654. *Photochemical Transformations. Part XIX.* Some Photosensitive Protecting Groups*

By D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby

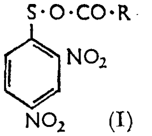
The photolysis of 2,4-dinitrobenzenesulphenyl esters affords carboxylic acids in high yield. The initial step in this photolysis has been defined.

The photolysis of phenolic esters has been further investigated. The esters of fluorene-9-carboxylic acid and xanthen-9-carboxylic acid afford reasonable yields of phenols with concomitant fragmentation of the acid residue.

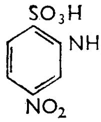
The potential advantages of protecting groups which can be removed photochemically under neutral conditions have been emphasised. A preliminary report of some aspects of our work has appeared.[1]

Removable protecting groups are of importance in many phases of modern synthesis. At present all useful protecting groups are removed by ordinary thermal chemical reactions. In principle, however, it should be possible to design protecting groups which could be removed by photolysis under completely neutral and very mild conditions. At the time when we were first considering this possibility there were no publications on the topic. However, shortly before our preliminary Communication,[1] the first example of a possible photosensitive protecting group was published.[2] We describe first a protecting group for carboxylic acids.

2,4-Dinitrobenzenesulphenyl acetate (I; R = Me) is readily prepared.[3] On irradiation with a mercury-arc lamp in benzene or ether solution the acetate was rapidly photolysed to furnish acetic acid, identified as its *p*-bromophenacyl ester, in at least 90% yield. In benzene solution the other products of the reaction were impure 2-amino-4-nitrobenzenesulphonic acid (II) (19%), 2,2′,4,4′-tetranitrodiphenyl disulphide (III) (6%), and 2,4-dinitrodiphenyl sulphide (IV; R = H) (73%). The first two compounds were precipitated from solution during the photolysis. The photolysis of 2,4-dinitrobenzenesulphenyl hexanoate (I; R = C_5H_{11}) and phenylacetate (I; R = $PhCH_2$) proceeded similarly, hexanoic aid (98% by titration) and phenylacetic acid (88%, crystalline) being formed. The non-acidic products in these last two photolyses were given only cursory attention.



(I)



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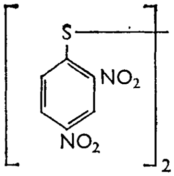

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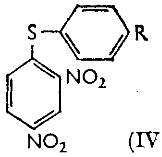

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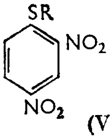

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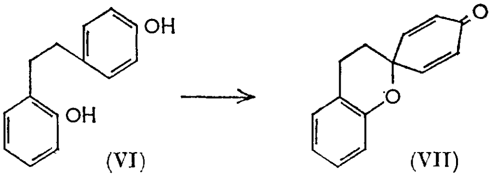

(VI) (VII)

In contrast to the photochemical sensitivity of sulphenyl esters of type (I), the methyl derivative (V; R = OMe) and the benzyl derivative (V; R = $PhCH_2$) were recovered unchanged after prolonged irradiation. The analogous chloro-compound (V; R = Cl), on the other hand, was again very sensitive to light.

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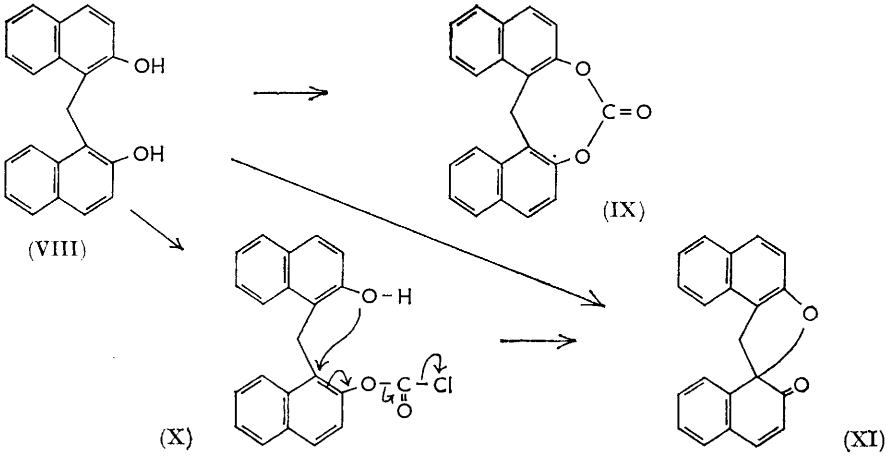
* Part XVIII, D. H. R. Barton and A. N. Starratt, *J.*, 1965, 2444.

[1] D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *Tetrahedron Letters*, 1962, 1055.

[2] J. A. Barltrop and P. Schofield, *Tetrahedron Letters*, 1962, 697.

[3] A. J. Havlik and N. Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 1207.

We considered two possible initial photochemical processes. In the first, sulphenyl esters would cleave to furnish 2,4-dinitrobenzenesulphenyl radicals and acyloxy-radicals, for example the acetate radical. In the second, the cleavage would be ionic in character, and 2,4-dinitrobenzenesulphenyl cations and acylate anions, for example acetate anion, would result. The photolysis of 2,4-dinitrobenzenesulphenyl acetate was studied in more detail and it was shown that no carbon dioxide was produced. It seems improbable that acetate radicals could be involved for these should undergo at least partial decarboxylation.[4] Furthermore, no carbon dioxide was evolved during the photolysis of the phenylacetate ester (I; R = $PhCH_2$), although the phenylacetate radical is exceptionally easily decarboxylated.



The formation of 2,4-dinitrodiphenyl sulphide as a major product when benzene was used as a solvent is consistent with either radical substitution by 2,4-dinitrobenzenesulphenyl radicals or with electrophilic substitution by the corresponding sulphenyl cations. Decisive evidence in favour of the intermediary of sulphenyl cations was obtained by the following experiment. The normal photolysis of the acetate (I; R = Me) was repeated in benzene containing 1 mol. of anisole. Working up as before gave 4-methoxy-2′,4′-dinitrodiphenyl sulphide (74%) and no 2,4-dinitrodiphenyl sulphide. It is clear that 1 mol. of anisole captures completely the 2,4-dinitrobenzensulphenyl moiety even in the presence of a large excess (1400 mol.) of benzene. Now, there is little difference between the rates of radical attack upon anisole and upon benzene,[5] whereas the rate ratio for electrophilic attack on anisole relative to benzene is at least 10^4. We consider that this proves that the initial photochemical step is a cleavage into 2,4-dinitrobenzenesulphenyl cations and acetate anions. The formation of the latter would, of course, account nicely for the absence of decarboxylation.

We also investigated the possibility that the product of photolysis might be a mixed anhydride between acetic acid and a sulphenic or sulphinic acid. However carefully the benzene was dried and traces of water removed from the apparatus, the photolysis still proceeded in the usual way. Furthermore, addition of excess (100 mol.) of cyclohexylamine at the end of the experiment did not affect the yield (89%) of acetic acid, and no cyclohexylacetamide resulted.

It cannot be stated at present whether the relatively small yield of impure 2-amino-4-nitrobenzenesulphonic acid is also associated with ionic cleavage or with a rearrangement of oxygen prior to a different mode of cleavage.

Now that the initial cleavage of sulphenyl esters has been demonstrated to be ionic in

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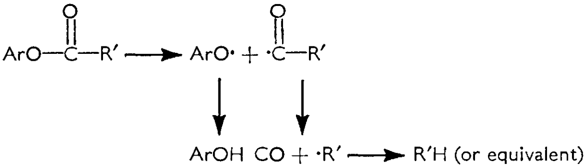
[4] M. S. Kharasch, J. L. Rowe, and W. H. Urry, *J. Org. Chem.*, 1951, **16**, 905.

[5] G. H. Williams, " Homolytic Aromatic Substitution," Pergamon Press, Oxford, 1960, p. 57.

character, it is understandable that derivatives (V; R = OMe) and (V; R = $PhCH_2$) are not sensitive to photolysis. The ease of rupture of the S–R bonds in such compounds should depend on the electronegativity of R and be in the order S–O·CO·Me and S–Cl > S–O–Me > S–CH_2Ph.

We now turn to the development of a protecting group for phenolic hydroxyl. Whilst the photochemical Fries rearrangement is by now well known [6] we had in mind the idea that phenolic esters should afford on photolysis phenoxy-radicals and aryl radicals which, if certain structural conditions were satisfied, should decarbonylate to relatively stable inert radicals. The phenoxy-radicals could then undergo conventional coupling reactions or, if a suitable hydrogen donor be present, be reduced to phenols. The process can be summarised as follows:



The Table lists a number of esters of 2-naphthol chosen so that the derived acyl radicals should undergo facile decarbonylation to afford stabilised radicals R′. It is clear that reasonable yields of pure phenol can be recovered from fluorene- and xanthen-9-carboxylic esters of 2-naphthol. Cholesteryl fluorene- and xanthen-9-carboxylate were recovered unchanged after prolonged irradiation, as was methyl fluorene-9-carboxylate. The photosensitivity of the phenolic esters is, therefore, due to the phenolic rather than the acidic moiety of the ester. In agreement with this, *p*-cresyl fluorene-9-carboxylate, unlike the corresponding 2-naphthyl ester, was not cleaved by irradiation in a Pyrex vessel. *p*-Cresyl and guaiacyl fluorene-9-carboxylate were photolysed in quartz to afford reasonable yields of the corresponding phenols. The proposed fragmentation of the R′CO fragment was confirmed in the case of 2-naphthyl fluorene-9-carboxylate by determination of the carbon monoxide evolved (90%).

In view of the recent work of Bentrude and Martin [7] on the anchimeric effect of sulphur or iodine atoms on radical cleavage reactions, it seemed reasonable to hope that the photolysis of phenolic esters might be subject to a similar acceleration. 2-Naphthyl *o*-(phenylthiomethyl)benzoate and *o*-iodobenzoate were prepared. Both esters photolysed rapidly (see Table) and gave high yields of phenolic material. The content of 2-naphthol was, however, small in both cases.

Ester	Irradiation time (hr.)	Type of flask	Base sol. fraction (%)	Pure phenol (%)
2-Naphthyl trichloroacetate	3	Quartz	40	22
2-Naphthyl triphenylacetate	1	Quartz	66	39
2-Naphthyl fluorene-9-carboxylate	4	Pyrex	74	60
2-Naphthyl xanthen-9-carboxylate	4	Pyrex	—	60
p-Cresyl fluorene-9-carboxylate	2	Quartz	71	58 *
Guaiacyl fluorene-9-carboxylate	2	Quartz	67	58
2-Naphthyl *o*-(phenylthiomethyl)benzoate	0·5	Quartz	81	10
2-Naphthyl *o*-iodobenzoate	4	Quartz	99	14

* Isolated as the 3,5-dinitrobenzoate.

Of the esterifying acids so far investigated, fluorene-9-carboxylic acid appears to be the most useful. A clear differentiation between the regeneration of phenolic and of non-phenolic hydroxyl groups can be secured.

In connection with model compounds for phenol oxidation studies we report briefly in the Experimental section the synthesis of the bisphenol (VI) by several different routes and

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[6] J. B. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 1960, 217; H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293.

[7] W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.*, 1962, **84**, 1561.

its oxidation to the spiro-dienone (VII). Also recorded is the phosgenation of methylenebis-2-naphthol (VIII) to give the cyclic carbonate (IX) when potassium carbonate was employed and the normal oxidation product (XI) of the bisphenol (VIII) when collidine was used as base. The formation of the enone (XI) can be formulated as a fragmentation reaction on intermediate (X).

EXPERIMENTAL

Melting points were taken on a Kofler hot-stage apparatus. Unless specified to the contrary, infrared spectra were taken for Nujol mulls.

General Procedure for the Photolysis of 2,4-Dinitrobenzenesulphenyl Esters.—The ester (250 mg.) in dry benzene or ether (125 ml.) contained in a Pyrex flask was irradiated under reflux in a nitrogen atmosphere with a 125 w high-pressure mercury lamp. A stream of nitrogen was passed through the flask and then through two wash-bottles in series containing 0·1N-sodium hydroxide. The reaction was followed by infrared or ultraviolet control and was complete in 1 hr. No carbon dioxide was evolved (titration). The appropriate (dark) thermal reactions were run in each case with no change being produced in the ester.

Photolysis of 2,4-Dinitrobenzenesulphenyl Acetate.—After photolysis of the ester[3,8] (250 mg.) the precipitate of impure 2-amino-4-nitrobenzenesulphonic acid[9] was removed by filtration. This was taken up in ethanol and reprecipitated with benzene to give the aminosulphonic acid (19%) as a brown amorphous powder identified by infrared comparison. Treatment with bromine in 50% sulphuric acid gave[10] 2,4,6-tribromo-3-nitroaniline, identified by m. p., mixed m. p., and infrared spectrum. In digesting the aminosulphonic acid with ethanol a small yellow precipitate remained undissolved. This was identified as 2,2′,4,4′-tetranitrodiphenyl disulphide[11] (6%) by infrared comparison.

The original benzene solution after photolysis was extracted with 2N-sodium hydroxide (4 × 50 ml.) and the extract acidified with 6N-sulphuric acid and steam-distilled. The distillate titrated for acetic acid (92%). Conversion into the *p*-bromophenacyl ester in the usual way confirmed (m. p., mixed m. p., and infrared comparison) that acetic acid was present.

The benzene layer was evaporated *in vacuo* to furnish a yellow solid. This was chromatographed over alumina (Grade III), eluting with 1 : 1 benzene–light petroleum (b. p. 40—60°), to give 2,4-dinitrodiphenyl sulphide[12] (73%), identified by m. p., mixed m. p., and infrared and n.m.r. comparison.

The photolysis of the acetate was repeated in ether with the same yield of acetic acid. It was also repeated in benzene containing anisole (1 mol.). Working up the benzene layer afforded 4-methoxy-2′,4′-dinitrodiphenyl sulphide (74%), identified by m. p., mixed m. p. (see below), and infrared and n.m.r. comparison.

In a further experiment the ester in benzene was irradiated in the usual way and then cyclohexylamine (100 mol.) was added and the solution refluxed for 10 min. Determination of the acetic acid produced (see above) gave 89%.

4-Methoxy-2′,4′-dinitrodiphenyl Sulphide.—*p*-Methoxybenzenethiol[13] (3·84 g.) in ethanol (50 ml.) was added to 1-chloro-2,4-dinitrobenzene (5·55 g.) in the same solvent (50 ml.). Aqueous sodium hydroxide (1N) was added dropwise with agitation until the solution was just alkaline, and then dilute hydrochloric acid (1N; 1 drop). The yellow precipitate was filtered off, digested with cold water, and refiltered. Crystallisation from benzene–ethanol gave *4-methoxy-2′,4′-dinitrodiphenyl sulphide* (84%) as needles, m. p. 116—117° (Found: C, 51·4; H, 3·4. $C_{13}H_{10}N_2O_5S$ requires C, 51·0; H, 3·3%).

The n.m.r. spectrum in carbon tetrachloride gave the following τ values: 1·02 (doublet, $J = 2{\cdot}5$ c./sec.; 1 proton), 1·90 (quartet, $J = 9$ and $J = 2{\cdot}5$ c./sec.; 1 proton), 2·51 and 2·98 (AB quartet, $J = 9$ c./sec.; 4 protons), 3·05 (doublet, $J = 9$ c./sec.; 1 proton), and 6·05 (singlet; 3 protons).

Photolysis of Other 2,4-Dinitrophenylsulphenyl Esters.—Prepared according to the general

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[8] R. E. Putnam and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 6526.

[9] N. Kharasch, W. King, and T. C. Bruice, *J. Amer. Chem. Soc.*, 1955, **77**, 931.

[10] R. L. Dhatta and J. C. Bhoumik, *J. Amer. Chem. Soc.*, 1921, **43**, 311.

[11] M. Claass, *Ber.*, 1912, **45**, 753.

[12] M. T. Bogert and R. L. Evans, *Ind. Eng. Chem.*, 1926, **18**, 301.

[13] C. M. Suter and H. L. Hansen, *J. Amer. Chem. Soc.*, 1932, **54**, 4100.

procedure of Havlik and Kharasch[3] 2,4-dinitrobenzenesulphenyl phenylacetate had m. p. 92—95° (decomp.), $\lambda_{max.}$ 352 and 303 (ε 3850 and 10,150, in ether), $\nu_{max.}$ (in $CHCl_3$) 1765, 1603, 1540, and 1350 cm.$^{-1}$, whilst 2,4-dinitrobenzenesulphenyl n-hexanoate had m. p. 74—78°, $\lambda_{max.}$ 282, 326, and 370 mμ (ε 6650, 8850, and 3150), $\nu_{max.}$ (in CCl_4) 1785, 1603, 1515, and 1340 cm.$^{-1}$.

2,4-Dinitrobenzenesulphenyl phenylacetate (680 mg.) in ether (300 ml.) was photolysed as above for 2 hr. (infrared control). The precipitate was removed by filtration and identified (cf. above) as crude 2-amino-4-nitrobenzenesulphonic acid. The ether solution was extracted with aqueous sodium hydroxide (2N; 3 × 30 ml.), and the extract acidified with sulphuric acid (6N) and extracted with ether. Removal of the ether *in vacuo* afforded an acid fraction which was taken up in benzene–ether (1 : 1) and filtered through silica (40 g.). The eluent (300 ml.) was evaporated to furnish crystalline phenylacetic acid (88%), identified by m. p., mixed m. p., and infrared spectrum. No carbon dioxide was evolved.

2,4-Dinitrobenzenesulphenyl n-hexanoate (580 mg.) in benzene (200 ml.) was photolysed as above for 2 hr. (disappearance of band at 1785 cm.$^{-1}$). The precipitate was filtered off and the solvent removed *in vacuo*. The residue was digested with light petroleum (b. p. 60—80°) and the solution extracted with aqueous sodium hydrogen carbonate. Acidification with 2N-sulphuric acid and re-extraction into ether gave n-hexanoic acid (61%), identified by infrared spectrum and by conversion into the *p*-bromophenacyl ester (m. p., mixed m. p., and infrared comparison). The precipitate formed during the photolysis (226 mg.) was crude 2-amino-4-nitrobenzenesulphonic acid.

In a further experiment, 2,4-dinitrobenzenesulphenyl n-hexanoate (345 mg.) in ether (200 ml.) was photolysed as above for 3 hr. (infrared control). After filtration, the ether was extracted with 2N-aqueous sodium hydroxide (3 × 30 ml.). The alkaline solution was made strongly acid with sulphuric acid (6N) and distilled. The volatile acid (98%), contained in the first 50 ml. of distillate, was converted into *p*-bromophenacyl n-hexanoate (83%) (m. p. and mixed m. p.) in the usual way.

2,4-Dinitrobenzenesulphenyl chloride is also as sensitive to irradiation as the other sulphenyl esters but affords tarry products. In contrast, 2,4-dinitrophenyl benzyl sulphide and 2,4-dinitrodiphenyl sulphide were recovered unchanged after prolonged irradiation in either benzene or ether.

2-*Naphthyl Triphenylacetate*.—Triphenylacetyl chloride[14] (1 mmole) in dry benzene (15 ml.) was added to 2-naphthol (1 mmole) in the same solvent (10 ml.) containing pyridine (1 ml.) and heated under reflux for 3 hr. The solution was washed with water, 2N-sodium hydroxide, 2N-hydrochloric acid, 2N-sodium carbonate, and water, and dried (Na_2SO_4). Removal of the solvent *in vacuo* and filtration in benzene through alumina (Grade III) gave 2-*naphthyl triphenylacetate*, needles (57%), m. p. 169—170° [from benzene–light petroleum (b. p. 40—60°)], $\nu_{max.}$ 1750 cm.$^{-1}$ (Found: C, 86·9; H, 5·7. $C_{30}H_{22}O_2$ requires C, 86·95; H, 5·35%).

2-*Naphthyl Fluorene*-9-*carboxylate*.—Fluorene-9-carboxylic acid chloride[15] (136·2 mg.) in dry benzene (15 ml.) was treated with 2-naphthol (86·4 mg.) in dry benzene (10 ml.) containing pyridine (1 ml.) and left for 1 hr. at room temperature. Filtration of the product in benzene through alumina (Grade III) and crystallisation from benzene–light petroleum (b. p. 40—60°) gave 2-*naphthyl fluorene*-9-*carboxylate* (65%), m. p. 143—144°, $\nu_{max.}$ 1755 cm.$^{-1}$ (Found: C, 85·75; H, 4·75. $C_{24}H_{16}O_2$ requires C, 85·7; H, 4·8%).

2-*Naphthyl Xanthen*-9-*carboxylate*.—This compound was prepared from xanthen-9-carboxylic acid chloride[16] and 2-naphthol exactly as for the fluorene analogue (see above). Recrystallised from acetone, 2-*naphthyl xanthen*-9-*carboxylate* formed needles (68%), m. p. 168—169°, $\nu_{max.}$ 1760 cm.$^{-1}$ (Found: C, 81·7; H, 4·45. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·6%).

Further Esters of Fluorene-9-*carboxylic Acid*.—Reaction of the acid chloride with *p*-cresol as for the procedure (see above) with 2-naphthol afforded p-*cresyl fluorene*-9-*carboxylate*, prisms (67%), m. p. 114—115° (from cyclohexane), $\nu_{max.}$ 1755 cm.$^{-1}$ (Found: C, 83·95; H, 5·25. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·35%).

Similar reaction of the acid chloride with guaiacol gave *guaiacycl fluorene*-9-*carboxylate*, large prisms (66%), m. p. 116—117° [from carbon tetrachloride–light petroleum (b. p. 40—60°)], $\nu_{max.}$ 1760 cm.$^{-1}$ (Found: C, 80·15; H, 5·05. $C_{21}H_{16}O_3$ requires C, 79·75; H, 5·1%).

[14] L. W. Jones and C. D. Hurd, *J. Amer. Chem. Soc.*, 1921, **43**, 2422.

[15] D. Vorlander and A. Pritzsche, *Ber.*, 1913, **46**, 1793.

[16] J. W. Cusic, U.S.P. 2,650,230 (*Chem. Abs.*, 1954, **48**, 11,500).

Similarly, *cholesteryl fluorene-9-carboxylate* was prepared. Recrystallised from benzene–light petroleum (b. p. 40—60°) this (61%) formed needles, m. p. 179—180°, $\nu_{max.}$ 1730 cm.$^{-1}$ (Found: C, 85·05; H, 9·3. $C_{41}H_{54}O_2$ requires C, 85·05; H, 9·4%).

Methyl fluorene-9-carboxylate (91%), needles, m. p. 63° (from methanol), $\nu_{max.}$ 1730 cm.$^{-1}$, was obtained according to the procedure of Tucker.[17]

Cholesteryl Xanthen-9-carboxylate.—Prepared from xanthen-9-carboxylic acid chloride and cholesterole, as for the 2-naphthol analogue (see above), *cholesteryl xanthen-9-carboxylate* (68%) crystallised from ethyl acetate as plates, m. p. 165—166°, $\nu_{max.}$ 1720 cm.$^{-1}$ (Found: C, 82·75; H, 9·0. $C_{41}H_{54}O_3$ requires C, 82·8; H, 9·15%).

General Procedure for the Irradiation of Carboxylic Esters.—The ester (about 0·5 mmole), in dry oxygen and peroxide-free solvent (125 ml.) in a Pyrex or quartz flask (250-ml.) equipped with a Hershberg stirrer, a nitrogen inlet, and an efficient reflux condenser, was irradiated with a Phillips 125 w high-pressure mercury arc lamp (57236F/21). The course of the photolysis was followed by ultraviolet and/or infrared measurements.

For each compound studied an appropriate thermal blank reaction was run for several times the period employed in the photolysis. In no case was there any thermal reaction.

The photolysis products were separated (2N-sodium hydroxide) into base-soluble and base-insoluble portions. The latter were discarded.

Irradiation of 2-Naphthyl Trichloroacetate and Triphenylacetate.—The trichloroacetate[18] (0·5 mmole) in dry ether (125 ml.) was irradiated under reflux in a quartz flask for 3 hr. (disappearance of infrared band at 1775 cm.$^{-1}$). The product was separated by extraction with 2N-aqueous sodium hydroxide into phenolic and non-phenolic fractions. The former (29 mg.) was chromatographed over alumina (Grade III). Elution with benzene–ether (4 : 1) gave 2-naphthol (21 mg.) (m. p., mixed m. p., and infrared spectrum).

The triphenylacetate (see above), irradiated and further processed in the same way, gave 2-naphthol (39%).

Irradiation of 2-Naphthyl Fluorene-9-carboxylate and Xanthen-9-carboxylate.—2-Naphthyl fluorene-9-carboxylate was irradiated in a Pyrex flask and further processed in the same way as for 2-naphthyl trichloroacetate (see above), to furnish 2-naphthol (60%).

In a further experiment, the exit gases were passed over iodine pentoxide at 120° and through saturated barium hydroxide (100 ml.). The yield of carbon monoxide determined iodometrically was 93%, and gravimetrically (as barium carbonate) 87%.

2-Naphthyl xanthen-9-carboxylate was irradiated in a Pyrex flask and further processed as for 2-naphthyl trichloroacetate (see above), to furnish 2-naphthol (60%).

Irradiation of Various Esters of Fluorene-9-carboxylic Acid.—All irradiations and further processing of the products were carried out as for 2-naphthyl trichloroacetate (see above). The *p*-cresyl ester (see above) gave *p*-cresol, isolated as the 3,5-dinitrobenzoate (58%). The guaiacyl ester, irradiated in a quartz flask for 2 hr., gave guaiacol (58%). Cholesteryl fluorene-9-carboxylate was unchanged after prolonged irradiation in both ether (96% recovery) and methylcyclohexane (94% recovery). Methyl fluorene-9-carboxylate was likewise recovered unchanged after prolonged irradiation in dry ether (94% recovery).

Irradiation of Cholesteryl Xanthen-9-carboxylate.—The ester (297 mg.) in dry ether (125 ml.) was irradiated in a quartz flask for 6 hr. with no diminution in the intensity of the ester band at 1720 cm.$^{-1}$. Removal of the solvent *in vacuo* and crystallisation from ethyl acetate gave unchanged ester (93%).

Preparation and Irradiation of 2-Naphthyl o-*(Phenylthiomethyl)benzoate*.—Phthalide (109 mg.) in dry dimethylformamide (25 ml.) containing sodium hydride (60 mg.) and thiophenol (0·089 ml.) was heated under reflux for 4 hr. Crystallisation of the product from cyclohexane–light petroleum (b. p. 60—80°) furnished o-*(phenylthiomethyl)benzoic acid* as plates (71%), m. p. 109—110°, $\nu_{max.}$ 1710 cm.$^{-1}$ (Found: C, 68·9; H, 4·9. $C_{14}H_{12}O_2S$ requires C, 69·05; H, 5·0%). This acid was treated with oxalyl chloride in benzene under reflux and the product treated with 2-naphthol in the usual way. Crystallisation from cyclohexane–light petroleum (b. p. 40—60°) gave 2-*naphthyl* o-*(phenylthiomethyl)benzoate*, m. p. 84—85°, $\nu_{max.}$ 1740 cm.$^{-1}$ (Found: C, 78·15; H, 4·8. $C_{24}H_{18}O_2S$ requires C, 77·85; 4·8%).

Irradiation of this ester for 30 min. in ether in a quartz flask (infrared control) afforded 2-naphthol (9%).

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[17] S. H. Tucker, *J.*, 1949, 2182.

[18] J. Houben and W. Fischer, *Ber.*, 1927, **60**, 1759.

Preparation and Irradiation of 2-Naphthyl o-*Iodobenzoate*.—*o*-Iodobenzoyl chloride [19] was treated with 2-naphthol in the usual way, to furnish 2-*naphthyl* o-*iodobenzoate*, prisms, m. p. 85—86° [from ethyl acetate–light petroleum (b. p. 40—60°)], $\nu_{max.}$ 1740 cm.$^{-1}$ (Found: C, 54·2; H, 2·9. $C_{17}H_{11}IO_2$ requires C, 54·55; H, 2·95%).

Irradiation in a quartz flask for 4 hr. (infrared control) gave 2-naphthol (14%).

3-(p-*Acetoxyphenyl*)*coumarin and* 2,4′-*Diacetoxystilbene*-β-*carboxylic Acid*.—*p*-Hydroxyphenylacetic acid (1·124 g.) and redistilled salicylaldehyde (0·576 ml.) in acetic anhydride (3·2 ml.) and triethylamine (0·8 ml.) were heated under reflux for 5 hr. On cooling to room temperature, 3-p-*acetoxyphenylcoumarin* separated and was filtered off. Recrystallised from ethanol–acetone this formed needles (57%), m. p. 181—182°, $\nu_{max.}$ 1720 and 1770 cm.$^{-1}$ (Found: C, 73·2; H, 4·15. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%).

The filtrate was diluted with water and extracted with ether. Further processing of the ethereal extract in the usual way and crystallisation of the product from aqueous ethanol gave 2,4′-*diacetoxystilbene*-β-*carboxylic acid* as needles (14%), m. p. 177—178°, $\nu_{max.}$ 1695 and 1760 cm.$^{-1}$ (Found: C, 66·6; H, 5·3. $C_{19}H_{16}O_6$ requires C, 67·1; H, 4·7%).

4-*Acetoxy*-2′-*benzyloxystilbene*-α-*carboxylic Acid*.—*p*-Hydroxyphenylacetic acid (750 mg.) and salicylaldehyde benzyl ether in acetic anhydride (3·2 ml.) and triethylamine (0·7 ml.) were heated under reflux for 5 hr. The mixture was poured into water and extracted with ether. The ethereal extract was washed with saturated sodium hydrogen carbonate and dried (Na_2SO_4). Removal of the solvent *in vacuo* and crystallisation of the product from ethanol–light petroleum afforded 4-*acetoxy*-2′-*benzyloxystilbene*-α-*carboxylic acid* as needles (54%), m. p. 163—175°, $\nu_{max.}$ 1670 and 1770 cm.$^{-1}$ (Found: C, 74·4; H, 5·1. $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·2%). The wide m. p. range suggests a mixture of stereoisomers. Separation was not attempted.

2,4′-*Dihydroxybibenzyl*.—(*a*) 4-Acetoxy-2′-benzyloxystilbene-α-carboxylic acid (see above) (236·4 mg.) in redistilled quinoline (2·5 ml.) was heated with copper chromite [20] (23·6 mg.) at 210—220° for 1·25 hr. The product was poured into 2N-hydrochloric acid (excess) and extracted with ether. The ether was removed *in vacuo*, and the residue in dry pyridine (10 ml.) was treated with acetic anhydride (5 ml.) and kept at room temperature overnight. The crude 4-acetoxy-2′-benzyloxystilbene thus produced could not be crystallised. A portion (110 mg.) in ethanol (25 ml.) was hydrogenated over 10% palladised charcoal (10 mg.) for 5 hr. (2 mol. uptake). Crystallisation of the product from benzene–light petroleum (b. p. 40—60°) gave 4-*acetoxy*-2′-*hydroxybibenzyl* as needles (91%), m. p. 93—95° (Found: C, 75·0; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). This acetoxy-phenol (250 mg.) was heated under reflux in 10% aqueous sodium hydroxide (50 ml.) for 1·5 hr. (all dissolved). Working up in the usual way and crystallisation of the product from benzene–light petroleum (b. p. 40—60°) gave 2,4′-*dihydroxybibenzyl* as needles (93%), m. p. 132—133° (Found: C, 77·4; H, 6·5. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%).

(*b*) 4-Benzyloxybenzyl chloride (820 mg.) in benzene (10 ml.) was treated with triphenylphosphine (830 mg.) in the same solvent (10 ml.) at room temperature. The crystalline precipitate was filtered off and recrystallised from benzene, to furnish 4-*benzyloxybenzyltriphenylphosphonium chloride* (essentially quantitative), m. p. 242—243° (Found: ionic Cl, 7·0. $C_{32}H_{28}ClOP$ requires Cl, 7·2%).

Sodium (46 mg.) was dissolved in ethanol (50 ml.) and 4-benzyloxybenzyltriphenylphosphonium chloride (990 mg.) added. Salicylaldehyde benzyl ether (424 mg.) in ethanol (25 ml.) was then run in and the mixture stirred at room temperature for 24 hr. Filtration and recrystallisation from benzene–light petroleum (b. p. 40—60°) afforded 2,4′-*dibenzyloxystilbene* as needles (53%), m. p. 124—125° (Found: C, 85·3; H, 6·1. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·15%). This stilbene (250 mg.) in ethanol (50 ml.) was hydrogenated over 10% palladised charcoal (25 mg.) for 5 hr. (3 mol. uptake). Crystallisation of the product from benzene–light petroleum (b. p. 40—60°) gave 2,4′-dihydroxybibenzyl (93%) (see above).

(*c*) 4-Benzyloxybenzyl chloride (670 mg.) and triethyl phosphite (0·472 ml.) were heated at 160° for 90 min. (no further evolution of ethyl chloride). Distillation of the product gave 4-benzyloxybenzyl diethyl phosphonate (85%), b. p. 185°/0·4 mm. This ester (345 mg.) was treated [21] with salicylaldehyde benzyl ether (219 mg.) and sodium methoxide (796 mg.) in dry dimethylformamide (10 ml.) and left overnight at room temperature. The mixture was poured

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[19] L. C. Raiford and H. P. Lankelma, *J. Amer. Chem. Soc.*, 1925, **47**, 1121.

[20] *Org. Synth.*, Coll. Vol. II, p. 142.

[21] E. J. Sens and C. V. Wilson, *J. Org. Chem.*, 1961, **26**, 5243.

into ice–water and the product filtered off. Recrystallisation from benzene–light petroleum (b. p. 40—60°) gave 2,4'-dibenzyloxystilbene (75%) identical with material described above.

Oxidation of 2,4'-Dihydroxybibenzyl.—2,4'-Dihydroxybibenzyl (533 mg.) in 2N-sodium hydroxide (300 ml.) was added dropwise with good stirring during 90 min. to a mixture of ether (200 ml.) and water (600 ml.) containing potassium ferricyanide (6 g.) under nitrogen. The ether layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. Chromatography of the residue over alumina (Grade III), and crystallisation from benzene–light petroleum (b. p. 40—60°), gave the *oxidation product* (VII) as needles (11%), m. p. 135—136°, $\nu_{max.}$ 1665 cm.$^{-1}$ (Found: C, 79·3; H, 5·9. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%).

Phosgenation of Methylenebis-2-naphthol.—(*a*) Methylenebis-2-naphthol (250 mg.) in dry toluene (100 ml.) containing suspended anhydrous potassium carbonate (1 g.) was heated under reflux for 5 hr. while phosgene was passed continuously. Removal of the solvent *in vacuo* and crystallisation from benzene gave the *cyclic carbonate* (IX) as prisms (67%), m. p. 235—236°, $\nu_{max.}$ 1765 cm.$^{-1}$ [Found: C, 80·65; H, 4·25%; *M* (Rast), 343. $C_{22}H_{14}O_3$ requires C, 80·95; H, 4·3%; *M*, 326].

(*b*) Dry benzene (75 ml.) was saturated with phosgene at the b. p., and further phosgene passed during the addition of methylenebis-2-naphthol (201·8 g.) and collidine (0·1735 ml.) in dry benzene (50 ml.). Th solution was then heated under reflux for a further 15 min., filtered, and the solvent removed *in vacuo*. The product was chromatographed over alumina (Grade V). Elution with benzene–light petroleum (b. p. 40—60°) (1 : 1) gave the cyclic carbonate (IX) already described (46%). Elution with benzene afforded the known [22] oxidation product (XI) of methylenebis-2-naphthol (24%). Recrystallised from ethanol this had m. p. 171—172° and was identified by mixed m. p. and comparative infrared spectra.

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[22] R. Pummerer and E. Cherbuliez, *Ber.*, 1914, **47**, 2957.