphoxide so greatly increases the basicity of potassium t-butoxide that olefinic hydrocarbons, at least as judged by their isomerisation reactions, can be readily converted into

* The following Papers are to be regarded as Parts of this Series: Part I, *J.*, 1962, 1578; Part II, *J.*, 1962, 4743; Part III, *J.*, 1964, 3312.

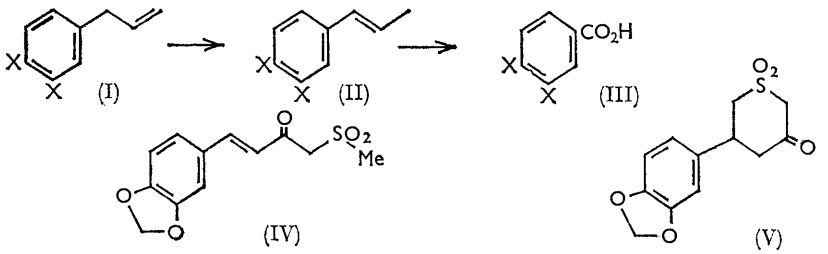
[1] D. H. R. Barton, S. K. Pradhan, S. Sternhell, and J. F. Templeton, *J.*, 1961, 255.

[2] E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J.*, 1962, 1578.

[3] A. Schriesheim, J. E. Hofmann, and C. A. Rowe, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 3731; A. Schriesheim and C. A. Rowe, *ibid.*, 1962, **84**, 3160; A. Schriesheim, R. J. Muller, and C. A. Rowe, jun., *ibid.*, 1962, **84**, 3164; A. Schriesheim, C. A. Rowe, jun., and L. Naslund, *ibid.*, 1963, **85**, 2111; S. Bank, C. A. Rowe, jun., and A. Schriesheim, *ibid.*, p. 2115.

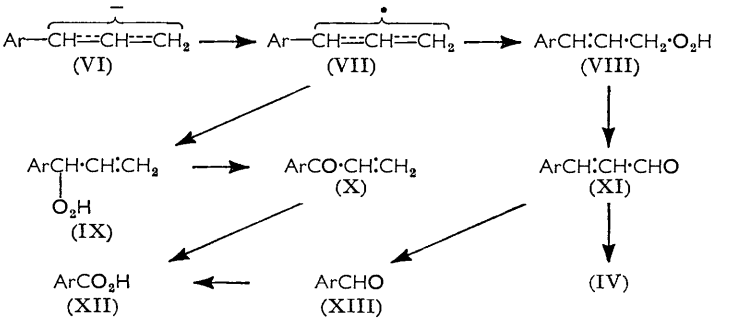
their anions. Using the dimethyl sulphoxide–t-butyl alcohol–potassium t-butoxide system we have shown that 1- and 3-arylpropenes are readily autoxidised.[4] Without the dimethyl sulphoxide no oxidation took place.

Autoxidation of safrole (I; XX = O·CH_2·O) gave piperonylic acid (III; XX = O·CH_2·O) (42%). The reagent rapidly isomerised safrole to isosafrole (II; XX = O·CH_2·O), and autoxidation of the latter afforded piperonylic acid in the same yield. In a similar manner, allylbenzene (I; X = H) and eugenol methyl ether (I; X = OMe) afforded benzoic acid and veratric acid (III; X = OMe), respectively. 1,2-Dihydronaphthalene, in contrast, gave naphthalene in high (89%) yield.



The neutral fraction obtained from the oxidation of safrole and isosafrole was examined in some detail When the oxidation was conducted in the presence of ten equivalents of potassium t-butoxide during 7 hr , very little isosafrole remained unoxidised. A sulphone, $C_{12}H_{12}SO_5$, was readily isolated from the neutral fraction, although formed in small and variable ($\leqslant$5%) yield. This compound was an αβ-unsaturated ketone ($\nu_{max.}$ 1650) and showed ultraviolet absorption [$\lambda_{max.}$ 352 mμ (ε 27,300)] similar to that of piperonylideneacetone which was measured for comparison [$\lambda_{max.}$ 343 mμ (ε 20,100)]. These data suggested the constitution (IV), which was in full accord with the n.m.r. spectrum (see Experimental section). A synthesis of the sulphone (IV) from the potassium t-butoxide catalysed condensation of phenyl 3,4-methylenedioxycinnamate with dimethyl sulphone confirmed the constitution. A second, isomeric sulphone was also formed in the condensation. This had physical properties in accord with the constitution (V). The autoxidation of isosafrole in the presence of dimethyl sulphone (6·5 mol.) gave an increased yield (*ca.* 10%) of the sulphone (IV).

Although there are several ways in which the formation of piperonylic acid and of the sulphone (IV) can be explained, the simplest is that the anion of safrole (VI) is converted



(Ar = 3,4-methylenedioxyphenyl, unless specified to the contrary)

into the radical (VII) which captures oxygen to give the hydroperoxides (VIII) and (IX). Decomposition of the former would afford 3,4-methylenedioxycinnamaldehyde (XI) and of the latter the vinyl ketone (X). Michael addition of water and reversed aldol cleavage

[4] Cf. T. J. Wallace, A. Schriesheim, and N. Jacobsen, *Chem. and Ind.*, 1964, 1316; *J. Org. Chem.*, 1964, **29**, 2907.

applied to the cinnamaldehyde (XI) would afford piperonaldehyde (XIII), which we have shown to be oxidised to piperonylic acid (XII) under the usual autoxidation conditions. The condensation of aldehyde (XI) with dimethyl sulphoxide (or dimethyl sulphone) followed by further oxidation would also give the sulphone (IV). In order to ascertain the relative importance of the vinyl ketone (X) and of the aldehyde (XI) in the scheme discussed above, the autoxidation of acrylophenone (X; Ar = Ph) and of cinnamaldehyde (XI; Ar = Ph) was investigated. The former, which can undergo Michael addition of water followed by further oxidation at the methylene α to the ketone group, gave a good yield of benzoic acid, whereas cinnamaldehyde afforded only a little benzoic acid. Cinnamyl alcohol, which could also be an intermediate in the scheme, likewise afforded little benzoic acid. It appears, therefore, that the degradations to aromatic acids proceed largely through vinyl ketones of type (X) and that relatively little terminal peroxidation to give (VIII) is involved. The formation of sulphone (IV) does, however, require some participation of the latter process.

We have also studied the autoxidation of 1,1,3-triphenylprop-1-ene (XIV), with results which are of some mechanistic significance. The nature of the principal products varied with the reaction time, but in all cases benzoic acid and the benzophenone–dimethyl sulphoxide adduct (XV) [5] were formed, these products corresponding to a complete degradation of the molecule and being comparable to the autoxidations already described. Short autoxidation gave, in addition to these products, a hydrocarbon, $C_{42}H_{34}$. By direct comparison with synthetic specimens this was shown to be a 1 : 1 complex of *meso*- and racemic 1,1,3,4,6,6-hexaphenylhexa-1,5-diene (XVI). In addition, 1,3,3-triphenylprop-2-en-1-one (XVII), 1,3,3-triphenylprop-2-en-1-ol (XVIII), and 1,1,3-triphenylprop-2-en-1-ol (XIX) were formed. Autoxidation during 24 hr. gave the 1 : 1 hydrocarbon complex (XVI), the alcohol (XIX), and a sulphone (XX), as well as the usual cleavage products. The absence of the unsaturated ketone (XVII) would be in agreement with the view that the cleavage products are derived, at least in part, through further transformations of this compound. The constitution of the sulphone (XX), deduced from spectra (see Experimental section), was confirmed by its synthesis from sodium methylsulphinate and 3-chloro-1,1,3-triphenylprop-1-ene.[6]

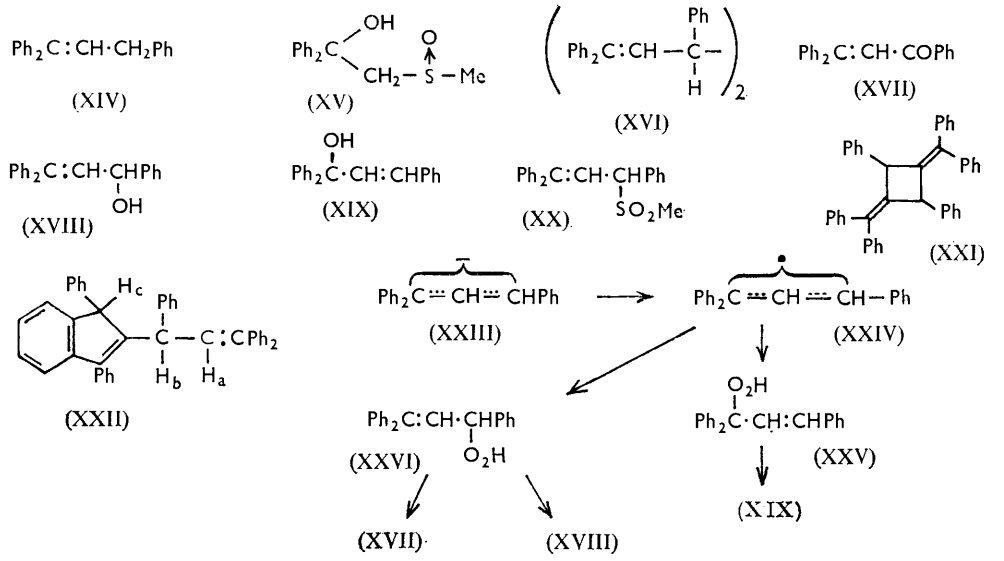
The two alcohols (XVIII) and (XIX) were difficult to characterise, but both gave the known hydrocarbon, $C_{42}H_{32}$, described by Ziegler *et al.*,[6,7] on acid-catalysed dehydration. Both alcohols were finally identified by comparison with synthetic specimens.[6,7] The n.m.r. spectrum of the hydrocarbon $C_{42}H_{32}$ showed that it does not have the constitution (XXI) assigned to it earlier.[8] The revised constitution (XXII) (or double-bond isomer) would satisfy the n.m.r. evidence. Thus, the spectrum showed resonance attributable to 29 aromatic protons between 2·6 and 3·3 τ, a doublet (1H) due to H_a at 4·14 τ (J = 11 c./sec.), a doublet (1H) due to H_b at 5·04 τ (J = 11 c./sec.), and a singlet (1H) at 5·56 τ for H_c. The sulphone (XX) also gave the hydrocarbon (XXII) on treatment with acid.

The results of the autoxidation of 1,1,3-triphenylprop-1-ene can be explained by anion (XXIII) formation, conversion into the radical (XXIV), transformation into the two hydroperoxides (XXV) and (XXVI), reduction [9] of these to the two alcohols (XVIII) and (XIX), and dehydration of hydroperoxide (XXVI) to the unsaturated ketone (XVIII). The formation of the dimeric hydrocarbon (XVI) and of the sulphone (XX) appears to be of particular mechanistic significance. As is well known, the products from anion autoxidation can be explained by direct attack of the anion on oxygen [10] or by the formation of the corresponding radical with transfer of one electron to oxygen to form $\cdot O_2^-$. The

[5] G. A. Russell, E. G. Janzen, H. D. Becker, and F. J. Smentowski, *J. Org. Chem.*, 1962, **84**, 2652.
[6] K. Ziegler, K. Richter, and B. Schnell, *Annalen*, 1925, **443**, 161.
[7] K. Ziegler, H. Grabbe, and F. Ulrich, *Ber.*, 1924, **57**, 1983.
[8] C. Dufraisse, A. Etienne, and B. Goffinet, *Compt. rend.*, 1954, **238**, 861.
[9] Cf. H. M. E. Cardwell and F. J. McQuillin, *J.*, 1955, 525.
[10] Cf. Y. Sprinzak, *J. Amer. Chem. Soc.*, 1958, **80**, 5449; A. F. Bickel, H. R. Gersman, and H. J. M. Nieuwenhuis, *Tetrahedron Letters*, 1963, 1383.

production of the dimeric hydrocarbon (XVI) must certainly be due to the radical mechanism.

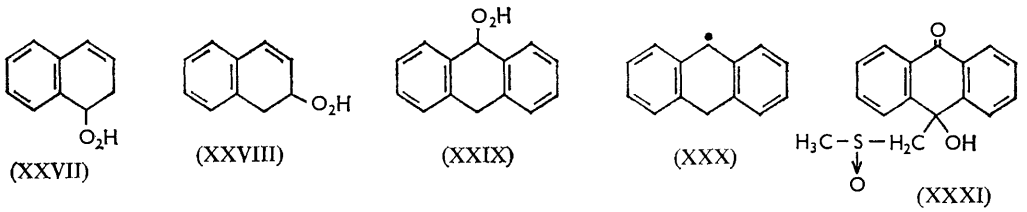
Autoxidation of the alcohol (XVIII) under the usual conditions gives only a trace (*ca.* 2%) of the sulphone (XX), and, as expected, the alcohol (XVIII) does not react with sodium methylsulphinate to give this derivative. However, short oxidation of 1,1,3-triphenylprop-1-ene in the presence of sodium methylsulphinate (5 mol.) does afford the



sulphone (XX) in improved yield (12%). Clearly, the methylsulphinate anion is oxidised to the $MeSO_2$· radical which then captures the radical (XXIV) to give the sulphone (XX).

The dehydrogenation of 1,2-dihydronaphthalene to naphthalene (see above) is also difficult to explain on the direct anion + oxygen ⟶ hydroperoxide theory. The expected intermediates would then be the hydroperoxides (XXVII) and (XXVIII) which should have given, under the alkaline conditions, 1- and 2-naphthol, respectively. A relevant case of aromatisation during alkaline autoxidation of an αβ-unsaturated ketone has recently been reported and shown not to involve hydroperoxide formation.[11]

We considered that the alkaline autoxidation of 9,10-dihydroanthracene could provide a clear distinction between the direct oxygen-displacement theory and the radical-intermediate theory. Reaction of the anion from 9,10-dihydroanthracene should afford either the hydroperoxide (XXIX) (oxygen displacement) or the radical (XXX). The latter, by further anion formation and electron abstraction by oxygen would then afford anthracene.



The hydroperoxide (XXIX) under the basic conditions of the oxidation was expected to form anthrone and thence anthraquinone. Since the hydroperoxide (XXIX) is a known compound [12] we were encouraged to make the relevant experiments.

[11] K. Crowshaw, R. C. Newstead, and N. A. J. Rogers, *Tetrahedron Letters*, 1964, 2307.
[12] H. Hock and F. Ernst, *Chem. Ber.*, 1959, **92**, 2732.

Autoxidation of 9,10-dihydroanthracene gave anthracene (61%) and the dimethyl sulphoxide adduct (XXXI) of anthraquinone (27%). An authentic specimen of the latter was prepared by condensation of dimethyl sulphoxide with anthraquinone under basic conditions. Similar autoxidation of the hydroperoxide (XXIX) gave anthracene (43%) and the dimethyl sulphoxide adduct (XXXI) (39%). The results did not, therefore, provide a clear distinction between alternative theories. However, the ratio of anthracene to adduct (XXXI) is different in the two autoxidations, which suggests that only part, if any, of the hydrocarbon can be produced through the hydroperoxide (XXIX).

Added, January 27th, 1965. Professor G. A. Russell (Iowa State University) has informed us that he and his colleagues have also studied the alkaline autoxidation of selected hydrocarbons, especially dihydroanthracene. Insofar as comparisons can be made, the separate investigations are in factual and interpretative accord.

Experimental

Melting points were determined on a Kofler hot-stage apparatus. Unless specified to the contrary ultraviolet absorption spectra were determined in ethanol and infrared spectra in Nujol. N.m.r. spectra were taken in deuterochloroform on a Varian A60 spectrometer on permanent loan from the Wellcome Foundation. The phrase " in the usual way " refers to dilution with water, acidification, extraction into ether, washing with saturated aqueous sodium hydrogen carbonate, and evaporation of the dried (Na_2SO_4) solvent on a water-bath *in vacuo*. Light petroleum refers to the fraction of b. p. 60—80°. The uptake of oxygen is given at 20°/760 mm. All autoxidations were carried out at room temperature.

Autoxidation of Safrole.—Safrole (redistilled; 1·41 g.) in dimethyl sulphoxide (48 ml.) and t-butyl alcohol (12 ml.) containing potassium t-butoxide (6·82 g.) was shaken under oxygen for 4 hr. (607 ml. uptake) and worked up in the usual way to furnish an oil (490 mg.). Trituration with benzene gave a yellow solid (40 mg.). A portion (23 mg.), chromatographed over alumina (Grade I), eluting with benzene–chloroform (3 : 2), afforded the *sulphone* (IV) (19 mg.), prisms, m. p. 179—180° (from ethanol), $\lambda_{max.}$ 256, 305, and 352 mμ (log ε 4·22, 4·14, and 4·44), $\nu_{max.}$ 1650 (αβ-unsat. ketone), 1150 and 1300 (sulphone) cm.$^{-1}$ [Found: C, 53·6; H, 4·3; O, 29·5; *M* (osmometric), 275. $C_{12}H_{12}O_5S$ requires C, 53·7; H, 4·5; O, 29·8%; *M*, 268]; n.m.r. singlet at 6·9 τ (3H), two singlets at 5·74 and 3·92 τ (both 2H), and a complex between 2·5 and 3·2 τ (5H).

After removal of the sulphone the residual material (see above) was chromatographed over alumina (Grade I) in benzene. Elution with the same solvent gave isosafrole (410 mg.). Acidification of the sodium hydrogen carbonate washing (see preliminary section above) gave 3,4-methylenedioxybenzoic acid (570 mg.), m. p. 227—228° (from ethanol) (mixed m. p. and infrared spectrum).

Autoxidation of Isosafrole.—Isosafrole (redistilled; 1·33 g.) in dimethyl sulphoxide (48 ml.) and t-butyl alcohol (12 ml.) containing potassium t-butoxide was shaken with oxygen for 375 min. (673 ml. uptake). Working up as above gave 3,4-methylenedioxybenzoic acid (760 mg.), the sulphone (IV) (22 mg.), and unchanged isosafrole (530 mg.).

Autoxidation as above, but without the dimethyl sulphoxide, caused no uptake of oxygen.

Isosafrole (500 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·6 g.) was shaken with oxygen for 7 hr. Working up as above gave 3,4-methylenedioxybenzoic acid (410 mg.), the sulphone (IV) (31 mg.), and no unchanged isosafrole.

Isosafrole (500 mg.), dimethyl sulphone (2·16 g.), and potassium t-butoxide (6·1 g.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) were shaken with oxygen (418 ml. uptake). Separation into acid and neutral fractions gave piperonylic acid (290 mg.) and the sulphone (IV) (100 mg. crude, 64 mg. pure).

Synthesis of the β-Oxosulphone (IV).—3,4-Methylenedioxycinnamic acid[13] (10 g.) was converted into the acid chloride with thionyl chloride. This product, in phenol (5 g.) and pyridine (100 ml.), was heated under reflux for 12 hr. Dilution with water (300 ml.), extraction into chloroform, and further working up in the usual way gave the *phenyl ester* (13·2 g.), needles, m. p. 104° (from ethanol) (Found: C, 72·1; H, 4·7. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

[13] I. A. Pearl and D. L. Beyer, *J. Org. Chem.*, 1951, **16**, 216.

Phenyl 3,4-methylenedioxycinnamate (2·73 g.) in dimethyl sulphoxide (20 ml.) containing dimethyl sulphone (1·89 g.) and potassium t-butoxide (2·53 g.) was stirred at 55—60° (bath) for 2 hr. Dilution with water (60 ml.), acidification with hydrochloric acid (6N), and extraction with chloroform gave, at the interface, a mixture (550 mg.) of the sulphone (V) (280 mg.) and 3,4-methylenedioxybenzoic acid. A further quantity (130 mg.) of this acid was obtained by washing the chloroform extract with aqueous sodium hydrogen carbonate. Removal of the chloroform *in vacuo* afforded an oil (2·33 g.) which gave a crystalline product (810 mg.) on trituration with benzene. A portion (257 mg.) of the crystals was chromatographed in benzene over alumina (Grade I). Elution with benzene–chloroform (4 : 1) and (7 : 3) gave the β-oxosulphone (IV) (see above) (144 mg.) (m. p., mixed m. p., and infrared spectrum). Further elution with benzene–chloroform (7 : 3) afforded the *sulphone* (V) (96 mg.), prisms, m. p. 212—215° (from ethyl acetate), $\nu_{max.}$ 1720 (ketone) and 1315 and 1210 cm.$^{-1}$ (sulphone) (Found: C, 53·3; H, 4·1; O, 30·2. $C_{12}H_{12}O_5S$ requires C, 53·7; H, 4·5; O, 29·8%).

Autoxidation of Allylbenzene.—Allylbenzene (540 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (4·3 g.) was shaken with oxygen for 80 min. (425 ml. uptake). Working up in the usual way gave benzoic acid (365 mg.).

Autoxidation of Eugenol Methyl Ether.—Eugenol methyl ether (500 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·4 g.) was shaken with oxygen for 215 min. (388 ml. uptake). Working up in the usual way gave an acidic product (370 mg.) which gave veratric acid (220 mg.) on crystallisation from water. The neutral fraction (100 mg.) was not examined further.

Autoxidation of 1,2-*Dihydronaphthalene.*—The hydrocarbon (540 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·4 g.) was shaken with oxygen for 6 hr. (310 ml. uptake). Working up in the usual way afforded naphthalene (480 mg.) (m. p., mixed m. p., and infrared spectrum).

Autoxidation of Acrylophenone (X; Ar = Ph).—The unsaturated ketone [14] (580 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·47 g.) was shaken under oxygen for 22 hr. (307 ml. uptake). The acid fraction (460 mg.) was essentially pure benzoic acid (m. p., mixed m. p., and infrared spectrum). The neutral product (148 mg.) was not investigated further.

Autoxidation of Cinnamaldehyde and of Cinnamyl Alcohol.—Cinnamaldehyde (acid free; 600 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·71 g.) was shaken under oxygen for 16 hr. (290 ml. uptake). The acid fraction (348 mg.) on extraction with hot water and cooling gave benzoic acid (22 mg.) containing some cinnamic acid (infrared spectrum). Sublimation *in vacuo* gave pure cinnamic acid (6·4 mg.). The neutral product (22 mg.) was not investigated further.

Autoxidation of cinnamyl alcohol gave the same results. Cinnamic acid alone subjected to identical autoxidation conditions was recovered quantitatively unchanged.

Autoxidation of Piperonaldehyde.—The aldehyde (540 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·51 g.) was shaken under oxygen for 4 hr. (252 ml. uptake). Separation into neutral and acid fractions gave, in the latter, piperonylic acid (340 mg.), identified by m. p., mixed m. p., and infrared spectrum.

Autoxidation of 1,1,3-*Triphenylprop*-1-*ene.*—(*a*) The hydrocarbon [15] (520 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·7 g.) was shaken with oxygen for 250 min. (105 ml. uptake). Working up in the usual way gave benzoic acid (50 mg.) and a neutral fraction (510 mg.). Chromatography of the latter over alumina (Grade III) gave, on elution with benzene, the *hydrocarbon complex* (XVI) (100 mg.), m. p. 186—190° and 212—14° (from chloroform–ethanol), $\lambda_{max.}$ 261 mμ (ε 33,700, in cyclohexane) [Found: C, 93·4; H, 6·6; *M* (osmometric), 569. $C_{42}H_{34}$ requires C, 93·6; H, 6·35; *M*, 538]. Admixture with the complex prepared by synthesis (see below) gave no depression in m. p. and identical ultraviolet and infrared spectra.

Further elution with benzene afforded 1,3,3-triphenylprop-2-en-1-one (34 mg.) (m. p., mixed m. p., and infrared spectrum).[16] Further elution with benzene gave 1,1,3-triphenylprop-2-en-1-ol [6] (43 mg.) (m. p., mixed m. p., and infrared spectrum) and then 1,3,3-triphenylprop-2-en-1-ol [7] (76 mg.) (infrared spectrum and thin-layer chromatography). Intermediate fractions in

[14] C. Mannich and G. Heilner, *Ber.*, 1922, **55**, 356.
[15] W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, 1.
[16] D. Vorländer, J. Osterburg, and O. Meye, *Ber.*, 1923, **56**, 1136.

the chromatogram contained mixtures of the two alcohols (thin-layer chromatography). The 1,3,3-triphenylprop-2-en-1-ol was characterised by acid-catalysed dehydration to the known hydrocarbon, $C_{42}H_{32}$.[6,7] The sulphone (XX) gave the same hydrocarbon under the same acid conditions.

Elution with ether–ethanol (93 : 7) gave the benzophenone–dimethyl sulphoxide adduct [5] (110 mg.) (m. p., mixed m. p., and infrared spectrum).

(*b*) 1,1,3-Triphenylprop-1-ene (510 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (4·9 g.) was shaken with oxygen for 24 hr. (uptake 684 ml.). Working up in the usual way gave benzoic acid (117 mg.). The neutral fraction (420 mg.) was chromatographed over alumina (Grade III). Elution with benzene gave the hydrocarbon (XVI) (62 mg.), 1,1,3-triphenylprop-2-en-1-ol (30 mg.) and then the *sulphone* (XX), needles, m. p. 140—141° (from ethanol), $\lambda_{max.}$ 259 mμ (ε 13,500), $\nu_{max.}$ 1310 and 1140 (sulphone) cm.$^{-1}$ [Found: C, 75·4; H, 5·8; O, 9·0; S, 9·05; *M* (osmometric), 361. $C_{22}H_{20}O_2S$ requires C, 75·8; H, 5·8; O, 9·2; S, 9·2%; *M*, 348], n.m.r. singlet (3H) at 7·52 τ ($CH_3{\cdot}SO_2$), a doublet at 5·35 τ (J = 11 c./sec.) (1H), a doublet at 3·47 τ (J = 11 c./sec.) (1H), and resonance due to aromatic protons between 2·5 and 2·9 τ (15H).

Further elution with benzene gave only oily fractions but elution with ether–ethanol (93 : 7) afforded the benzophenone–dimethyl sulphoxide adduct [5] (190 mg.).

Autoxidation of 1,3,3-*Triphenylprop*-2-*en*-1-*ol*.—The alcohol (400 mg.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) containing potassium t-butoxide (3·57 g.) was shaken with oxygen for 24 hr. (560 ml. uptake). Working up in the usual way gave benzoic acid (108 mg.) and a neutral fraction (250 mg.). Chromatography of the latter over alumina (Grade III) afforded, as crystalline products, the sulphone (XX) (9·4 mg.) and the benzophenone–dimethyl sulphoxide adduct (142 mg.).

Synthesis of the Sulphone (XX).—Sodium methylsulphinate (370 mg.) and 3-chloro-1,1,3-triphenylprop-1-ene (310 mg.) in tetrahydrofuran (25 ml.) were heated under reflux for 15 hr. The product was chromatographed over alumina (Grade III) in benzene. Elution with this solvent gave the hydrocarbon [6,7] $C_{42}H_{32}$ (222 mg.). Further elution with benzene afforded the sulphone (XX) (83 mg.), needles, m. p. 140—141° (from ethanol) (m. p., mixed m. p., and infrared spectrum).

The possible, but improbable, interaction of sodium methylsulphinate and 1,3,3-triphenylprop-2-en-1-ol was also studied. The alcohol (240 mg.) and sodium methylsulphinate (340 mg.) in dimethyl sulphoxide (25 ml.) did not react in 24 hr. at room temperature. Potassium t-butoxide (500 mg.) was added and the solution set aside for a further 24 hr. After working up in the usual way the product (209 mg.) was chromatographed over alumina (Grade I). After initial oily fractions, elution with benzene–light petroleum (4 : 1) gave 1,3,3-triphenylpropan-1-one (110 mg.). Further elution afforded no evidence for the presence of the easily crystallised sulphone (XX).

Autoxidation of 1,1,3-*Triphenylprop*-1-*ene in the Presence of Sodium Methylsulphinate*.—The olefin (490 mg.), sodium methylsulphinate (1·24 g.), and potassium t-butoxide (3·4 g.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) were shaken in oxygen for 4 hr. (97 ml. uptake). Separation into acidic and neutral fractions gave benzoic acid (32 mg.) and an oil (500 mg.), respectively. The latter was chromatographed over alumina (Grade III). Elution with benzene furnished the hydrocarbon complex (XVI) (97 mg.). Further elution with benzene gave oily fractions that were not further investigated, and then the sulphone (XX) (63 mg.). Further elution with ether–ethanol (93 : 7) afforded the benzophenone–dimethyl sulphoxide adduct (98 mg.).

Identical autoxidation of 1,3,3-triphenylprop-2-en-1-ol (560 mg.) in the presence of sodium methylsulphinate (1·26 g.) gave benzoic acid (145 mg.) and a neutral product (310 mg.). Chromatography of the latter gave only a trace of sulphone (XX) (as detected by thin-layer chromatography) as well as the benzophenone–dimethyl sulphoxide adduct (113 mg.).

Synthesis of Racemic and meso-1,1,3,4,6,6-*Hexaphenylhexa*-1,5-*diene*.—(*a*) Synthesis of the 1 : 1-complex (XVI). 3-Chloro-1,1,3-triphenylprop-1-ene (650 mg.) and magnesium (48 mg.) in anhydrous ether (20 ml.) were heated under reflux under nitrogen for 3 hr. Crystallisation of the product from ethanol gave the 1 : 1 complex (XVI) (320 mg.) as flat needles, m. p. 186—190° and 212—214°, identical (mixed m. p. and infrared spectra) with the hydrocarbon from autoxidation of 1,1,3-triphenylprop-1-ene (see above).

(*b*) *meso*-Dimethyl ββ′-diphenyladipate [17] (1·4 g.) in ether (50 ml.) was added dropwise to phenylmagnesium bromide (from 4·1 g. of bromobenzene) in ether (200 ml.), and the solution heated under reflux for 3 hr. Crystallisation of the product from ethanol gave meso-1,1,3,4,6,6-*hexaphenylhexane*-1,6-*diol* (1·34 g.) as flat needles, m. p. 188—196° (Found: C, 87·9; H, 6·9; O, 5·5. $C_{42}H_{38}O_2$ requires C, 87·8; H, 6·7; O, 5·6%).

This diol (510 mg.) in glacial acetic acid (20 ml.) and concentrated sulphuric acid (0·4 ml.) was heated on a steam-bath for 15 min. Cooling to room temperature gave meso-1,1,3,4,6,6-*hexaphenylhexa*-1,5-*diene* (400 mg.), m. p. 221—222° (from chloroform–ethanol) (Found: C, 93·3; H, 6·5. $C_{42}H_{34}$ requires C, 93·6; H, 6·35%).

In the same way, racemic dimethyl ββ′-diphenyladipate [17] (720 mg.) gave a non-crystalline diol (1·1 g.) which on dehydration afforded racemic 1,1,3,4,6,6-*hexaphenylhexa*-1,5-*diene* (170 mg.) plates, m. p. 196° (from ethanol) (Found: C, 93·7; H, 6·3%).

A 1 : 1 mixture of these two hydrocarbons was identical (m. p., mixed m. p., and infrared spectrum) with the 1 : 1 complex (XVI) described above.

Autoxidation of 9,10-*Dihydroanthracene*.—9,10-Dihydroanthracene (500 mg.) and potassium t-butoxide (3·51 g.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) were shaken with oxygen for 40 min. (135 ml. uptake). The product was diluted with water and acidified with hydrochloric acid. The white precipitate formed was filtered off (305 mg.) and shown to be anthracene by comparison of infrared spectra and mixed m. p. determination. The filtrate was extracted with chloroform. The dried ($MgSO_4$) extract gave an oil (460 mg.) that, after 12 hr. *in vacuo*, afforded a crystalline residue (206 mg.), needles (132 mg.), m. p. 170—171° (from chloroform–light petroleum) (Found: C, 67·15; H, 5·0%; *M*, 293. $C_{16}H_{14}O_3S$ requires C, 67·1; H, 49·95%; *M*, 286). The compound showed strong infrared absorption at 1060 (sulphoxide), 1603, 1668 (aryl ketone), and 3100 cm.$^{-1}$ (OH). It was identified as the adduct (XXXI) by the following synthesis.

Anthraquinone (500 mg.) and potassium t-butoxide (3·5 g.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml) were shaken for 45 min., diluted with water, acidified with hydrochloric acid, and extracted into chloroform. The dried, evaporated extract (570 mg.) crystallised from chloroform–light petroleum as needles, m. p. 170—171°, identical with the sulphoxide obtained above (mixed m. p. and infrared spectrum).

Autoxidation of 9-*Hydroperoxy*-9,10-*dihydroanthracene*.—The hydroperoxide [12] (480 mg.) and potassium t-butoxide (3·5 g.) in dimethyl sulphoxide (24 ml.) and t-butyl alcohol (6 ml.) were shaken with oxygen for 48 min. (68 ml. uptake). Dilution with water and acidification with hydrochloric acid gave anthracene (0·216 g.). The filtrate, after removal of anthracene, was extracted with chloroform. The oil obtained by removal of solvents (12 hr. *in vacuo*) afforded (XXXI) (194 mg.) on crystallisation from chloroform–light petroleum.

We thank the Government Grants Committee of the Royal Society and the D.S.I.R. for financial assistance.

IMPERIAL COLLEGE, LONDON S.W.7. [*Received, December 14th*, 1964.]

[17] M. P. Oommen and A. I. Vogel, *J.*, 1930, 2148.