The Trapping of Carbon Radicals. The Competition of Oxygen and Iodine for the 1,1-Diphenylethyl Radical

By **Simon C. W. Hook,*** The Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NP
Brian Saville, Department of Chemistry, University of South Carolina, South Carolina 29208

Carbon-centred radicals react rapidly with oxygen and numerous radical-scavenging compounds. The competition between oxygen and radical scavengers for a tertiary alkyl radical has been studied under conditions that simulate the initiation step of a hydrocarbon autoxidation. Iodine effectively captures the 1,1-diphenylethyl radical in the presence of oxygen, the resultant alkyl iodide undergoing decomposition by loss of hydrogen iodide to give the corresponding olefin. An approximate value of $k(O_2)/k(I_2) = 6$ for the relative reactivity of the 1,1-diphenylethyl radical towards oxygen and iodine has been obtained.

THE conventional methods for inhibiting hydrocarbon autoxidations include the removal of alkylperoxyl radicals by reaction with a hydrogen donor molecule (AH), normally an amine or phenol [equation (4)].

$$\text{initiation} \longrightarrow R\cdot \qquad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (2)$$

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot \qquad (3)$$

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot \qquad (4)$$

In this way a chain [equations (2) and (3)] is broken and the oxidation retarded. One other possible approach to the problem of inhibiting hydrocarbon oxidations may lie in competitively diverting the alkyl radicals (R·) from reaction with oxygen. The advantages of this system include not only destruction of radical chains but also the reduced levels of peroxy-compounds should lead to a considerable reduction in initiation processes. It is with this concept in mind that we have devised a scheme to screen potential alkyl radical scavengers in a system that approximates to the initiation step of a hydrocarbon autoxidation.

The trapping of alkyl radicals has been known since the advent of free radical chemistry. Gomberg[1] in his studies of the triphenylmethyl radical noted that it reacted rapidly with both oxygen and iodine. The addition of iodine to triarylmethyl radicals was found to be reversible and the degree of association varying with individual triarylmethyl, with in general 20—40% of the iodine being free.[2]

$$2Ar_3C\cdot + I_2 \rightleftharpoons 2Ar_3CI \qquad (5)$$

More recently Brown[3] has found that iodine acts as a powerful inhibitor in the autoxidation of organoboranes. It was proposed that oxygen reacts with the organoborane producing alkyl radicals [equation (6)]; these in turn combine with oxygen giving the corresponding alkylperoxyl radical [equation (7)] which displaces an alkyl radical from the organoborane so completing the chain [equation (8)]. However iodine traps the alkyl radicals [equation (9)] producing an alkyl iodide and iodine atoms which are incapable of propagating the chain.

$$R_3B + O_2 \longrightarrow R\cdot \qquad (6)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (7)$$

$$RO_2\cdot + R_3B \longrightarrow RO_2BR_2 + R\cdot \qquad (8)$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot \text{ no chain} \qquad (9)$$

These results indicate that at certain concentrations iodine is able to compete effectively with oxygen for alkyl radicals.

In addition to iodine, *p*-benzoquinones,[4,5] nitrobenzenes,[6] and many stable free-radicals[7] for example diphenylpicrylhydrazyl,[7a] galvinoxyl,[8] and cyclic di-t-alkylnitroxides[7b,9] have been used as effective alkyl radical trapping agents. More recently e.s.r. spectroscopy has shown that 'spin traps'[10] can be usefully employed in capturing short lived radical intermediates and it has been reported[11] that 2-methyl-2-nitrosopropane traps alkyl and aryl radicals in the presence of oxygen.

In order to investigate the trapping of carbon radicals in the presence of oxygen we have studied the capture of a tertiary alkyl radical in an environment approximating to that found in the initial stage of a hydrocarbon autoxidation.

The method involves the production of alkyl radicals without the evolution of gaseous side-products such as nitrogen from azoalkanes or carbon dioxide from peroxyoxalates. The radical precursor selected was 2,2,3,3-tetraphenylbutane which undergoes homolysis of the central carbon–carbon bond at a convenient rate

---

[1] M. Gomberg, *Ber.*, 1900, **33**, 3150; *J. Amer. Chem. Soc.*, 1900, **22**, 757.

[2] M. Gomberg, *Chem. Rev.*, 1925, **1**, 91.

[3] M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 1506; H. C. Brown and M. M. Midland, *Chem. Comm.*, 1971, 699.

[4] L. F. Fieser and A. E. Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2060; A. E. Oxford, *J. Chem. Soc.*, 1942, 577.

[5] A. F. Bickel and W. A. Waters, *J. Chem. Soc.*, 1950, 1764; G. S. Hammond and G. B. Lucas, *J. Amer. Chem. Soc.*, 1955, **77**, 3249.

[6] R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 1960, 1653.

[7] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, New York, 1968 (*a*) ch. 4, p. 154; (*b*) ch. 5, p. 224 and references therein.

[8] P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, 1962, **84**, 2596.

[9] I. T. Brownlie and K. U. Ingold, *Canad. J. Chem.*, 1967, **45**, 2427; E. G. Rozantzev and M. B. Neiman, *Tetrahedron*, 1964, **20**, 131.

[10] (*a*) M. J. Perkins, 'Essays in Free-radical Chemistry,' Chem. Soc. Special Publication No. 24, ch. 5, 1970; (*b*) E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; (*c*) C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

[11] T. W. Bentley, J. A. John, R. A. W. Johnstone, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1973, 1039.

at 60°[12,13] [equation (10)]. The 1,1-diphenylethyl

$$Ph_2CMe{-}CMePh_2 \longrightarrow 2Ph_2\dot{C}Me \qquad (10)$$

radical (I) then reacts with oxygen to give the corresponding peroxyl radical [equation (11)], and in the

$$(I) + O_2 \xrightarrow{\text{fast}} Ph_2C(Me)O_2\cdot \qquad (11)$$

presence of a plentiful supply of a hydrogen donor (AH) the peroxyl radical is converted quantitatively to the hydroperoxide [equation (12)].

$$PhC(Me)O_2\cdot + AH \xrightarrow{\text{fast}} Ph_2C(Me)O_2H + A\cdot \qquad (12)$$

Mahoney,[13] using the above stoicheiometric uptake of oxygen, has studied the rate of dissociation of the butane in chlorobenzene (AH = 2,6-di-t-butyl-*p*-cresol) and found it to be independent of oxygen pressure. The rate is first order in the butane and independent of the concentration of AH, hence induced decomposition is negligible. In our study, using the same hydrogen donor in a 20-fold excess over the butane, a first-order rate constant of $2{\cdot}15 \times 10^{-4}\ s^{-1}$ at 60° in chlorobenzene was obtained; this is in good agreement with the value of $2 \times 10^{-4}\ s^{-1}$ found by Mahoney.[13] An average value of 100·3% (Figure 1) for oxygen uptake, based on conversion to the hydroperoxide [equation (13a)] was obtained over a number of experiments; the results varied by ±2·5% due to the incremental step requirements dictated by the automatic oxygen absorption apparatus[14] used.

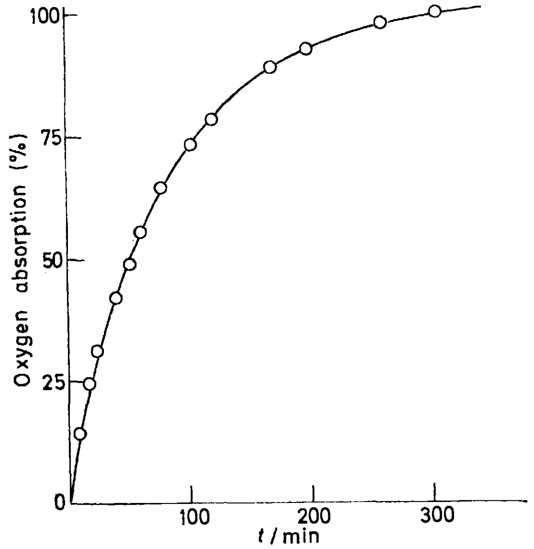
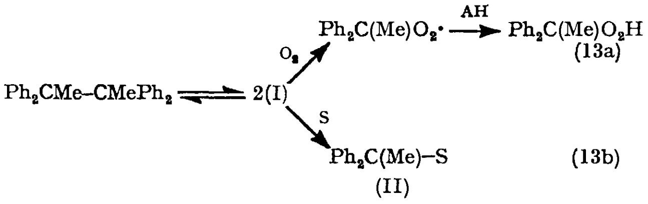


FIGURE 1 The absorption of oxygen by 2,2,3,3-tetraphenylbutane (2×10^{-3}M) in chlorobenzene containing 2,6-di-t-butyl-*p*-cresol (4×10^{-2}M) at 60°

The effect of adding a potential radical trap is to set up a competition between oxygen and the radical trap (S) for the 1,1-diphenylethyl radical (Scheme 1). If species (II) cannot participate further in an oxidation system then the extent of radical capture will be reflected by a reduction in the ratio moles of oxygen absorbed/moles of butane decomposed.



SCHEME 1

Removal of the 1,1-diphenylethylperoxyl radical by the species S will not be reflected in the oxidation stoicheiometry but may well be a possible route by which the radical trap is consumed.

The results obtained for a range of potential radical traps are shown in Table 1. Oxidations were performed using both air and oxygen, the concentration of the radical trap being fixed at twice the concentration of 2,2,3,3-tetraphenylbutane, thus providing one mole of S per mole of 1,1-diphenylethyl radicals. All oxidation reactions were run for six hours to ensure complete decomposition of the butane.

TABLE 1

The extent of oxidation of 2,2,3,3-tetraphenylbutane (TPB) (2×10^{-3}M) in chlorobenzene, in the presence of 200 mole % radical trap and 2,6-di-t-butyl-*p*-cresol (4×10^{-2}M) (60°; atmospheric pressure)

Radical trap	Oxidant	Oxidation extent (%)
	O_2–Air	100
Iodine	O_2	92
	Air	80
p-Benzoquinone	O_2	100
	Air	97
Chloranil	O_2	97·5
	Air	95·5
m-Dinitrobenzene	O_2	100
	Air	100
Galvinoxyl	O_2	*
	Air	*
2,2,6,6-Tetramethyl-4-oxopiperidine	O_2	98
1-oxyl	Air	97
α-Phenyl-*N*-methylnitrone	O_2	97
	Air	95
2-Methyl-2-nitrosopropane	O_2	†
	Air	†

* Galvinoxyl rapidly consumed by 2,6-di-t-butyl-*p*-cresol.
† All oxidation runs gave values well in excess of 100% reflecting new oxygen-consuming species being formed.

The concentration of the potential alkyl radical scavengers was then increased ten-fold in all cases, and 50-fold for the nitrone, nitroxide, and iodine. No significant changes were found except with iodine. The extent of oxidation of 2,2,3,3-tetraphenylbutane in the presence of increasing amounts of iodine is shown in Table 2.

Analysis of the products of the oxidation of tetraphenylbutane–iodine shows the presence of 1,1-diphenylethylene and almost total absence of 1,1-diphenylethane. The yields of the ethylene and the ethane and the extent

---

[12] K. Ziegler, *Annalen*, 1942, **551**, 150.
[13] L. R. Mahoney, *J. Amer. Chem. Soc.*, 1966, **88**, 3035.
[14] M. E. Cain and G. T. Knight, *Chem. and Ind.*, 1971, 1125.

of oxidation, for a wide range of tetraphenylbutane : iodine ratios, are shown in Table **3** and Figure **2**.

TABLE 2

The extent of oxidation by air of 2,2,3,3-tetraphenylbutane (TPB) (2×10^{-3}M) in the presence of iodine and 2,6-di t-butyl-*p*-cresol (4×10^{-2}M) (60°; solvent, chlorobenzene)

Molar ratio I_2 : TPB	Extent of oxidation (%)
0	100
2	80
10	56
15	42
20	33·4
25	28
40	20
100	20

The formation of hydrogen iodide, and the presence of iodine, made hydroperoxide determinations impractical.

TABLE 3

The products of reactions of 2,2,3,3-tetraphenylbutane (TPB) with oxygen and iodine (solvent, chlorobenzene, 60°)

10^5 TPB (mol)	10^4 I_2 (mol)	10^4 2,6-TBPC (mol)	Chlorobenzene (cm³)	10^5 1,1-Diphenylethane (mol) [%]	10^5 1,1-Diphenylethylene (mol) [%]	Oxidation (%)
6·475		12·95	32·5	*	*	100
5·52 †			2	4·06 ‡ [36·8]	4·72 [42·8]	
6·475	1·295	12·95	32·5	0·16 [1·24]	1·77 [13·6]	80
6·475	6·475	12·95	32·5	0·55 [4·24]	6·31 [43·6]	56
6·475	12·95	12·95	32·5	*	10·10 [77·8]	33·4
6·475	25·90	12·95	32·5	*	11·99 [92·5]	20

TBPC = 2,6-Di-t-butyl-*p*-cresol.

* Trace quantities; no qualitative estimation possible. † Injected directly onto g.l.c. column at 150° ‡ Ethane : ethylene ratio 1 : 1·16.

No reaction between iodine and 2,6-t-butyl-*p*-cresol was observed over the range of iodine concentrations studied.

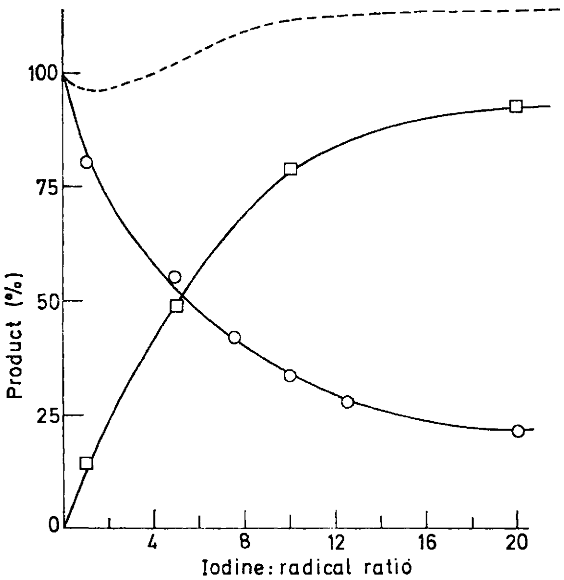


FIGURE 2 The variation of product concentrations with an increase in the initial concentration of iodine for the oxidation of 2,2,3,3-tetraphenylbutane (2×10^{-3}M) in chlorobenzene: temperature 60°; □ 1,1-diphenylethylene; ○ percentage oxidation of 2,2,3,3-tetraphenylbutane; □ + ○ = - - - -

DISCUSSION

It is apparent (Table 2) that of the compounds investigated only iodine is able to compete effectively with oxygen for the 1,1-diphenylethyl radical. In general the experimental system proved satisfactory for screening alkyl radical traps but in two cases, that of 2-methyl-2-nitrosopropane and galvinoxyl, interference by side reactions led to results that could not be satisfactorily interpreted.

The thermal and photolytic instability of the nitrosobutane has been noted previously [10a] and the increased extent of oxidation above 100% in the presence of 2-methyl-2-nitrosopropane can be ascribed to its thermal dissociation [equation (14)]. The t-butyl radical so

$$\mathrm{Bu^tNO} \longrightarrow \mathrm{Bu^t\cdot} + \mathrm{NO\cdot} \qquad (14)$$

formed reacts rapidly with oxygen [equation (15)] and in the presence of 2,6-di-t-butyl-*p*-cresol gives the hydroperoxide. When this side-reaction is added to the oxidation of the 1,1-diphenylethyl radicals the overall

$$\mathrm{Bu^t\cdot} + \mathrm{O_2} \longrightarrow \mathrm{Bu^tO_2\cdot} \xrightarrow{\mathrm{AH}} \mathrm{Bu^tOOH} \qquad (15)$$

extent of oxidation is increased to well in excess of the value for **2**,**2**,**3**,**3**-tetraphenylbutane alone.

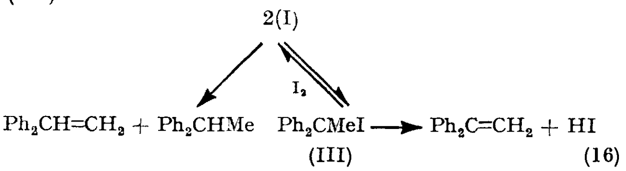
Galvinoxyl was rapidly consumed on addition to a solution of 2,6-di-t-butyl-*p*-cresol in chlorobenzene giving hydrogalvinoxyl and as such could not be investigated as a radical scavenger in this system.

It is most unfortunate that this method is unable to answer the two questions, *viz.*, does 2-methyl-2-nitrosopropane compete effectively with oxygen for alkyl radicals, and is galvinoxyl a more efficient scavenger of alkyl radicals than iodine?

The main conclusion that can be drawn from the results obtained with *m*-dinitrobenzene, the quinones, the cyclic nitroxide, and α-phenyl-*N*-methylnitrone is that even when the concentration of radical trap exceeds that of oxygen (the concentration of oxygen in chlorobenzene at 60° was calculated to be 4×10^{-3}M) by fifty times, the reaction of the 1,1-diphenylethyl radical with oxygen is many times faster than the trapping reactions of any of these compounds.

The capture of the 1,1-diphenylethyl radical by iodine

(Scheme 2) leads to the formation of the tertiary iodide (III).



SCHEME 2

The instability of tertiary alkyl iodides has been well known for at least 70 years.[1,2] Gomberg observed that triphenylmethyl iodide was in equilibrium with the triphenylmethyl radical and iodine. Subsequent workers [15-17] have confirmed the ease of dissociation of triphenylmethyl iodide and have noted its considerable readiness to liberate iodine on exposure to light in a variety of media. There appears to be no evidence for the existence of 1,1-diphenyl-1-iodoethane (III) although both the corresponding chloride [18] and bromide [19] have been prepared. The chloride is reported [18] to lose hydrogen chloride very rapidly. Therefore it appears likely that the transient 1,1-diphenyl-1-iodoethane can undergo decomposition by two routes [equations (17) and (18)].

$$\text{(III)} \overset{K_{17}}{\rightleftharpoons} \text{(I)} + \text{I}\cdot \qquad (17)$$

$$\text{(III)} \longrightarrow \text{HI} + Ph_2C{=}CH_2 \qquad (18)$$

If the iodide decomposes exclusively by route (17) then ultimately all the 1,1-diphenylethyl radicals can react with oxygen and be removed in the upper branch of Scheme 1 [equation (13a)]. The overall effect would be to cause the oxidation of 2,2,3,3-tetraphenylbutane and iodine to proceed to completion (100%) at a reduced rate dependent on the equilibrium constant K_{17}. However, if the iodide decomposes by loss of HI [equation (18)] this will be reflected in the total oxygen absorption figure and in corresponding formation of 1,1-diphenylethylene.

It is also possible that the ethylene could arise by disproportionation of the 1,1-diphenylethyl radicals. It was found that when 2,2,3,3-tetraphenylbutane was injected directly onto a g.l.c. column at 150° that 1,1-diphenylethane and 1,1-diphenylethylene were formed in the ratio 1 : 1·16 (Table 3). This value is consistent with the disproportionation of these radicals and compares well with the value of 1·01 for the cumene : α-methylstyrene ratio obtained for cumyl radicals derived from azocumene by injection into a g.l.c. port at 170°.[20] However the oxidation of 2,2,3,3-tetraphenylbutane alone yielded only trace quantities of ethane and ethylene and with the addition of iodine although some ethane could be detected the yields are sufficiently low (Table 3) for us to conclude that the disproportionation of 1,1-diphenylethyl radicals is unimportant in these oxidations. Therefore we submit that the 1,1-diphenylethylene is derived exclusively from 1,1-diphenyl-1-iodoethane by loss of HI. For a balance of the competing reactions (13a) and (16), a combination of the yield of 1,1-diphenylethylene and the extent of oxidation should equal 100%. However, the overall yield increases with an increase in the concentration of iodine (Figure 2 and Table 3) and for the most part exceeds 100%. The possible explanation for this high value may be the well known reaction of HI with oxygen yielding iodine and water, thus giving a higher oxidation value. This reaction cannot be taking place quantitatively in these oxidations for this would lead to a considerably higher overall yield value. It is therefore likely that the major portion of the HI is removed by other routes including its reaction with the hydroperoxide.

The results are consistent with capture of the 1,1-diphenylethyl radical by iodine in the presence of oxygen. The efficiency of the trapping process cannot be readily quantified in this instance as the oxidation figure is composed of more than one reaction; however using data from Table 3 for I_2 : TPB ratios from 2 to 10, an approximate value of $k(O_2)/k(I_2) = 6$ has been obtained. This figure assumes simple competition between oxygen and iodine for the 1,1-diphenylethyl radical and does not take into account any complicating side reactions. The exact extent of decomposition of the iodide by the two possible routes is also in some doubt but it appears to proceed largely by loss of HI.

This work has shown that iodine can compete effectively with oxygen for alkyl radicals and it is therefore not impossible that other substances might be found which are capable of competitively removing similar radicals in hydrocarbon autoxidation thus providing a new approach to the inhibition of such processes.

EXPERIMENTAL

Materials.—*m*-Dinitrobenzene, chloranil, *p*-benzoquinone, and iodine were commercial samples used without additional purification. Galvinoxyl was prepared by the method of Bartlett and Funahashi.[8] α-Phenyl-*N*-methylnitrone was prepared from *anti*-benzaldoxime by the method of Buehler.[21]

2,2,6,6-*Tetramethyl*-4-*oxopiperidine* 1-*oxyl*.[22] Phorone (50 g) was dissolved in aqueous ammonia (*d* 0·88; 180 cm^3) and stirred for 12 days. The excess of ammonia was gently evaporated and the solution acidified with hydrochloric acid. Unchanged phorone was extracted into ether (3 × 50 cm^3) and the aqueous phase made alkaline. 2,2,6,6-Tetramethyl-4-piperidone was extracted into ether, dried, and the ether removed (29·7 g, 34·6%), m.p. 36°. The piperidone was oxidised to the nitroxide by the method of Allies.[23] 2,2,6,6-Tetramethyl-4-piperidone (15 g) was dis-

---

[15] H. G. Lewis and E. G. Owen, *J. Chem. Soc.* (*B*), 1967, 422; *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 277 (*Chem. Abs.*, 1968, **69**, 26,529d).

[16] M. A. Pak, D. N. Shigorin, and G. A. Ozerova, *Izvest. Akad. Nauk S.S.S.R. Ser. Fiz.*, 1968, **32**, 1442 (*Chem. Abs.*, 1968, **69**, 101,7432).

[17] K. M. Harmon and F. E. Cummings, *J. Amer. Chem. Soc.*, 1965, **87**, 539.

[18] H. C. Brown and M. H. Rei, *J. Org. Chem.*, 1966, **31**, 1090.

[19] N. P. Bogonostseva, *Uchenye Zapiski, Kazan Gosudarst Univ., im V.I. Ul'yanova Lenina*, 1956, 116, No. 2, 71 (*Chem. Abs.*, 1957, **51**, 6581g).

[20] S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1966, **88**, 137.

[21] E. Buehler, *J. Org. Chem.*, 1967, **32**, 261.

[22] J. Guareschi, *Ber.*, 1895, **28**, 160.

[23] P. G. Allies, Ph.D. Thesis, London, 1968.

solved in water (80 cm^3) and dodecatungstophosphoric acid (40 mg) and hydrogen peroxide (100 vol; 30 cm^3) were added. The solution was set aside for 7 days, saturated with sodium chloride, and extracted with ether (2 × 30 cm^3). The ether extract was washed with N-sulphuric acid (2 × 30 cm^3) and saturated sodium chloride solution, dried, and the ether distilled off. The crude 1-oxyl was recrystallised from light petroleum (7·21 g, 50%), m.p. 36° (lit.,[23] 36°) (Found: C, 63·7; H, 9·55; N, 8·35. Calc. for $C_9H_{16}N_2O$: C, 63·5; H, 9·5; N, 8·2%).

2-*Methyl*-2-*nitrosopropane*. Oxidation [24] of t-butylamine gave 2-methyl-2-nitropropane (64%) which was reduced [25] to *N*-t-butylhydroxylamine (52·5%). Oxidation [26] of the latter gave dimeric 2-methyl-2-nitrosopropane (69%), m.p. 83° (lit.,[26] 83—84°).

2,2,3,3-*Tetraphenylbutane*. 1,1-Diphenylethyl chloride was prepared by the method of Schoepfe and Ryan [27] (65%). Freshly prepared lithium shot (1·12 g, 0·16 mol) was suspended in redistilled tetrahydrofuran (80 cm^3), 1,1-diphenylethyl chloride (35 g, 0·16 mol) in tetrahydrofuran (40 cm^3) was added, and the reaction stirred for 18 h at room temperature. The crude product was obtained after removal of the excess of lithium and solvent and was recrystallized from benzene–methanol to yield pure 2,2,3,3-tetraphenylbutane (5·9 g, 20·2%), m.p. 122—123° (lit.,[28] 122—123°) (Found: C, 93·1; H, 7·3. Calc. for $C_{28}H_{20}$: C, 92·8; H, 7·2%), τ 7·98 (6H, 2 × CH_3) and 2·65—3·18 (20H, 4 × Ph).

1,1-*Diphenylethylene*. A commercial sample was redistilled under reduced pressure, b.p. 104° at 1·5 mmHg.

1,1-*Diphenylethane*. The condensation [29] of styrene and benzene in the presence of concentrated sulphuric acid gave 1,1-diphenylethane (34%), b.p. 68—69° at 0·005 mmHg (lit.,[30] 82° at 0·01 mmHg).

Chlorobenzene. G.P.R. Grade was redistilled under nitrogen before use and stored under nitrogen over magnesium sulphate.

Oxidation Procedure.—Oxidations under both air and oxygen were performed using a chlorobenzene solution of 2,2,3,3-tetraphenylbutane (2 × 10^{-3}M) containing 2,6-di-t-butyl-*p*-cresol (4 × 10^{-3}M). Potential radical traps were included, concentrations varying from 4 × 10^{-3} to 2 × 10^{-2}M. Oxidations using 2-methyl-2-nitrosopropane were conducted in the dark. All oxidations were performed using the automatic oxidation apparatus described by Cain and Knight.[14]

G.l.c. Analysis.—Analysis of oxidation products was carried out on a Philips PV4000 series chromatograph using a 6 ft × 4 mm column of 3% DEGS on 80—100 mesh Chromosorb G (ammonia washed) at 148°.

[4/1725 *Received*, 16*th August*, 1974]

---

[24] N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Amer. Chem. Soc.*, 1965, **78**, 4003.

[25] P. A. S. Smith, H. R. Ahil, and R. L. Baumgarten, *J. Amer. Chem. Soc.*, 1964, **86**, 1139.

[26] W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 6522.

[27] C. S. Schoepfe and J. D. Ryan, *J. Amer. Chem. Soc.*, 1932, **54**, 3687.

[28] E. Muller and G. Roscheisen, *Chem. Ber.*, 1957, **90**, 543.

[29] T. I. Yurzhenko and V. A. Puchin, *Nauch. Zapiski L'vov. Politekh. Inst.*, 1957, **62**, 333; E. M. Terent'eva, P. I. Sanin, T. G. Stepantseva, M. M. Kusakov, N. A. Shimanko, and V. I. Sidorenko, *Neftekhimiya*, 1961, **1**, 141.

[30] T. Garofano, A. Arcoleo, and M. C. Natoli, *Atti. Accad. Sci., Lettre Arti Palermo*, 1965, **24**, 235 (*Chem. Abs.*, 1966, **64**, 1257f).