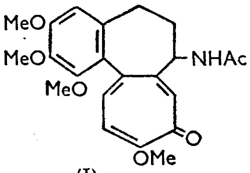
556. *Photochemical Transformations of Tropolones. Part I. Tetra-O-methylpurpurogallin.*

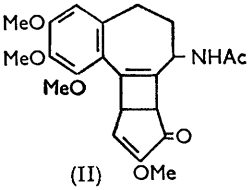
By E. J. Forbes and R. A. Ripley.

Dilute aqueous-alcoholic solutions of tetra-*O*-methylpurpurogallin (III) in sunlight give a number of products, including methyl 6,7,8-trimethoxy-1-naphthoate (VI). The course of the reaction is discussed.

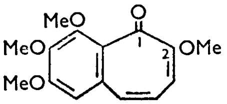
Apart from a recent communication on γ-tropolone methyl ether[1] the photosensitivity of simple tropolones appears to have passed unreported. Of the more complex tropolones, only colchicine (I) has been investigated. It is converted in aqueous solution by sunlight into three isomers,[2] two of which have been shown to have stereoisomeric structures[3] (II), for which confirmatory evidence has been adduced by Gardner *et al.*[4] These results demonstrate that at least the tropolone ring has been involved in the transformations. For closer study we have investigated the action of light on a number of simple tropolones and the readily available tetra-*O*-methylpurpurogallin (III). The last compound gave an unexpected result.



(I)



(II)



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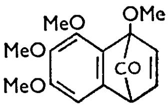

(IV)

Aqueous-alcoholic solutions of tetra-*O*-methylpurpurogallin were irradiated in Pyrex tubes initially with a mercury vapour lamp. Ultraviolet spectroscopic data indicated that much starting material remained even after 165 hours. This suggested that, since the tropolone methyl ether absorbs strongly and over a wide range of frequencies in the near ultraviolet region, the use of sunlight might be more efficacious. When dilute solutions of the ether (III) were exposed to quite moderate sunlight under nitrogen, spectroscopic evidence indicated that no starting material remained after 2—3 weeks.

The residues from the methylene chloride extracts of these solutions were chromatographed. The first fractions afforded a colourless crystalline material, m. p. 81—82°. Elemental analysis and a methoxyl determination show that it is a photo-isomer of the ether (III). Its ultraviolet spectrum (see Figure) closely resembles that of the final irradiated solution and differs from that of the starting material. Its infrared spectrum showed a single band in the carbonyl region at 1748 cm.$^{-1}$, which suggested a saturated five-ring ketone and was consistent with one of our possible products (IV). We were not, however, able to obtain any carbonyl derivatives even under forcing conditions, and the compound was unaffected by sodium borohydride. It absorbed 2 mols. of hydrogen catalytically, but no crystalline product could be isolated; the infrared spectrum of the

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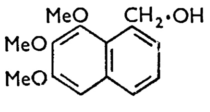
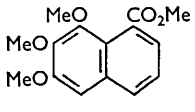
[1] Chapman and Pasto, *J. Amer. Chem. Soc.*, 1958, **80**, 6685.
[2] Grewe and Wulf, *Chem. Ber.*, 1951, **84**, 621.
[3] Forbes, *J.*, 1955, 3864.
[4] Gardner, Brandon, and Haynes, *J. Amer. Chem. Soc.*, 1957, **79**, 6334.

crude product differed appreciably from that of the starting material in the finger-print region, but the " carbonyl " band remained unaltered at 1748 cm.$^{-1}$. The photo-isomer in carbon tetrachloride slowly absorbed 2 mols. of bromine. The compound was recovered unchanged after 3 hours' boiling with alcoholic potassium hydroxide though the sequel shows that it is in fact an ester.

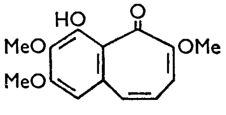
Structure (IV) implies considerable steric hindrance to reactions at the carbonyl centre and could be consistent with our findings in this respect. Reaction with lithium aluminium hydride would, however, be expected and could lead to the naphthalene (V) *via* an intermediate aldehyde. The alcohol (V) could well be obtained from the known



(V)

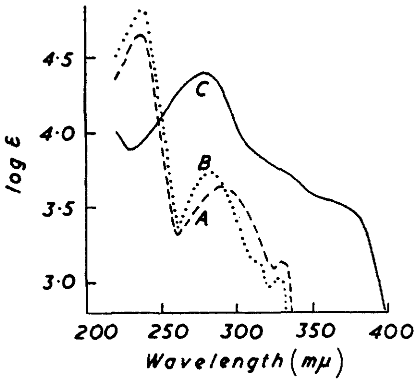


(VI)



(VII)

ester (VI) which had been synthesised by Haworth, Moore, and Pauson.[5] This ester (VI) has m. p. 80—81° practically identical with that of our photo-isomer. The two compounds were shown to be identical when we prepared the ester from tri-*O*-methylpurpurogallin (VII); [5] and they yielded the same product on reduction with lithium aluminium hydride. The structure of this compound (V) was established by its elemental analysis, methoxyl determination, the presence of a band at 3600 cm.$^{-1}$ (hydroxyl) and the absence of a band in the carbonyl region of the infrared spectrum.



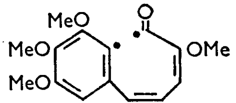
Light absorption in ethanol of (A) methyl 6,7,8-*trimethoxy*-1-*naphthoate,* (*B*) 1-*hydroxymethyl*-6,7,8-*trimethoxynaphthalene, and* (*C*) *tetra*-O-*methylpurpurogallin.*

The structure (VI) accounts also for the " carbonyl " band at 1748 cm.$^{-1}$. Steric hindrance between the ester and the *peri*-methoxyl group forces the ester group out of the plane of the ring so that it is hardly conjugated with the ring. Its infrared absorption will thus be typical of a saturated rather than a phenyl-conjugated ester. This steric effect accounts also for the close similarity between the ultraviolet spectra of the ester (VI) and the alcohol (V) (see Figure). The unusual resistance of the ester to hydrolysis has already been described by Haworth *et al.*[5]

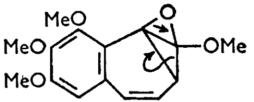
In our preparation of the ester (VI) from tri-*O*-methylpurpurogallin (VII), the rearrangement of the tropolone is carried out in ethylene glycol, rather than in ethanol in a sealed tube.[5] This is more convenient but the yield is not increased. Our attempts to convert the tropolone (III) directly into the ester (VI), with sodium methoxide in methanol, gave only the trimethyl ether (VII). The stability of this tropolone (III) towards alkali was demonstrated when some of it was recovered after treatment with alcoholic potassium hydroxide. This experiment gave also 6,7,8-trimethoxy-1-naphthoic acid.

[5] Haworth, Moore, and Pauson, *J.*, 1949, 3271.

Since the methyl ester (VI) is unaccompanied by the analogous ethyl ester although ethanol is present in great excess, the photochemical transformation must be intramolecular. This contrasts with the ionic conversion of tropolones into benzenoid compounds which is intermolecular.[6] The intramolecular reaction appears to be unique and has two possible courses. The first involves initial fission of the tropolone ring to a diradical (VIII). Cyclisation to a six-membered ring and migration of the methoxyl group complete the process. The second and perhaps more likely course would involve the formation of a high-energy intermediate such as (IX) followed by a rearrangement of electrons. Fission of the tropolone ring as such and migration of a methoxyl group are not involved. Moreover, by this mechanism $C_{(2)}$ of the tropolone ring is displaced, whereas by the first mechanism $C_{(1)}$ is displaced to form the side-chain. This point will be settled by isotopic carbon studies. Other products of the reaction are being examined, also the influence of solvents on the course of the reaction.



(VIII)



(IX)

EXPERIMENTAL

Infrared and ultraviolet spectra were measured respectively in carbon disulphide and ethanol.

*Irradiation of Tetra-*O*-methylpurpurogallin.*—(a) *By use of a mercury-vapour lamp* (Hanovia UVS 500). A solution of tetra-*O*-methylpurpurogallin[7] (100 mg.) in 20% v/v aqueous ethanol (50 c.c.) was irradiated under nitrogen. The ultraviolet spectrum of the solution was measured at intervals, and showed that much starting material remained after 165 hr.

(b) *In sunlight.* Tetra-*O*-methylpurpurogallin, m. p. 93—94° (3·0 g.), was dissolved in a mixture of oxygen-free water (700 c.c.) and ethanol (300 c.c.). The warmed solution (*ca.* 50°) was sealed up in a long glass tube under nitrogen. After 28 days' exposure to moderate summer sunlight the clear solution (which had darkened somewhat) was extracted with methylene chloride (3 × 200 c.c.). The combined extracts were dried rigorously ($MgSO_4$) and evaporated under reduced pressure (at *ca.* 25°). The residual gum (2·9 g.), which did not crystallise, was chromatographed in dry benzene on neutral alumina (Brockmann III—IV). Eluting the column with benzene gave 7 fractions (total 1·42 g.). Further elution with benzene containing 2% of methanol gave only a non-crystalline solid.

When boiled with light petroleum (b. p. 40—60°), fraction 1 gave a solid which on recrystallisation from light petroleum (charcoal) afforded colourless prisms of methyl 6,7,8-trimethoxy-1-naphthoate, m. p. 81—82° (Found: C, 65·4; H, 6·1; OMe, 44·3. Calc. for $C_{15}H_{16}O_5$: C, 65·2; H, 5·8; 4OMe, 44·9%), $\lambda_{max.}$ 238 and 290 mμ, (ε 45,660 and 4560 respectively), $\nu_{max.}$ 1748 cm.$^{-1}$. The compound showed no m. p. depression on admixture with an authentic specimen.

Fractions 2—7 were combined and again chromatographed on neutral alumina with benzene as eluent, giving (*a*) a further quantity of the photo-isomer (total 0·45 g., 15%, of pure material), (*b*) an amorphous compound (CO band at 1710 cm.$^{-1}$), and (*c*) a non-crystalline solid which appears to be polymeric.

1-*Hydroxymethyl*-6,7,8-*trimethoxynaphthalene* (V).—Methyl 6,7,8-trimethoxy-1-naphthoate (196 mg.) in dry ether (10 c.c.) was added to a cooled suspension of lithium aluminium hydride (200 mg.) in dry ether (10 c.c.). The mixture was heated under reflux for 2 hr., cooled, treated with water and dilute sulphuric acid, and extracted with ether. The extract was dried and evaporated, and the residue was chromatographed in dry benzene on neutral alumina (Brockmann III—IV). Elution with benzene gave 1-*hydroxymethyl*-6,7,8-*trimethoxynaphthalene* which crystallised from benzene–light petroleum in plates (95 mg.), m. p. 85—86° (Found: C, 67·7; H, 6·5; OMe, 37·2. $C_{14}H_{16}O_4$ requires C, 67·6; H, 6·5; OMe, 37·5%). The compound showed no m. p. depression on admixture with that obtained by reduction of the irradiation

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[6] Pauson, *Chem. Rev.*, 1955, **55**, 1.

[7] Haworth, Moore, and Pauson, *J.*, 1948, 1045.

product with lithium aluminium hydride. Both specimens had $\nu_{max.}$ 3600 cm.$^{-1}$, $\lambda_{max.}$ 237 and 285 mμ (ε 64,870 and 6000 respectively).

Methyl 6,7,8-*Trimethoxy*-1-*naphthoate*.—Tri-*O*-methylpurpurogallin (Haworth *et al.*[6]) (3 g.) was heated with potassium hydroxide (5 g.) in ethylene glycol (45 c.c.) under nitrogen for 4 hr. at 160—170°, cooled, acidified with dilute hydrochloric acid, and extracted with ether. The extract was evaporated. A solution of the residue in 10% sodium hydroxide was warmed with methyl sulphate at 50° for 30 min. Next morning the slightly acidic solution was washed with 2N-sodium carbonate, dried, and evaporated to give a residue, which distilled at 165°/0·8 mm. A solution of the distillate in benzene was chromatographed on neutral alumina. Elution with benzene gave methyl 6,7,8-trimethoxy-1-naphthoate, prisms, m. p. 81—82° (from light petroleum).

When this experiment was conducted according to the directions of Haworth *et al.*[5], chromatography of the methylated product gave, in addition to the expected ester (VI), a second compound which crystallised from light petroleum in needles, m. p. 111—112°, depressed on admixture with the ester (VI) (Found: C, 67·6; H, 6·2; OMe, 37·4. $C_{14}H_{16}O_4$ requires C, 67·6; H, 6·5; 3OMe, 37·5%). Infrared and ultraviolet light absorption were almost identical with those of tetramethylpurpurogallin. M. p. behaviour established their non-identity.

6,7,8-*Trimethoxy*-1-*naphthoic Acid*.—Tetra-*O*-methylpurpurogallin (4·0 g.), potassium hydroxide (2·5 g.), and methanol (35 c.c.) were heated together in a sealed tube at 165° for 2·5 hr. Saturation of the cooled mixture with carbon dioxide gave a resin. The supernatant liquid was decanted, diluted with water, and extracted overnight with ether. Evaporation of the extract gave a solid (400 mg.) which was obtained crystalline from aqueous ethanol. One further crystallisation from benzene–cyclohexane afforded colourless needles of 6,7,8-trimethoxy-1-naphthoic acid, m. p. 146—147°. Haworth *et al.*[5] give m. p. 145—146°.

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