455. *Triarylmethanes. Part III.* Influence of Substitution on Quinone Formation from Naphthyldiphenylmethane Derivatives.*

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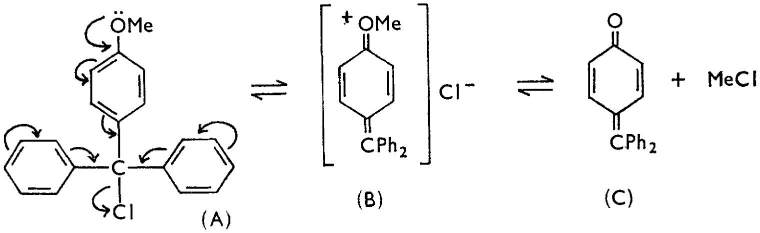
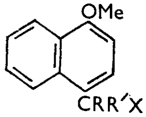
In the formation of the quinonoid naphthafuchsones from naphthyldiphenylmethyl chlorides, an *o*-methyl group in a phenyl group inhibits formation of the carbonium ion and thus of the fuchsone. *p*-Methoxyl groups favour this reaction by their tautomeric effect; and *o*-methoxyl groups form hydrogen bonds which restore planarity and so permit the reaction to proceed.

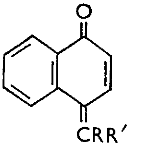
The formation and stability of naphthafuchsones from naphthyldiphenylmethyl chlorides depend on the position and nature of the substituents in the rings.[1,2] In this paper we report a study of the effects of some substituents, basing our interpretation upon what we consider the probable mechanism of the reaction, as follows: A *p*-methoxytriarylmethyl chloride dissociates, owing to hyperconjugative effects[3,4] as in (A), into a chloride ion and a positive ion whose predominant resonance form[5,6] is as in (B); the methyl group then separates with a positive charge, yielding methyl chloride and the product (C).[7]

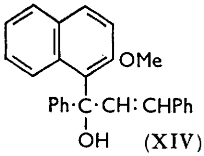




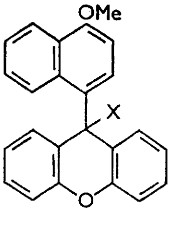
(*a*) X = OH. (*b*) X = Cl.

	R	R	
(I)	Ph	Ph	(XVI)
(II)	o-HO·C_6H_4	Me	
(III)	Ph	CH:CHPh	
(IV)	Ph	o-Me·C_6H_4	
(V)	o-MeC_6H_4	o-Me·C_6H_4	
(VI)	Ph	p-MeO·C_6H_4	(XVII)
(VII)	p-MeO·C_6H_4	p-MeO·C_6H_4	(XVIII)
(VIII)	p-MeO·C_6H_4	o-Me·C_6H_4	
(IX)	Ph	o-MeO·C_6H_4	(XIX)
(X)	o-Me·C_6H_4	o-MeO·C_6H_4	(XX)
(XI)	p-MeO·C_6H_4	o-MeO·C_6H_4	(XXI)
(XII)	o-MeO·C_6H_4	o-MeO·C_6H_4	(XXII)
(XIII)	Ph	o-HO·C_6H_4	(XXIII)





(XIV)



(XV)

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* Part II, *Egypt. J. Chem.*, 1959, **2**, 311.

[1] Anderson and Thomas, *J. Amer. Chem. Soc.*, 1943, **65**, 234.

[2] Fries and Empson, *Ber.*, 1909, **42**, 3375.

[3] de la Mare, Hughes, and Ingold, *J.*, 1948, 17.

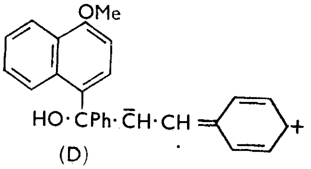
[4] Straus and Dutzman, *J. prakt. Chem.*, 1921, **103**, 1.

[5] Pauling, *Proc. Nat. Acad. Science, U.S.A.*, 1939, **25**, 577.

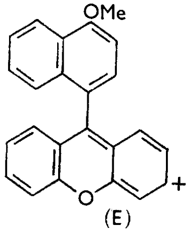
[6] Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2102.

[7] Sandorfy, *Compt. rend.*, 1951, **7**, 633.

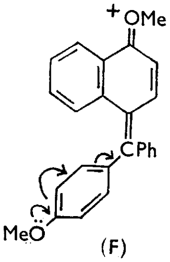
We studied compounds (I)—(XV). These, either as alcohols or chlorides, gave the naphthafuchsones (XVII)—(XXIII). We explain the failures in the other cases as follows. The two aryl groups in the alcohol (II*a*) do not provide sufficient electron density at the methyl-carbon atom for ionisation, so in glacial acetic acid this compound loses water and yields the ethylene. In compound (III*a*) the resonance form (D) prevents reaction, and similarly for compound (XIV). Compound (XV*a*) gives, as predominant form, the ion (E) and here the charge does not involve the methoxyl group.[8] In compounds (IV*b*), (V*b*),[9] and (VIII*b*), the failure is due to the *o*-methyl groups which prevent co-planarity of the molecules.[7,10]



(D)

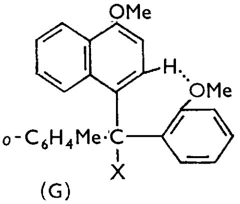


(E)

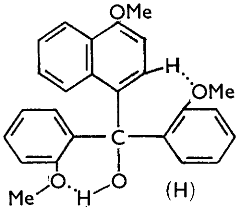


(F)

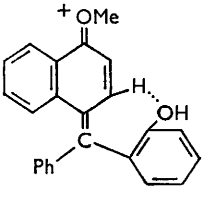
It is noteworthy that when methoxyl groups are present in a phenyl group, it is the methoxyl group from the naphthalene residue that is lost in fuchsone formation. We explain this by the predominance of the form (F).



(G)



(H)



(I)

It remains only to explain why *o*-methoxyl and *o*-hydroxyl groups do not have the same inhibiting effect as the *o*-methyl group. For this we postulate hydrogen-bonding, as in (G), (H), and (I). The transformation of the alcohol (XI*a*) directly to the fuchsone (XXI) involves the formation of a second hydrogen bond as in (H) which facilitates the ionisation of the alcoholic hydroxyl group, the alcohol (XIII*a*) then passing into a fuchsone (XXIII) by forming a hydrogen bond between the same phenolic hydroxyl group and a naphthalene hydrogen atom as in (I).

The *p*-methoxynaphthafuchsone (XVII) exists in two (*cis* and *trans*) forms. Each, when recrystallised, reverts to a mixture of the two, presumably owing to the partial single-bond nature of the ethylenic linking. The *o*-methoxy-isomer was obtained in only one form, and this too may be explained if hydrogen-bonding is assumed.

EXPERIMENTAL

4-*Methoxy*-1-*naphthyl* o-*Tolyl Ketone*.—*o*-Toluoyl chloride (15·4 g.) in carbon disulphide (equal volume) was added to anhydrous aluminium chloride (13·5 g.) and 1-methoxynaphthalene (15·8 g.) in carbon disulphide (300 c.c.) with stirring at <10°. The next day the mixture was stirred and refluxed for 2 hr., then cooled and poured into ice and water acidified with hydrochloric acid. The organic layer was separated and washed and the solvent driven off in steam. The solid residue crystallised (15 g.) from ethanol containing little ether. Recrystallised from

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[8] Gomberg, *Chem. Rev.*, 1925, **1**, 125.

[9] Elkaschef, *Egypt. J. Chem.*, 1959, **2**, 311; Thesis, Paris, 1953.

[10] Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1942, **64**, 1774.

ethanol, it gave the *ketone*, m. p. 92—93°, giving a blood-red colour with sulphuric acid (Found: C, 82·3; H, 5·6. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

α-(4-*Methoxy*-1-*naphthyl*)-2-*methyl*-α-*phenylbenzyl Alcohol* (IV*a*).—To a solution of phenylmagnesium bromide [from bromobenzene (3·14 g.)] in dry ether, a benzene solution of the above ketone (2·76 g.) was added. The mixture was left overnight, refluxed for 3 hr., then decomposed with ammonium chloride and ice. The organic layer and an ethereal extract of the aqueous layer were united, washed, dried (Na_2SO_4), and evaporated. The resulting *alcohol* solidified (2·1 g.) nnder cold ethanol containing a few drops of ether and crystallised from ethanol in yellow prisms, m. p. 132°, giving a yellow colour with concentrated sulphuric acid (Found: C, 84·9; H, 6·0. $C_{25}H_{22}O_2$ requires C, 84·7; H, 6·3%).

α-(4-*Methoxy*-1-*naphthyl*)-2-*methyl*-α-*phenylbenzyl Chloride* (IV*b*).—An ethereal solution of the alcohol (IV*a*) (1·7 g.) and acetyl chloride (1·2 g.), on being refluxed for 2 hr., afforded, on cooling, the crystalline chloride, which was washed with light petroleum (b. p. 70—80°), melted at 138°. The yield was almost quantitative.

This chloride (IVb), when fused at 180° (bath-temperature) for 15 min. and then crystallised from light petroleum (b. p. 110—120°), gave the alcohol (IV*a*), m. p. and mixed m. p. 132°, presumably owing to hydrolysis by moisture.

α-(4-*Methoxy*-1-*naphthyl*)-α-p-*methoxyphenyl*-2-*methylbenzyl Alcohol* (VIII*a*).—The above ketone (2·76 g.) and *p*-methoxyphenylmagnesium bromide (from *p*-bromoanisole, 3·74 g.), in reaction as above, afforded an oil that solidified (1·5 g.) under ethanol containing drops of ether on cooling. Recrystallised from ethanol, this *alcohol* had m. p. 185° and gave an orange-yellow colour with concentrated sulphuric acid (Found: C, 80·8; H, 6·0. $C_{26}H_{24}O_3$ requires C, 81·3; H, 6·3%).

With acetyl chloride (1·2 g.) this alcohol (1·8 g.) gave the chloride (1·5 g.), m. p. 186°. When fused at 190° (bath-temperature) and crystallised from light petroleum (b. p. 110—120°) it gave back the alcohol, m. p. and mixed m. p. 185°.

Similar reactions gave α-(4-*methoxy*-1-*naphthyl*)-α-o-*methoxyphenyl*-2-*methylbenzyl alcohol*, pale yellow, m. p. 161° (from ethanol), giving a blood-red colour with concentrated sulphuric acid (Found: C, 81·7; H, 6·4%). It gave a colourless chloride (X*b*), m. p. 172°.

o-*Methoxy*-o′-*methyl*-α-*naphthafuchsone* (XX).—The chloride (X*b*) was fused at 180° (bath-temperature) till evolution of methyl chloride ceased (*ca.* 15 min.). The fused mass crystallised from light petroleum (b. p. 110—120°), then from ethanol; the *fuchsone* was obtained in nearly theoretical yield as yellow prisms, melting at 175° and giving a violet colour wbth concentrated sulphuric acid (Found: C, 85·5; H, 5·8. $C_{25}H_{20}O_2$ requires C, 85·2; H, 5·7%).i

4-*Methoxy*-1-*naphthyl* p-*Methoxyphenyl Ketone*.—Prepared as its analogue, but from α-methoxynaphthalene (15·8 g.) and *p*-anisoyl chloride (17·0 g.), this *ketone*, obtained from the carbon disulphide layer, crystallised from ethanol (charcoal) as pale yellow needles (15·0 g.), m. p. 107°. It gives blood-red colour with concentrated sulphuric acid (Found: C, 78·1; H, 5·6. $C_{19}H_{16}O_3$ required C, 78·1; H, 5·5%).

α-(4-*Methoxy*-1-*naphthyl*)-4-*methoxy*-α-*phenylbenzyl Alcohol* (VI*a*).—Phenylmagnesium bromide [prepared from bromobenzene (15·7 g.)] and the preceding ketone (14·6 g.) in a reaction as above with 3 hours' boiling and decomposition with ammonium chloride gave an oil that on washing with light petroleum (b. p. below 50°) and cooling under ether afforded a solid *alcohol* (10 g.) which, recrystallised from ethanol, had m. p. 124° and gave a blue colour in concentrated sulphuric acid (Found: C, 81·3; H, 6·2. $C_{25}H_{22}O_3$ requires C, 81·1; H, 5·9%). It gave a chloride, m. p. 156° (decomp.).

p-*Methoxy*-α-*naphthafuchsone* (XVII).—The chloride (VIb) (3·4 g.) was fused at 180° (bath-temperature) until evolution of gas ceased (*ca.* 15 min.). Crystallisation from ether–light petroleum (b. p. $<50°$) gave a mixture of brown and bright red crystals. This mixture could not be resolved by fractional crystallisation or chromatography, but only mechanically. The red *fuchsone* (1 g.) melted at 142° (Found: C, 84·8; H, 5·3. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4%); the brown *isomer* (1 g.) melted at 157° (Found: C, 85·0; H, 5·5%). A rapidly cooled solution in light petroleum (b. p. 70—80°) afforded an apparently homogeneous solid with m. p. 136° similar to that of the mixed m. p. of the separate isomers. Both isomers gave a brownish-red colour with concentrated sulphuric acid.

α-(4-*Methoxy*-1-*naphthyl*)-$\alpha\alpha$-*di*-p-*methoxyphenylmethanol* (VII*a*).—The ketone (14·6 g.) with a Grignard reagent from *p*-bromoanisole (18·7 g.) in a reaction as above gave an oil. When washed with light petroleum (b. p. $<50°$) and cooled under ether this gave a solid *alcohol*

(8·5 g.) that, crystallised from methanol, had m. p. 145° and gave a deep violet colour with concentrated sulphuric acid (Found: C, 77·8; H, 6·4. $C_{26}H_{24}O_4$ requires C, 78·0; H, 6·0%). It gave a chloride, m. p. 148°.

pp′-*Dimethoxy-α-naphthofuchsone* (XVIII).—Fusion of the chloride (VIIb) (4·0 g.) at 170° gave an oil that failed to crystallise. A solution of the oil in 1 : 1 benzene–light petroleum (b. p. 70—80°) was chromatographed through alumina. Elution of the red band and evaporation afforded a solid *fuchsone* that crystallised from the solvent mixture in bright red aggregates (2·0 g.), m. p. 196°, giving a rose-red colour with concentrated sulphuric acid (Found: C, 81·4; H, 5·3. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·4%).

4-*Methoxy-α-*o*-methoxyphenyl-α-*(4-*methoxy-*1-*naphthyl*)*benzyl alcohol*, similarly prepared and recrystallised from ether–ethanol, had m. p. 135—136° and gave a bluish-green colour with concentrated sulphuric acid (Found: C, 77·5; H, 6·3. $C_{26}H_{24}O_4$ requires C, 78·0; H, 6·0%). It gave an oily chloride and thence, at 170—180°, a *fuchsone* which recrystallised from methanol in deep orange needles, m. p. 139—140°, giving a deep violet colour with concentrated sulphuric acid (Found: C, 81·2; H, 5·5. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·4%).

α-(4-*Methoxy*-1-*naphthyl*)-2-*methoxy-α-phenylbenzyl Alcohol* (IX*a*).—A Grignard reagent from *o*-bromoanisole (18·7 g.) and 1-benzoyl-4-methoxynaphthalene [11] (13·1 g.) gave an oil that, after being washed with light petroleum (b. p. below 50°), solidified (13 g.) under ether at 0°. This *alcohol* recrystallised from ether–ethanol in pale yellow crystals, m. p. 160°, giving a bluish-violet colour with concentrated sulphuric acid (Found: C, 80·8; H, 6·3%).

o-*Methoxy-α-naphthafuchsone* (XIX).—The oily chloride (IXb) (3·7 g.) was heated at 170—180°. The oil obtained was purified by chromatography; it slowly crystallised (1·5 g.) under methanol–ether and recrystallised from ether–light petroleum (b. p. $<50°$) in bright yellow prisms, m. p. 118°, giving a violet colour with concentrated sulphuric acid (Found: C, 85·4; H, 5·4%).

o-*Hydroxyphenyl* 4-*Methoxy*-1-*naphthyl Ketone*.—To 1-methoxynaphthalene (15·8 g.) and aluminium chloride (27·0 g.) in carbon disulphide (*ca.* 300 c.c.) at $-5°$, salicyloyl chloride (15·7 g.) was added at $<2°$, and the whole was stirred for 5 hr. The next day it was stirred for 2 hr. at room temperature. It was decomposed as usual. The carbon disulphide layer was filtered from a by-product, m. p. 249° (from chloroform), and the carbon disulphide was removed in steam. The oily residue solidified (15·0 g.) under cold ether–ethanol (1 : 1 v/v). Recrystallised from light petroleum (b. p. 100—120°) this *ketone* gave pale yellow leaflets, m. p. 128°, giving a red colour with sulphuric acid (Found: C, 77·7; H, 4·9. Calc. for $C_{18}H_{14}O_3$: C, 77·7; H, 5·1%).

Using only one mol. of aluminium chloride gave products which melted at 138° (from ethanol) and 249° (from chloroform).

2-*Hydroxy-α-*(4-*methoxy*-1-*naphthyl*)-*α-phenylbenzyl Alcohol* (XIII*a*).—The preceding ketone (2·78 g.) with phenylmagnesium bromide [prepared from bromobenzene (4·71 g.)] in a reaction as before, with decomposition with acetic acid, afforded a solid *alcohol* (2 g.) which, crystallised from benzene, had m. p. 180° (decomp.), containing one mol. of benzene (Found: C, 82·4; H, 6·0. $C_{24}H_{20}O_3,C_6H_6$ requires C, 82·9 H, 6·0%), or crystallised from ethanol, had m. p. 174° (decomp.) with 0·5 mol. of ethanol (Found: C, 79·7; H, 5·7. $C_{24}H_{20}O_3,\frac{1}{2}C_2H_5{\cdot}OH$ requires C, 79·2; H, 6·1%), giving a violet colour with concentrated sulphuric acid.

o-*Hydroxy-α-naphthafuchsone* (XXIII).—Refluxing a solution of the alcohol (XIII*a*) (1 g.) in glacial acetic acid (25 c.c.) for 15 min. and cooling afforded a solid *fuchsone* (0·5 g.) which crystallised from light petroleum (b. p. 70—80°) in pale yellow prisms, m. p. 170°, giving a greenish-yellow colour with concentrated sulphuric acid (Found: C, 84·9; H, 5·2. $C_{23}H_{16}O_2$ requires C, 85·2; H, 5·0%).

2-*Hydroxy-α-*(4-*methoxy*-1-*naphthyl*)-*α-methylbenzyl Alcohol* (II*a*).—In a reaction as before, *o*-hydroxyacetophenone (4·5 g.) and a Grignard reagent from 1-bromo-4-methoxynaphthalene (23·7 g.) in ether only and after decomposition with acetic acid, afforded the *alcohol* (3·2 g.) which recrystallised from benzene–light petroleum (b. p. below 50°) as prisms, m. p. 167° (decomp.). It does not dissolve in alkali, and it gives an orange-brown colour with concentrated sulphuric acid (Found: C, 77·4; H, 6·3. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%).

2-*Hydroxy-α-*(4-*methoxy*-1-*naphthyl*)*styrene* (XXIV).—A solution of the alcohol (II*a*) (1 g.) in acetic acid (25 c.c.) was refluxed for 20 min., diluted with water, and cooled, give a *styrene* (0·7 g.) that, crystallised from ether–light petroleum (b. p. $<50°$) and then from light petroleum

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[11] Julian and Gist, *J. Amer. Chem. Soc.*, 1935, **57**, 2030.

(b. p. 70—80°), had m. p. 110° and gave a reddish-brown colour with sulphuric acid (Found: C, 82·3; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

9-(4-*Methoxy*-1-*naphthyl*)*xanthhydrol* (XV).—A solution of xanthone (3·92 g.) in dry benzene (50 c.c.) and a Grignard reagent from 1-bromo-4-methoxynaphthalene (9·56 g.) in dry ether (60 c.c.) in a reaction as before gave a precipitate that was collected and added to a solid isolated from the organic layer. The solid *xanthhydrol* (4 g.) crystallised from benzene in needles, m. p. 245° (Found: C, 81·4; H, 5·1. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%).

9-*Chloro*-9-(4-*methoxy*-1-*naphthyl*)*xanthen* (XV*b*).—Obtained as above, this chloride, m. p. 205°, was obtained in nearly theoretical yield. On fusion, this product gave a mixture of a black and a white compound that could not be separated.

4-*Methoxy*-1-*naphthyl Styryl Ketone*.—Cinnamoyl chloride (16·7 g.), added to 1-methoxynaphthalene (15·8 g.) and aluminium chloride (13·5 g.) in carbon disulphide (*ca.* 300 c.c.) at <10°, gave an oil that crystallised from chloroform–ethanol (1 : 1 v/v). This *ketone* (12 g.) recrystallised from the same solvent as deep yellow needles, m. p. 93°, which with concentrated sulphuric acid give a red colour (Found: C, 83·1; H, 5·5. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

α-(4-*Methoxy*-1-*naphthyl*)-α-*phenylcinnamyl Alcohol* (III*a*).—Phenylmagnesium bromide from bromobenzene (6·28 g.) and the styryl ketone (5·76 g.) as before afforded a solid *alcohol* (5 g.) that crystallised from benzene–light petroleum (b. p. 70—80°) as needles, m. p. 141—142°, giving an orange-yellow colour with concentrated sulphuric acid (Found: C, 85·5; H, 6·1. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·1%).

This compound, refluxed for 2 hr. with acetyl chloride as before or for 4 hr. with acetic anhydride–acetic acid (1 : 2 v/v), gave back the starting substances on cooling in both cases.

α-(2-*Methoxy*-1-*naphthyl*)-α-*phenylcinnamyl Alcohol* (XIV).—A Grignard reagent prepared from bromobenzene (6·28 g.) and 2-methoxynaphthyl styryl ketone [12] (5·78 g.) in a reaction as above gave an oily *alcohol* that crystallised (4 g.) from ethanol and recrystallised therefrom in colourless needles, m. p. 96°, giving a yellow colour with concentrated sulphuric acid (Found: C, 85·0; H, 6·0. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·1%). This also yielded no chloride.

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[*Received, March 9th,* 1959.]

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[12] Koelsch and Anthes, *J. Org. Chem.*, 1941, **6**, 558.