Autoxidation of Polysubstituted Isoindoles

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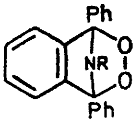
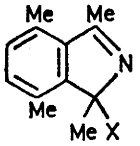
Autoxidation of *N*-substituted 1,3,4,7-tetramethylisoindoles to the corresponding phthalimides is described. A mechanism proposed to account for the loss of methyl groups from the 1- and 3-positions is supported by studies of the thermal decomposition of some anthracene 9,10-peroxides.

ISOINDOLES are known to be air-sensitive,[1] and autoxidation products of various types have been described. 1,2,3-Triphenylisoindole reacts photochemically with oxygen forming a cyclic peroxide adduct (1a);[2] a similar peroxide (1b) has been suggested as an intermediate in the oxidation in air of 2-methyl-1,3-diphenylisoindole to *o*-dibenzoylbenzene.[3] Air oxidation products from 2-methylisoindole have not been characterised,[4] but 2-n-butylisoindole is autoxidised to the corresponding *N*-substituted phthalimide, phthalimidine, and 3-hydroxyphthalimidine.[5] Isoindoles without an *N*-substituent show two further types of behaviour, exemplified by the formation of an oxidative coupling product [6] from 1-phenylisoindole in air, and that of the tertiary 1*H*-isoindolyl alcohol (2a) and hydroperoxide (2b) from 1,3,4,7-tetramethylisoindole (3e) and air or oxygen, respectively.[7]

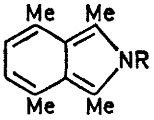


(1) a; R = Ph
b; R = Me

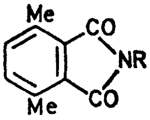


(2) a; X = OH
b; X = O·OH

We report that the action of air or oxygen converts the isoindoles (3a—d) into the corresponding phthalimides (4a—d), the reaction involving loss of methyl groups from the 1- and 3-positions. We first obtained *N*-phenyl-3,6-dimethylphthalimide (4d) from an unsuccessful attempt to add benzyne to the isoindole (3d). It appeared likely that the imide arose from autoxidation during work-up of unchanged isoindole (3d), an explanation that was readily confirmed by aerating solutions of



(3) a; R = Me
b; R = Et
c; R = $PhCH_2$
d; R = Ph
e; R = H



(4) a; R = Me
b; R = Et
c; R = $PhCH_2$
d; R = Ph

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[1] J. D. White and M. E. Mann, *Adv. Heterocyclic Chem.*, 1969, **10**, 113.

[2] W. Theilacker and W. Schmidt, *Annalen*, 1957, **605**, 43.

[3] W. Theilacker and W. Schmidt, *Annalen*, 1955, **597**, 95.

[4] G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Annalen*, 1951, **572**, 1.

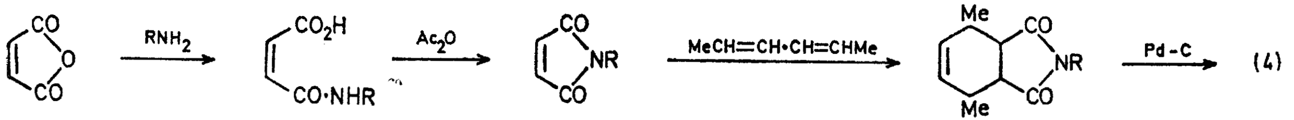
[5] J. K. Kochi and E. A. Singleton, *Tetrahedron*, 1968, **24**, 4649.

[6] R. I. Fryer, B. Brust, J. V. Earley, and L. H. Sternbach, *J. Chem. Soc.* (*C*), 1967, 366.

[7] C. O. Bender and R. Bonnett, *Chem. Comm.*, 1966, 198; C. O. Bender, R. Bonnett, and R. G. Smith, *J. Chem. Soc.* (*C*), 1970, 1251.

the latter and observing the formation of the imide (4d) by g.l.c.

N,3,6-Trimethylphthalimide (4a) was isolated in 18% yield by evaporation and column chromatography after passage of oxygen through a solution of 1,2,3,4,7-pentamethylisoindole (3a) in refluxing tetrahydrofuran; the phthalimides (4b and c) were similarly obtained from the isoindoles (3b and c). In each case the oxygenated solution before work-up showed i.r. absorption characteristic of a hydroxy-group, although no hydroxy-compound could be isolated; tests with acidified potassium iodide proved the absence of hydroperoxides analogous to (2b). Superficial formation of the corresponding phthalimides could be shown after exposure of crystals of the isoindoles (3a—d) to air. Autoxidation in solution is accompanied by the instantaneous development of intense red or violet colours, which later become dark blue. Incompletely oxidised samples of the isoindoles (3a and c) in methanol examined in an e.s.r. spectrometer showed no absorption indicative of free radicals. The autoxidation (3c) ⟶ (4c) in refluxing tetrahydrofuran was shown to occur in the dark, although conversion was faster in diffused daylight.

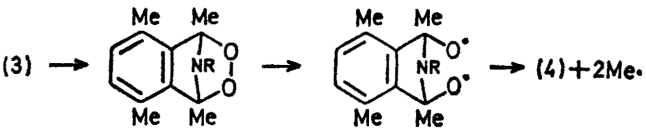


SCHEME 1

The assignment of structures (4a—d) to the autoxidation products is supported by elemental analysis and spectroscopic evidence. All four phthalimides show two carbonyl group absorptions (1700—1750 cm^{-1}) and an absorption for aromatic carbon–hydrogen bonds in *ortho*-positions (*ca.* 830 cm^{-1}): the latter is a feature of the i.r. spectra of the isoindoles (3a, c, and d).[8] The mass spectra of the phthalimides (4a and d) show many similarities to the spectra recorded for *N*-methyl- and *N*-phenyl-phthalimide, respectively, including the loss of CO$_2$ from the molecular ion;[9] unlike the other compounds, but like *N*-ethylphthalimide,[9] compound (4b) easily loses a methyl group to give the base peak, *m/e* 188. Another fragmentation pattern common to compounds (4a, c, and d) is loss of CO; also stepwise or concerted loss of NR and CO is observed in the mass spectra of compounds (4a—d) to give an ion, *m/e* 132, which breaks down further to *m/e* 104 by loss of CO (appropriate metastable peaks observed). There is also a significant M — OH peak in the mass spectra of compounds (4c and d); the same feature has been noted in the spectra of *N*-biphenyl-2-yl- and *N*-(2,6-dimethylphenyl)-phthalimide, but not in that of *N*-phenylphthalimide,[9] and its occurrence with compounds (4c and d) is attributable to abstraction of hydrogen atoms from the 3- and 6-methyl groups.

Further proof of structure was obtained by comparison with authentic samples of the phthalimides (4b—d) synthesised independently *via* the route shown (Scheme 1). The Diels–Alder adducts of hexa-2,4-diene and *N*-substituted maleimides were mixtures of stereoisomers which were not characterised, but were aromatised directly to the desired products. The identity of synthetic materials with autoxidation products confirmed the unexpected loss of the 1- and 3-methyl groups from the isoindoles (3a—d). The only previous reports of phthalimide formation concern those from *N*-n-butylisoindole[5] (with oxygen) and from *N*-methylisoindole[4] (with potassium permanganate), for which no carbon–carbon bond breakage is necessary.

A mechanism (Scheme 2) which accounts for the conversion of isoindoles (3) into phthalimides (4) involves the initial formation of cyclic peroxides analogous to those (1a and b) already referred to.[2,3] We repeated the autoxidation of compound (3c) in aqueous butanol containing a trace of hydrochloric acid, expecting to identify 2,3-diacetyl-1,4-dimethylbenzene, benzylamine, and hydrogen peroxide arising by hydrolysis of the peroxide (*cf.* ref. 3), but only the phthalimide (4c) was obtained, unaccompanied by any new products. On the other hand, after u.v. irradiation of 1,2,3,4,7-pentamethylisoindole (3a) in carbon disulphide during passage of oxygen, neither the expected peroxide (*cf.* ref. 2) nor *N*,3,6-trimethylphthalimide (4a) was obtained, but only a small quantity of an indigo-coloured material, as yet unidentified.



SCHEME 2

We envisage that decomposition of the intermediate peroxide takes place *via* alkoxyl radicals, from which methyl radicals are eliminated from the 1- and 3-positions (Scheme 2). The analogous disproportionation of tertiary alkoxyl radicals is a well known reaction,[10] giving rise to ketonic products, and methyl radicals attributable to the step Bu^{t}O• ⟶ Me• + Me$_2$CO have been detected[11] in the reduction of t-butyl hydroperoxide by titanium(III) ions. The mechanism proposed for the formation of decane-1,10-dicarboximide on

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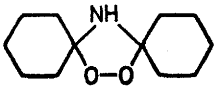
[8] C. O. Bender and R. Bonnett, *J. Chem. Soc.* (*C*), 1968, 3036.

[9] R. A. W. Johnstone, B. J. Millard, and D. S. Millington, *Chem. Comm.*, 1966, 600; J. L. Cotter and R. A. Dine-Hart, *ibid.*, p. 809; T. W. Bentley and R. A. W. Johnstone, *J. Chem. Soc.* (*C*), 1968, 2354.

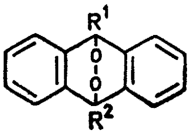
[10] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239; P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. Reaction Kinetics*, 1967, **4**, 63; C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, pp. 388, 443.

[11] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119; M. F. R. Mulcahy, J. R. Steven, and J. C. Ward, *Austral. J. Chem.*, 1965, **18**, 1177.

pyrolysis of 1,1′-peroxydicyclohexylamine (5) [12] and the reported formation of anthraquinone on pyrolysis of the transannular anthranol peroxides (6a—c) [13] provide further precedents for our suggested reaction path. The



(5)



(6) a; $R^1 = Me, R^2 = OH$
b; $R^1 = Ph, R^2 = OH$
d; $R^1 = PhCH_2, R^2 = OH$
d; $R^1 = Me, R^2 = H$
e; $R^1 = R^2 = Et$

peroxides (6d and e) prepared photochemically from 9-methyl- and 9,10-diethyl-anthracene also gave anthraquinone on heating, in agreement with our expectations. On the other hand, 9,10-diarylanthracene 9,10-peroxides decompose thermally by elimination of oxygen, often accompanied by luminescence.[14] 1,3-Diarylisoindoles, which apparently are not autoxidised to the corresponding phthalimides, are now being studied.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls and calibrated with polystyrene. ^1H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were recorded with an A.E.I. MS12 low-resolution spectrometer operating at 70 eV, with a direct insertion probe. G.l.c. analyses were performed on a column (1·6 m) containing silicone gum rubber SE 30 as stationary phase at 220°. Alumina for chromatography was Laporte type H.

Hexa-2,4-diene was a mixture of *trans,trans-* and *cis,trans-*isomers (Emmanuel). *N*-Phenylmaleamic acid, m.p. 198—200° (lit.,[15] 201—202°), and *N*-phenylmaleimide, m.p. 86—87° (lit.,[15] 88—89°), were obtained as reported.[15] The same procedure with benzylamine and maleic anhydride gave *N*-benzylmaleamic acid, m.p. 130—134° (lit.,[16] 138°), and *N*-benzylmaleimide, m.p. 68—69° (lit.,[17] 68—69°).

N-*Ethyl*-3,6-*dimethylphthalimide* (4b).—Hexa-2,4-diene (3·0 g) and *N*-ethylmaleimide (B.D.H.) (4·5 g) in a sealed tube were heated at 130—140° for 20 h. The tube was cooled and opened, and the glassy contents were then reheated at 280° for 3 h with palladium–charcoal (10%; 5·0 g). G.l.c. analysis then indicated *ca.* 75% dehydrogenation of the intermediate tetrahydrophthalimide. The mixture was extracted with chloroform, the extract was filtered, and the filtrate was chromatographed on a column of alumina (100 g) prepared in light petroleum (b.p. 60—80°). Elution with light petroleum–benzene (1 : 1 v/v) afforded the *phthalimide* (4b) (2·25 g, 55%) as needles, m.p. 102—103° [from light petroleum–benzene (1 : 4 v/v)] (Found: C, 71·1; H, 6·5; N, 7·0. $C_{12}H_{13}NO_2$ requires C, 70·9; H, 6·5; N, 6·9%), $\nu_{max.}$ 1750 and 1700br (C=O), 1400, 1355, 1200, 1035, 900, 835, and 760 cm^{-1}, τ 2·72 (2H, s, ArH), 6·32 (2H, q, $N{\cdot}CH_2$), 7·37 (6H, s, $ArCH_3$), and 8·77 (3H, t, $CH_3{\cdot}CH_2$), *m/e* 203 (M^+, 50%), 204 (6), 189 (12), 188 (100, *M* – Me), 132 (7), 104 (7), 103 (9), and 77 (10), *m** 174 ($203 \longrightarrow 188$) and 82 ($132 \longrightarrow 104$).

N-*Benzyl*-3,6-*dimethylphthalimide* (4c).—The intermediate tetrahydrophthalimide was prepared similarly from hexa-2,4-diene (1·25 g) and *N*-benzylmaleimide (2·8 g) and then dehydrogenated (*ca.* 60% by g.l.c. analysis) with palladium–charcoal (10%; 0·3 g) at 280° for 15 min. Chromatography of the crude product on alumina (150 g) gave the *phthalimide* (4c) (0·2 g, 5%) as needles, m.p. 125—126° [from light petroleum (b.p. 40—60°)–benzene (1 : 3 v/v)] (Found: C, 76·8; H, 5·7; N, 5·2. $C_{17}H_{15}NO_2$ requires C, 77·0; H, 5·7; N, 5·3%), $\nu_{max.}$ 1745 and 1700 (C=O), 1435, 1345, 1070, 950, 830, 770, 760, and 710 cm^{-1}, τ 2·5—2·9 (7H, m, ArH), 5·24 (2H, s, CH_2), and 7·40 (6H, s, $2 \times CH_3$), *m/e* 265 (M^+, 100%), 266 (19), 264 (10), 248 (4, *M* – OH), 247 (7), 237 (4, *M* – CO), 222 (6), 188 (7, *M* – Ph), 187 (26), 160 (4, *M* – NCH_2Ph), 159 (19), 133 (7), 132 (7), 105 (9), 104 (16), 103 (13), 91 (55, $PhCH_2^+$), 78 (8), and 77 (16), *m** 232 ($265 \longrightarrow 248$), 212 ($265 \longrightarrow 237$), 135 ($187 \longrightarrow 159$), 132 ($265 \longrightarrow 187$), and 82 ($132 \longrightarrow 104$).

3,6-*Dimethyl*-N-*phenylphthalimide* (4d).—The intermediate tetrahydrophthalimide was prepared from hexa-2,4-diene (1·25 g) and *N*-phenylmaleimide (2·6 g) and then dehydrogenated (*ca.* 90% by g.l.c. analysis) with palladium–charcoal at 280° for 30 min. Chromatography of the crude product on alumina afforded the *phthalimide* (4d) (0·3 g, 8%), as needles, m.p. 133—134° [from light petroleum (b.p. 40—60°)–benzene] (Found: C, 76·5; H, 5·3; N, 5·3. $C_{16}H_{13}NO_2$ requires C, 76·5; H, 5·2; N, 5·6%), $\nu_{max.}$ 1755 and 1715br (C=O), 1595, 1510, 1230, 1115, 920, 905, 830, 765, and 700 cm^{-1}, τ 2·4—2·8 (7H, m, ArH) and 7·32 (6H, s, $2 \times CH_3$), *m/e* 251 (M^+, 100%), 252 (15), 250 (10), 234 (8, *M* – OH), 223 (44, *M* – CO), 222 (10), 208 (10), 207 (18, *M* – CO_2), 206 (9), 194 (6), 180 (8), 132 (5), 130 (7), 118 (5), 104 (21), 103 (26), 91 (10), 78 (15), and 77 (36), *m** 218 ($251 \longrightarrow 234$), 198 ($251 \longrightarrow 223$), 171 ($251 \longrightarrow 207$), and 82 ($132 \longrightarrow 104$).

Preparation of Isoindoles.—1,2,3,4,7-Pentamethylisoindole (3a) resulted from the condensation of hexane-2,5-dione with methylamine as described by Bender and Bonnett;[8] isoindoles (3c and d) were prepared by condensations between hexane-2,5-dione and the appropriate 1,2,5-trisubstituted pyrroles.[8] The latter procedure with 1-ethyl-2,5-dimethylpyrrole [18] afforded 2-*ethyl*-1,3,4,7-*tetramethylisoindole* (3b) (95% crude yield), obtained as a pale yellow solid, m.p. 87—90° (sealed tube), by sublimation at 120° and 1 mmHg (Found: C, 83·5; H, 9·5; N, 6·9. $C_{14}H_{19}N$ requires C, 83·5; H, 9·5; N, 7·0%), $\nu_{max.}$ 1760w, 1610, 1400, 1350, 1180, 1120, and 810s cm^{-1}, τ 3·70 (2H, s, ArH), 5·97 (2H, q, $N{\cdot}CH_2$), 7·33 and 7·46 (12H, two s, $ArCH_3$), and 8·75 (3H, t, $CH_3{\cdot}CH_2$), *m/e* 201 (M^+, 100%), 202 (15), 200 (35), 199 (10), 186 (23), 173 (18), and 172 (*M* – Et, 35), *m** 147 ($201 \longrightarrow 172$). Samples of these isoindoles were freshly sublimed for the autoxidation studies.

Autoxidation of 1,2,3,4,7-*Pentamethylisoindole* (3a).—A solution of the isoindole (3a) (2·2 g) in dry tetrahydrofuran (50 ml) was heated under reflux during passage of oxygen for

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[12] E. G. E. Hawkins, *J. Chem. Soc.* (*C*), 1969, 2663.

[13] P. L. Julian and A. Magnani, *J. Amer. Chem. Soc.*, 1934, **56**, 2174; P. L. Julian, W. Cole, and G. Diemer, *ibid.*, 1945, **67**, 1721.

[14] K. Gollnick and G. O. Schenck in ' 1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, London, 1967, p. 255 and references cited therein.

[15] M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, *Org. Synth.*, 1961, **41**, 93.

[16] M. Frankel, Y. Liwschitz, and Y. Amiel, *J. Amer. Chem. Soc.*, 1953, **75**, 330.

[17] P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, and A. R. Williams, *J. Org. Chem.*, 1961, **26**, 15.

[18] K. J. Reed, U.S.P. 2,725,378 (*Chem. Abs.*, 1957, **51**, 910b).

7 days. A portion of the solution after being redried ($MgSO_4$) showed $\nu_{max.}$ 3500 cm^{-1} (O–H); a test for peroxide was negative. The solvent was evaporated and the brown oil remaining was dissolved in chloroform (5 ml) and chromatographed on alumina (200 g). Light petroleum (b.p. 60—80°)–benzene (7 : 3 v/v) eluted N,3,6-*trimethylphthalimide* (4a) (0·4 g, 18%), and recrystallisation of this from benzene gave needles which sublimed above 70°, m.p. 161—162° (sealed tube) (Found: C, 70·0; H, 6·0; N, 7·2. $C_{11}H_{11}NO_2$ requires C, 69·8; H, 5·9; N, 7·4%), $\nu_{max.}$ 1745 and 1700 (C=O), 1605, 1510, 1270, 1060, 1010, 825, 810, and 760 cm^{-1}, τ 2·55—2·65 (2H, m, ArH), 6·90 (3H, s, $N{\cdot}CH_3$), 7·38 (6H, s, $ArCH_3$), *m/e* 189 (M^+, 100%), 190 (12), 188 (6), 161 (3, M – CO), 160 (6, M – NMe), 145 (5, M – CO_2), 133 (8), 132 (72, M – MeNCO), 104 (14, M – MeNCO – CO), 103 (12), 78 (6), and 77 (11), m^* 135 ($189 \longrightarrow 160$), 92 ($189 \longrightarrow 132$), and 82 ($132 \longrightarrow 104$).

Autoxidation of 2-*Ethyl*-1,3,4,7-*tetramethylisoindole* (3b).—A solution of the isoindole (3b) (0·7 g) in tetrahydrofuran (50 ml) was oxygenated at the b.p. for 14 days; g.l.c. analysis then indicated the presence of unchanged (3b) and a more volatile product (*ca.* 2 : 1 peak area ratio) with retention time identical to that of *N*-ethyl-3,6-dimethylphthalimide (4b). The solvent was evaporated off, and the residual oil was redissolved in the minimum amount of chloroform and chromatographed on alumina (5 g). Light petroleum–benzene (1 : 1 v/v) eluted *N*-ethyl-3,6-dimethylphthalimide (4b) (0·01 g), m.p. 97—99° (from light petroleum–benzene), i.r. and mass spectra identical with those of an authentic sample.

Autoxidation of 2-*Benzyl*-1,3,4,7-*tetramethylisoindole* (3c).—A solution of the isoindole (3c) (5·0 g) in dry tetrahydrofuran (20 ml) was heated under reflux while oxygen was bubbled through it for 24 h. The redried ($MgSO_4$) solution showed a broad i.r. absorption at 3600 cm^{-1} (O–H). Evaporation left a dark indigo-coloured oil, which was redissolved in chloroform and chromatographed on alumina (350 g). Elution with light petroleum (b.p. 60—80°)–benzene (3 : 7 v/v) afforded *N*-benzyl-3,6-dimethylphthalimide (4c) (0·2 g, 4%), m.p. and mixed m.p. 125—126°, i.r. spectrum and g.l.c. retention time identical with those of authentic material. Subsequent fractions eluted gave only brown oils.

Another sample of compound (3c) was oxygenated in the same way for 6 days, after which g.l.c. analysis showed the presence of unchanged isoindole (3c) (*ca.* 12%), the phthalimide (4c) (7%), and one other volatile component of intermediate retention time (*ca.* 1%) which was present in amounts too small for characterisation.

Another sample of the isoindole (3c) (6·0 g) in n-butanol (100 ml) containing a few drops of dilute hydrochloric acid was heated under reflux during passage of oxygen for 12 h. The solution turned red, then purple-brown, and eventually a dark indigo colour which interfered with the test for the presence of peroxides with acidified potassium iodide solution. G.l.c. analysis showed the presence of starting material (3c) and the phthalimide (4c) and the absence of benzylamine and other new volatile products.

Autoxidation of 1,3,4,7-*Tetramethyl*-2-*phenylisoindole* (3d).—A solution of the isodindole (3d) (2·0 g) in dry tetrahydrofuran (50 ml) was heated under reflux during passage of oxygen for 24 h. The redried ($MgSO_4$) solution showed $\nu_{max.}$ 3600br cm^{-1} (O–H); a peroxide test was negative. Evaporation left a brown oil, which was shown to contain unchanged (3d) and the phthalimide (4d) (identified by its retention time and by g.l.c.-mass spectrum).

9-*Methylanthracene* 9,10-*Peroxide* (6d).—9-Methyl anthracene was prepared as described [19] from anthrone [20] and methylmagnesium iodide; the crude product (76%) was chromatographed on Florisil, from which light petroleum eluted material recovered as pale yellow plates, m.p. 79—80° (lit.,[19] 80°). 9-Methylanthracene (1·5 g) was dissolved in carbon disulphide (500 ml) which had previously been saturated with oxygen, and this solution was irradiated (Hanovia 100 W medium-pressure mercury arc, water-cooled, with Pyrex filter) for 2 h. The solvent was evaporated off and the residual solid after trituration with a little carbon disulphide was recrystallised from ether to give the peroxide (6d) (0·23 g, 13%), m.p. 76—79° (decomp.) (lit.,[21] *ca.* 80°).

Pyrolysis of 9-*Methylanthracene* 9,10-*Peroxide* (6d).—1,2-Dimethoxyethane (10 ml) containing the peroxide (6d) (0·23 g) was refluxed for 2 h, after which time no change was apparent. The solvent was removed, and the residue was redissolved in toluene (10 ml) and refluxed for 3 h. After evaporation, the residual oil was triturated with a little methanol and repeatedly washed with ether to give a solid (0·02 g), $\nu_{max.}$ 1680 cm^{-1} (C=O), whose mass spectrum consisted of peaks attributable to 9-methylanthracene and anthraquinone. Sublimation at 210° gave a trace of anthraquinone, m.p. and mixed m.p. 284—287° (sealed tube).

9,10-*Diethylanthracene* 9,10-*Peroxide* (6e).—The reaction of anthraquinone with ethylmagnesium iodide gave 9,10-diethyl-9,10-dihydroxydihydroanthracene (83%) as a mixture of geometrical isomers, m.p. 158—160° (lit.,[22] 172°; 150 and 176° for *cis*- and *trans*-isomers [23]), τ 2·1—2·8 (8H, m, ArH), 7·71 (2H, s, OH, exchangeable in D_2O), 7·87 (4H, q, $ArCH_2$), and 9·80 (6H, t, $CH_3{\cdot}CH_2$). This mixture of isomeric diols, on treatment with tin(II) chloride and hydrochloric acid [23] gave 9,10-diethylanthracene (67%) as pale yellow needles, m.p. 145—146° (from dimethylformamide) (lit.,[23] 147°). Oxygen was slowly bubbled through a solution of 9,10-diethylanthracene (1·17 g) in carbon disulphide (1 l) for 5 days. The solvent was evaporated off and the residue was extracted with boiling light petroleum (b.p. 40—60°); the undissolved solid (0·37 g) was then recrystallised from xylene to give the peroxide (6e), m.p. 198—200° (decomp.) (lit.,[23] 214°).

Pyrolysis of 9,10-*Diethylanthracene* 9,10-*Peroxide* (6e).—A solution of the peroxide (6e) (0·35 g) in xylene (20 ml) was refluxed for 4 h and then cooled. The starting material was recovered, m.p. and i.r. spectrum unchanged. The xylene was evaporated off and the solid residue was redissolved in decalin (15 ml) and refluxed for 4 h. On cooling, anthraquinone (0·08 g, 30%) was obtained as needles, m.p. and mixed m.p. 285—287° (sealed tube), i.r. spectrum identical with that of an authentic sample.

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