

Aromatic Annulation by Reaction of Aryl Radicals with Dimethyl Acetylenedicarboxylate and Related Compounds

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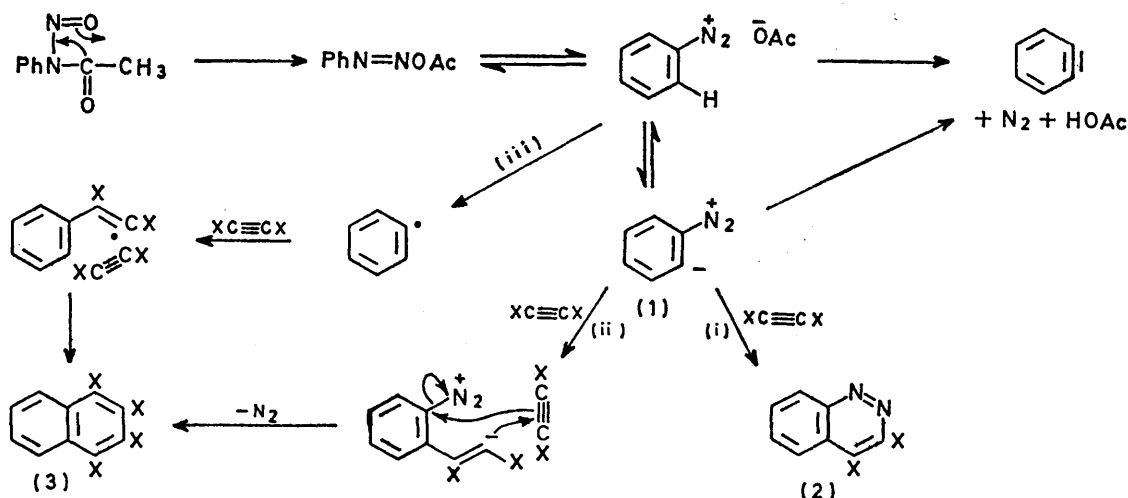
Phenyl radicals derived from *N*-nitrosoacetanilide, dibenzoyl peroxide, or di-*t*-butyl peroxide-triphenylarsine react with dimethyl acetylenedicarboxylate (DMAD) to give tetramethylnaphthalene-1,2,3,4-tetracarboxylates, the maximum yield being 0.5 mol per mol of radical source, obtained in the case of dibenzoyl peroxide. Substituted dibenzoyl peroxides [(XC₆H₄CO₂)₂; X = 2-NO₂, 2-Cl, 3-Cl, 3-Br, 3-Me, 4-Cl, 4-Br, 4-Me, or 4-CN] undergo this annulation less successfully to give the corresponding tetramethyl X-naphthalene-1,2,3,4-tetracarboxylates. Di-2-naphthoyl peroxide similarly gave a mixture of tetramethylantracene- and phenanthrene-1,2,3,4-tetracarboxylates, and dibenzoyl peroxide in ethyl propiolate gave a mixture of diethyl naphthalenedicarboxylates.

That the annulation probably proceeds *via* reaction of first-formed styryl radicals with DMAD followed by cyclisation is indicated by the additional formation of dimethyl diphenyl-maleate and -fumarate when dibenzoyl peroxide decomposed in a mixture of benzene and DMAD. In accord with this, decomposition of bis- α -methylcinnamoyl peroxide in DMAD gave a small yield of dimethyl 3-methylnaphthalene-1,2-dicarboxylate.

Di-2-thenoyl peroxide behaved differently on decomposition in DMAD, giving dimethyl thenoylmaleate (20%), the *trans*-isomer being absent, and trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (5%). A mechanism is advanced.

DURING investigation of the mechanism of formation of benzyne from *N*-nitrosoacetanilide and benzenediazonium acetate, the question of the reversible formation of the betaine (1) arose¹ (Scheme 1). We considered that if this 1,3-dipole were present it might be trapped by a dipolarophile such as dimethyl acetylenedicarboxylate to give the cinnoline (2) [Scheme 1, route (i)]. We now

the naphthalene (3) could have been formed *via* stepwise reaction of the betaine (1) with two molecules of DMAD [Scheme 1, route (ii)], or *via* a radical annelation reaction [route (iii)]. The products of the reaction of *N*-nitrosoacetanilide with DMAD in benzene point to the latter, radical route since they included dimethyl diphenyl-maleate (10%) and dimethyl diphenylfumarate (5%) in



SCHEME 1 X = CO₂Me

describe experiments carried out in this connection which, in the event, led to a new aromatic annulation reaction *via* aryl radicals, but did not help in resolving the original problem, which was subsequently resolved satisfactorily by other means.^{2,3}

Decomposition of *N*-nitrosoacetanilide in an excess of dimethyl acetylenedicarboxylate (DMAD) gave a large amount of intractable polymeric tar and tetramethyl naphthalene-1,2,3,4-tetracarboxylate (3) (17%). The cinnoline (2) was not detected. It was conceivable that

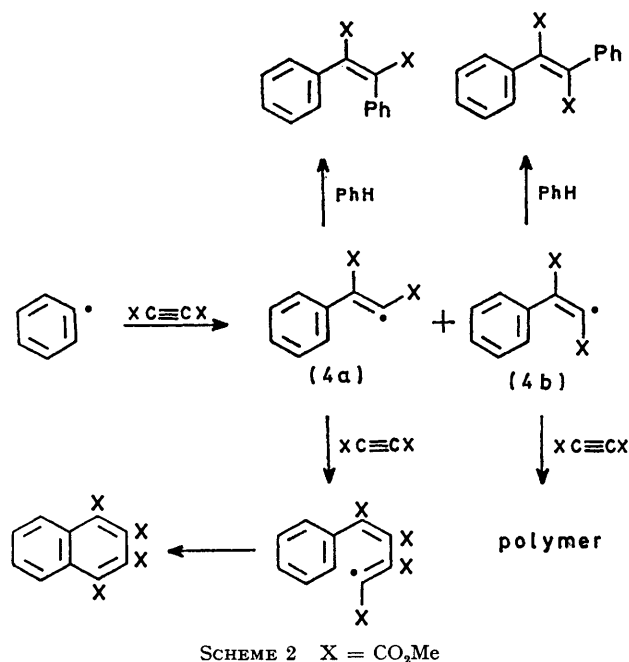
¹ J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, 4, 186.

² D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *J. Chem. Soc. (B)*, 1971, 1996.

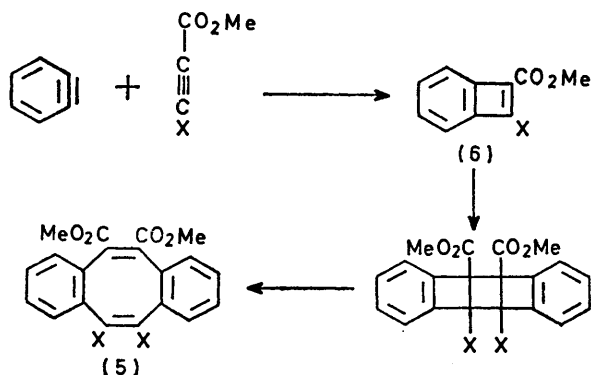
addition to biphenyl (7%) and the naphthalene (3) (15%). These results suggest a process such as that shown in Scheme 2, wherein a phenyl radical reacts to give a mixture of the isomeric styryl radicals (4a and b) which can react either with benzene to give the observed maleate and fumarate derivatives or with another molecule of DMAD to give substituted phenylbutadienyl radicals which can cyclise to give the observed naphthalene tetra-ester. In addition, competing radical-induced polymerisation reactions would be expected, as observed.

³ J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1974, 1321.

It is well known that the decomposition of *N*-nitrosoacetanilide is partitioned between radical and benzyne routes,¹ but the further possibility that the naphthalene



(3) arises *via* reaction of benzyne with DMAD was excluded by our demonstration that benzyne, formed from anthranilic acid in the presence of pentyl nitrite gave no naphthalene tetraester. The only detectable product, in this case, was tetramethyl dibenzo[*a,e*]cyclooctene-5,6,11,12-tetracarboxylate (5; $X = \text{CO}_2\text{Me}$) (3%) presumably formed *via* the benzocyclobutene (6) in a manner analogous to that proposed for the formation of the diester (5; $X = \text{H}$) from benzyne and methyl propiolate⁴ (Scheme 3).



The radical route to the naphthalene tetraester was confirmed when other sources of phenyl radicals gave the same product, namely the reactions of *t*-butyl peroxide

⁴ M. Stiles and U. Burkhardt, *J. Amer. Chem. Soc.*, 1964, **86**, 3396.

with triphenylarsine⁵ and the more familiar decomposition of dibenzoyl peroxide which gave, in neat DMAD, the best yield of naphthalene tetraester which we observed (0.5 mol per mol of peroxide). Decomposition of the peroxide in benzene mixed with DMAD led to a reduction of the yield of the naphthalene (3), with the formation of biphenyl and a 3 : 1 mixture of dimethyl diphenylmaleate and -fumarate.

The Table outlines the scope of this annelation reaction. All substituted peroxides investigated gave smaller or negligible yields of the naphthalene tetraester. The Table also shows that much of the aryloxy-unit is lost

Reactions of diaroyl peroxides [$(\text{Y}\text{C}_6\text{H}_4\text{CO}_2)_2$] with dimethyl acetylenedicarboxylate*

Y	Y		$\text{Y}\text{C}_6\text{H}_4\text{CO}_2\text{H}$	CO_2
	5-Y	6-Y		
H	50		3	72
2-NO ₂	0			
2-Cl	3		13	68
3-Cl	10	4		
3-Br	14.5	5.5		
3-Me	13	6	10	66
4-Cl		22	10	56
4-Br		18		
4-Me		16	11	62
4-CN		18		

* Yields in mol per 100 mol of peroxide.

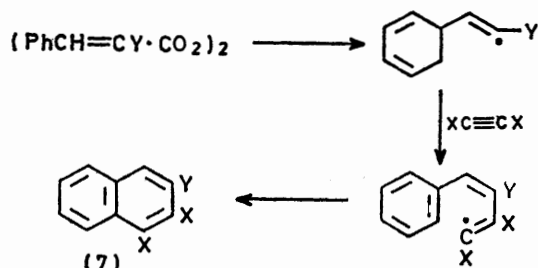
in the unidentified residue: only small amounts of the expected substituted benzoic acids are formed and the evolution of carbon dioxide is also low in each case. This suggests that in most cases trapping of the aryloxy radical by DMAD is competing successfully with (a) decarboxylation of the radical to give the required aryl radical, (b) addition of aryl to DMAD, and (c) addition of the subsequently formed arylstyryl radical to DMAD followed by cyclisation. No information is available concerning the relative effects of substituents in the aryl moiety on these factors.

The concept of radical participation is also supported by the observation that *m*-substituted peroxides give mixtures of 5- and 6-substituted tetramethyl naphthalene-1,2,3,4-tetracarboxylates in the ratios *ca.* 2—3 : 1, showing that intramolecular attack takes place more readily *ortho* rather than *para* to the substituent, it being well known that radical substitution in aromatic compounds (PhX) occurs more readily in the *ortho*- than the *para*-position.

We sought further confirmation of Scheme 2 by attempting to generate styryl radicals, by decomposition of dicinnamoyl peroxide, in DMAD to give dimethyl naphthalene-1,2-dicarboxylate (7; $\text{Y} = \text{H}$) (Scheme 4). We were defeated, however, by the low yield of styryl radicals available by this route, the preferred reaction

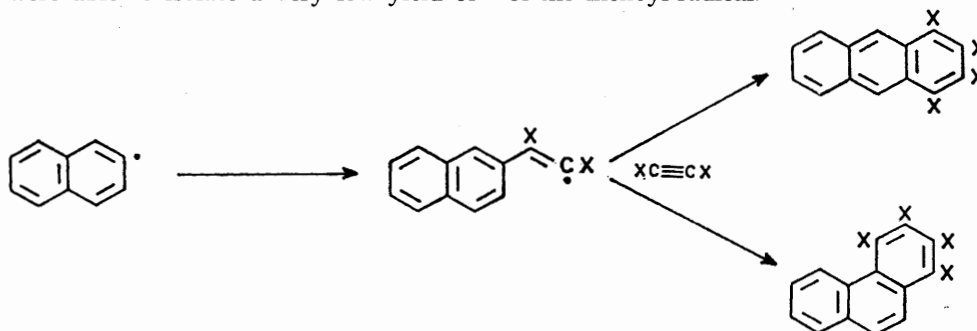
⁵ E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1972, **94**, 5932.

being induced decomposition not involving styryl radicals.⁶ Bis- α -methylcinnamoyl peroxide is reported to



SCHEME 4 X = CO₂Me

generate β -methylstyryl radicals in useful quantities, however,⁷ and in partial accord with this, and with Scheme 4, we were able to isolate a very low yield of



SCHEME 5 X = CO₂Me

material which had mass and ¹H n.m.r. spectra as expected for dimethyl 3-methylnaphthalene-1,2-dicarboxylate (7; Y = Me).

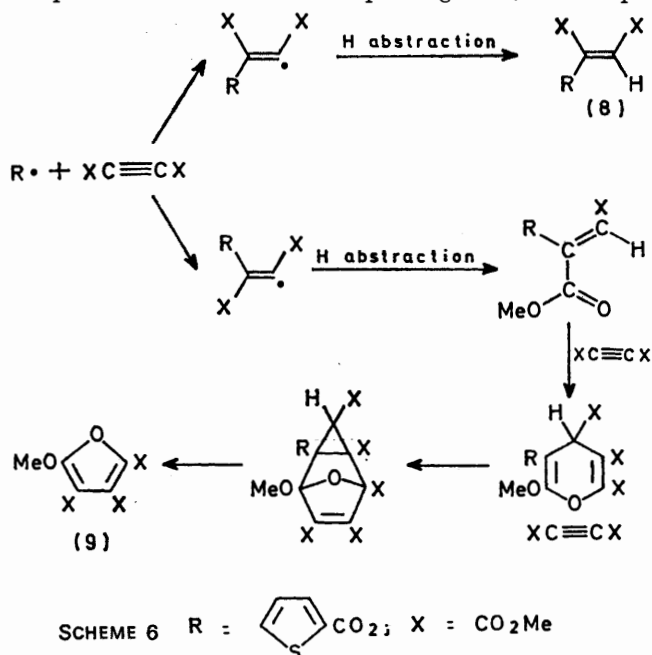
Attempts to extend the annelation to other systems were successful only in the cases of the reaction of dibenzoyl peroxide with ethyl propiolate, which gave a mixture of isomeric diethyl naphthalenedicarboxylates, and of di-2-naphthoyl peroxide in DMAD, which gave a low yield of a mixture identified as tetramethyl anthracene- and phenanthrene-1,2,3,4-tetracarboxylates (Scheme 5). Reactions with phenylacetylene and hex-1-yne did not give annelated products. Reaction of bis-(2-phenylbenzoyl) peroxide with DMAD gave dibenzo-[*b,d*]pyran-6-one (37%) in intramolecular reaction rather than the annelation product, dimethyl phenanthrene-9,10-dicarboxylate.


Reaction of di-2-thenoyl peroxide with neat DMAD proceeded quite differently (Scheme 6). The major product was dimethyl thenoylmaleate (8) (20%), produced together with trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (9) (0.05 mol per mol of peroxide), and identified by comparison of its physical and spectroscopic characteristics with published data.⁸ Previous workers

had obtained this compound from co-pyrolysis of DMAD with methyl fumarate (although not from methyl maleate) and had outlined a possible mechanism for its formation.⁸ Although the origin of this remarkable product in the reaction of dithenoyl peroxide with DMAD is not clear, a similar mechanism for its formation is advanced in Scheme 6. This accounts not only for the product (9) but also for the otherwise puzzling lack of dimethyl thenoylfumarate. Scheme 6 requires the reaction of the latter with DMAD in a Diels-Alder-type reaction, followed by cycloaddition of a second molecule of DMAD to this product. The intermediate thus formed undergoes an electrocyclic ring opening with extrusion of the cyclopropene unit to give (9). That these products were derived from the thenoyl radical is in accord with the known resistance to decarboxylation of the thenoyl radical.⁹

EXPERIMENTAL

Preparation of Materials.—Diaroyl peroxides, prepared by Cooper's method from the corresponding acids,¹⁰ had m.p.s



SCHEME 6 R =  CO₂; X = CO₂Me

⁶ N. Muramoto, T. Ochiai, O. Simamura, and M. Yoshida, *Chem. Comm.*, 1968, 717.

⁷ L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, 1966, **88**, 5213.

⁸ C. F. Huebner, E. Donoghue, L. Dortman, F. A. Stuber, N. Danielli, and E. Wenkert, *Tetrahedron Letters*, 1966, 1185.

⁹ (a) R. D. Sheutz and D. M. Teller, *J. Org. Chem.*, 1962, **27**, 410; (b) M. C. Ford and D. McKay, *J. Chem. Soc.*, 1957, 4620.

¹⁰ W. Cooper, *J. Chem. Soc.*, 1951, 3107.

in accord with the literature. Heterocyclic peroxides were prepared by adaptation of the carbodi-imide synthesis of Greene and Kazan,¹¹ exemplified as follows by the case of bis-2-thenoyl peroxide. A solution of 2-thenoic acid (3.84 g, 30 mmol) in dichloromethane (50 ml) was added dropwise to a stirred solution of dicyclohexylcarbodi-imide (6.39 g, 31 mmol) and H₂O₂ in ether (20 ml) at 0°, keeping the temperature below 5°. The solution was stirred for a further 30 min at room temperature, then the dicyclohexylurea was filtered off and washed with dichloromethane (3 × 50 ml). The organic layers were combined and ether was added to double the volume. The organic solution was washed successively with saturated aqueous ammonium sulphate (3 × 50 ml), aqueous 10% sodium carbonate (2 × 50 ml), and saturated aqueous sodium chloride (2 × 50 ml); the solvent was evaporated off at room temperature and the yellow residue was recrystallised from chloroform-cyclohexane (1 : 9) to give di-2-thenoyl peroxide as almost colourless plates (3.35 g, 88%), m.p. 99–100° (lit.,⁹ 100–101°). Also prepared by this route were bis-2-phenylbenzoyl peroxide, m.p. 103–104° (lit.,¹² 105–106°), and bis- α -methylcinnamoyl peroxide, m.p. 73–74° (decomp.) [lit.,⁷ 74–75° (decomp.)].

Reactions of Diaroyl Peroxides with Dimethyl Acetylenedicarboxylate (DMAD).—General method. The peroxide (5 mmol) was allowed to decompose at 80° under nitrogen in dimethylacetylenedicarboxylate (50 mmol). After 12 h, the excess of solvent was removed and the residue was examined by t.l.c. to determine the presence of any products and the best solvent system. The residue was adsorbed on alumina (25 g) and chromatographed on a dry column (60 × 3.5 cm), developed with either benzene or dichloromethane. The products were detected as either intense, fluorescent blue bands or dark heavily masked bands which were separated from alumina with methanol. Evaporation of the extracts yielded the crude product which was recrystallised from methanol to give the substituted naphthalene tetraester as a white crystalline solid, characterised by analysis and n.m.r. spectroscopy.*

In the cases of 3-substituted peroxides where both the 5- and 6-substituted naphthalenes were possible products, the ratio of isomers was determined by ¹H n.m.r. spectroscopy. Thus for a mixture of tetramethyl 5- and 6-methylnaphthalene-1,2,3,4-tetracarboxylates, direct comparison of the integral tracings for the respective methyl singlets gave the isomer ratio, the methyl singlet of the 5-isomer appearing downfield relative to that of the 6-isomer. When substituents gave no signal (e.g. Br or Cl) the signal due to the 5-proton of the 6-isomer was easily assigned as it appeared furthest downfield as a *meta*-coupled doublet. The integral tracing of this fixed signal was compared with that for other fixed signals and the ratio of isomers was determined by simple computation.

Pure samples of 5-isomers were obtained from mixtures of 5- and 6-isomers by chromatography. However a mixture of 5- and 6-methylnaphthalene tetraesters could not be separated by either chromatography or fractional crystallisation.

Separate experiments were performed to obtain the yields of substituted benzoic acids and carbon dioxide formed in these reactions by interposing an extraction step (aqueous

sodium hydrogen carbonate) and by use of a standard gas burette.

The results are summarised in the Table.

Reactions of Dibenzoyl Peroxide with DMAD in Benzene.—The peroxide (5.84 g, 20 mmol) was allowed to decompose in a solution of dimethyl acetylenedicarboxylate (8.5 g, 60 mmol) in benzene (200 ml) at the b.p. Removal of the solvents left an orange oil which was redissolved in chloroform and extracted with aqueous 10% sodium hydrogen carbonate (3 × 20 ml) to give benzoic acid (0.26 g, 12 mol per 100 mol of peroxide). The residue (7.0 g) was chromatographed on a dry alumina column (60 × 4 cm), developed with benzene, to give three main fractions. The first was a yellow oil which on recrystallisation from methanol gave a solid, identified as biphenyl (1.25 g, 40 mol per 100 mol of peroxide), m.p. and mixed m.p. 70°. The second was a yellow oil (0.2 g). G.l.c. (2% NPGS; 180°) indicated a number of components; two of these had retention times identical with those of authentic samples of dimethyl diphenyl-fumarate and -maleate (1 : 2.7). G.l.c.-mass spectrometry of the two components showed parent ions for both at *m/e* 296. The third fraction gave a yellow solid after recrystallisation from methanol and was shown to be tetramethylnaphthalene-1,2,3,4-tetracarboxylate (0.27 g, 4 mol per 100 mol of peroxide), m.p. and mixed m.p. 145–146°.

Reactions of Other Peroxides with Dimethyl Acetylenedicarboxylate.—(i) *Di-2-naphthoyl peroxide.* Di-2-naphthoyl peroxide (1.02 g, 3 mmol) was allowed to decompose at 80° under nitrogen in dimethyl acetylenedicarboxylate (7.1 g, 50 mmol). The excess of solvent was removed and the residue (2.1 g) was chromatographed on a dry alumina column (50 × 2 cm), developed with dichloromethane. A cream coloured solid (0.07 g, 6 mol per 100 m) was the only product recovered from the column and was identified as a mixture of tetramethyl anthracene- and phenanthrene-1,2,3,4-tetracarboxylates, *M*⁺ 410, τ (CDCl₃) 1.70–1.80 (1H, m, aromatic), 2.02–2.24 (3H, m, aromatic), 2.26–2.48 (2H, m, aromatic), and 5.98, 6.02, 6.07, and 6.08 (12H, 4s, 4 × CO₂Me). The appearance (τ ca. 6.0) of four singlets was compatible with the product being a mixture of two different carbocyclic tetraesters. From the ratio of the singlets at τ 5.98 and 6.02, the isomer ratio was determined as 3 : 2, respectively, and by analogy with 3-substituted benzoyl peroxides where the 5-substituted adduct predominated, the major isomer in this case was taken to be the phenanthrene tetraester. All attempts to separate either component from the mixture failed.

(ii) *Bis-2-phenylbenzoyl peroxide.* Bis-2-phenylbenzoyl peroxide (0.79 g, 2 mmol) was allowed to decompose at 100° under nitrogen in dimethyl acetylenedicarboxylate (4.3 g, 30 mmol). Standard work-up, which showed the absence of 2-phenylbenzoic acid, gave dibenzo[*b,d*]pyran-6-one (37 mol per 100 mol of peroxide), m.p. and mixed m.p. 90–92°, *m/e* 196 (*M*⁺) and 168 (*M*⁺ – CO) ν_{max} (Nujol) 1730 cm⁻¹ (C=O of lactone). No dimethyl phenanthrene-9,10-dicarboxylate was detected by g.l.c.-mass spectrometry either in the isolated solid or in the crude reaction mixture.

(iii) *Di-2-thenoyl peroxide.* Di-2-thenoyl peroxide (1.27 g, 5 mmol) was allowed to decompose at 80° under nitrogen in dimethyl acetylenedicarboxylate (7.1 g, 50 mmol). After 12 h, the excess of solvent was removed and the black residue

* Data are available as Supplementary Publication No. SUP 31320 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

¹¹ F. D. Greene and J. Kazan, *J. Org. Chem.*, 1963, **28**, 2168.

¹² J. K. Kochi and R. D. Gillman, *J. Amer. Chem. Soc.*, 1964, **86**, 5251.

was distilled to give a bright yellow oil (1.0 g), b.p. 120° at 0.05 mmHg, and a white crystalline solid which sublimed at the b.p. of the oil. T.l.c. analysis of the oil indicated two components, one of which had the same R_F value as the white solid. The two products were combined and chromatographed on a dry alumina column (60 × 2 cm), developed with dichloromethane, to give two fractions.

The first, a dark brown oil, was redistilled to give a yellow oil, b.p. 125° at 0.05 mmHg, which solidified on cooling. Recrystallisation from methanol gave a pale yellow solid (0.27 g, 20 mol per 100 mol of peroxide), identified as *dimethyl thenoylmaleate*, m.p. 75–76° (Found: C, 49.1; H, 3.7%; M^+ , 270.020054. $C_{11}H_{10}O_6S$ requires C, 48.9; H, 3.7%; M , 270.019804), τ ($CDCl_3$) 2.00–2.08 (1H, dd, aromatic), 2.24–2.33 (1H, dd, aromatic), 2.78–2.89 (1H, dd, aromatic), 3.22 (1H, s, vinylic), 6.25 (3H, s, CO_2Me), and 6.29 (3H, s, CO_2Me), ν_{max} (Nujol) 1730br (C=O) and 1655 cm^{-1} (C=C). This compound was assigned the *cis* structure on the basis of a comparison with the known *cis*- and *trans*-dimethyl diphenylmaleates, *viz.* CO_2Me (*trans*) τ 6.51; CO_2Me (*cis*) τ 6.20.

The second fraction, a sticky green solid (0.1 g), was recrystallised from chloroform-petroleum to give trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (0.07 g, 5 mol per 100 mol of peroxide), m.p. 117–119° (lit.⁸ 117–118°) (Found: M^+ , 272.052698. $C_{11}H_{12}O_8$ requires M , 272.053208), τ ($CDCl_3$) 5.78 (3H, s, OMe), 6.07 (3H, s, CO_2Me), 6.16 (3H, s, CO_2Me), and 6.22 (3H, s, CO_2Me), ν_{max} (Nujol) 1740, 1720, and 1705 cm^{-1} (C=O), λ_{max} 273 nm (log ϵ 4.92) [lit.⁸ 276 (log ϵ 4.18)].

Reactions of Phenyl Radicals from Various Sources with DMAD.—(i) *N-Nitrosoacetanilide*. *N*-Nitrosoacetanilide (14.0 g, 85.0 mmol) was allowed to decompose in benzene (137 g, 1.76 mol) containing dimethyl acetylenedicarboxylate (37.0 g, 0.26 mol) at room temperature. After a short induction period, a vigorous reaction set in and the reaction was quickly over. Work-up by fractional distillation and subsequent recrystallisation gave (i) biphenyl (0.90 g, 7 mol per 100 mol), m.p. and mixed m.p. 68–69°, (ii) cream crystals (3.60 g), m.p. 80–100°, and (iii) tetramethyl naphthalene-1,2,3,4-tetracarboxylate, m.p. 145–146° (15 mol per 100 mol). Fraction (ii) contained two components (1:1) (by g.l.c.). Fractional crystallisation from methanol gave a pure sample of the minor component, m.p. 141–141.5°, identified by comparison with an authentic specimen as dimethyl diphenylfumarate (Found: C, 73.2; H, 5.4; M^+ , 296. Calc. for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4%; M , 296), τ ($CDCl_3$) 2.64 (10H, s), and 6.50 (6H, s). Preparative g.l.c. gave the other component, m.p. 108–110°, similarly identified as dimethyl diphenylmaleate (lit.¹³ m.p. 110–112°). Hydrogenation of the mixture gave a mixture of (\pm)- and *meso*-dimethyl diphenylsuccinates, identified by comparison with an authentic mixture. The yields of the diphenyl-maleate and -fumarate were shown to be (g.l.c.) 5 and 10 mol per mol of *N*-nitrosoacetanilide, respectively.

A similar reaction in which *N*-nitrosoacetanilide was formed *in situ* from acetanilide and *p*-chlorobenzoyl nitrite¹⁴ gave similar results.

A reaction of *N*-nitrosoacetanilide and DMAD carried out in the absence of benzene gave tetramethyl naphthalene-1,2,3,4-tetracarboxylate in 17% yield.

(ii) *With t-butyl peroxide-triphenylarsine*. *t*-Butyl peroxide (0.76 g, 5 mmol) was allowed to decompose under

nitrogen at 120° in a stirred solution of triphenylarsine (3.06 g, 10 mmol) in dimethyl acetylenedicarboxylate (7.1 g, 50 mmol). After 12 h the solid black mass was examined by t.l.c. and the presence of tetramethyl naphthalene-1,2,3,4-tetracarboxylate was confirmed. Work-up as before gave the product (0.12 g, 3%), m.p. and mixed m.p. 144–146°.

Reaction of Pentyl Nitrite and Anthranilic Acid with Dimethylacetylenedicarboxylate in Benzene.—Anthranilic acid (5.0 g, 0.04 mol) in benzene (20 ml) was added dropwise to a boiling solution of pentyl nitrite (5.2 g) and dimethylacetylenedicarboxylate (16.0 g, 0.11 mol) in benzene (25 g, 0.32 mol). Standard work-up gave tetramethyl dibenzo[a,e]cyclo-octene-5,6,11,12-tetracarboxylate (0.48 g, 3.0 mol per 100 mol), m.p. 213–215° (decomp.) (Found: C, 65.7; H, 4.6%; M^+ , 436. $C_{24}H_{20}O_8$ requires C, 66.05; H, 4.6%; M , 436), ν_{max} (Nujol) 1720 cm^{-1} (C=O), τ ($CDCl_3$) 2.81 and 2.83 (8H, d) and 6.18 (12H, s). The crude product was examined by n.m.r. for trace amounts of tetramethyl naphthalene-1,2,3,4-tetracarboxylate, but this was absent, as were *cis*- and *trans*-dimethyl diphenylmaleate (0.2% yield would have been detected).

Reaction of Dibenzoyl Peroxide with Ethyl Propiolate.—Dibenzoyl peroxide (1.21 g, 5 mmol) was allowed to decompose in ethyl propiolate (4.9 g, 50 mmol) at 80°. After 12 h, the excess of solvent was distilled off and the residue (4.4 g) was chromatographed on a dry alumina column (60 × 4 cm), developed with benzene. The blue fluorescent segment was removed and washed with ether to give a brown oil (0.5 g) which was purified by distillation to give a tacky solid (0.37 g, 27 mol per 100 mol; b.p. 90° at 0.05 mmHg), identified as a mixture of at least two isomeric naphthalene diesters. G.l.c. analysis of the solid indicated two components. G.l.c.–mass spectrometry showed parent ions for each at m/e 272. High-speed liquid chromatography (Spherisorb A, 20 μ ; CH_2Cl_2) indicated two major components. The mixture showed τ ($CDCl_3$) 1.01–1.05 (1H, dd, aromatic), 1.27 (2H, s, aromatic), 1.94–2.74 (4H, m, aromatic), 5.40–5.65 (4H, s overlapping quartets, 2 × CO_2Et), and 8.45–8.66 (6H, 2 overlapping triplets, 2 × CO_2Et), ν_{max} (Nujol) 1720 cm^{-1} (C=O). The n.m.r. spectrum was compatible with a mixture of two naphthalene diesters; the low-field doublet indicated the presence of diethyl naphthalene-1,3-dicarboxylate; however it was not possible to determine which of the remaining diesters was responsible for the low-field singlet at τ 1.27.

Decomposition of Bis- α -methylcinnamoyl Peroxide in DMAD.—The peroxide (1.61 g, 5 mmol) was allowed to decompose in DMAD (7.2 g, 50 mmol) at 70° for 18 h. The blue (*sic*) solution was worked up by distillation and chromatography to give an oil containing two components, one major, which resisted all attempts at separation. G.l.c.–mass spectrometry, however, showed that the major component was dimethyl 3-methylnaphthalene-1,2-dicarboxylate [m/e 258 (M^+), 227 (–MeO), 199 (–CO), 168 (–MeO), and 140 (–CO); also 226 (–MeOH), 211 (–Me), and 139 (–CO₂, –CO)]. The n.m.r. spectrum of the mixture was also in accord with the presence of a major amount of this material: τ ($CDCl_3$) 1.8–2.9 (6H, m, aromatic), 6.05 (3H, s, CO_2Me), 6.10 (3H, s, CO_2Me), and 7.48 (3H, s, Me). The total yield was *ca.* 5 mol per mol of peroxide.

[4/2333 Received, 8th November, 1974]

¹³ W. Metlesics and H. Zeiss, *J. Amer. Chem. Soc.*, 1959, **81**, 4117.

¹⁴ B. D. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.