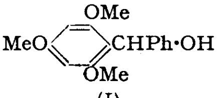
968. *Alkyl–Oxygen Fission in Carboxylic Esters. Part XI.** *Reactions of Secondary Alcohols containing the* 2 : 4 : 6-*Trimethoxyphenyl Radical.*

By J. Kenyon and R. F. Mason.

2 : 4 : 6-Trimethoxydiphenylmethanol and its acetate react exclusively by alkyl–oxygen fission and behave as powerful aralkylating agents.

Attempts to prepare a hydrogen phthalate or succinate were fruitless but the acetate was readily obtained. The alcohol undergoes deep-seated oxidation with cold hydrogen peroxide, to give a quinone, and under the influence of a trace of sulphuric acid suffers dismutation. A mechanism is proposed for the latter reaction which involves electrophilic attack by the carbonium cation on the methoxylated nucleus of an un-ionised methanol molecule.

The hydrolysis of carboxylic esters reveals that the introduction of a *p*-methoxyl group into a phenyl radical present in the alcohol moiety greatly increases the tendency to hydrolysis by alkyl–oxygen fission (*J.*, 1942, 605), a second methoxyl group, as in di-*p*-methoxyphenylmethanol, increasing this tendency still further (Balfe, Kenyon, and Thain, *J.*, 1952, 790). An extension of this study shows that 2 : 4 : 6-trimethoxydiphenylmethanol (I) reacts readily and exclusively by alkyl–oxygen fission : thus the alcohol itself acts as a powerful aralkylating agent towards a variety of compounds. The cumulative mesomeric effect of the methoxyl groups results in a large electron-availability at the methane carbon atom and this leads to incipient ionisation with liberation of the trimethoxydiphenylmethyl cation. This behaviour is shown also by 1-(2 : 4 : 6-trimethoxyphenyl)ethanol and by α-naphthyl-2 : 4 : 6-trimethoxyphenylmethanol and, in a more pronounced degree, by the acetate of (I).


(I)

The alcohol (I) and its acetate act as aralkylating agents. Thus, with alcohols and thiols in hot chloroform, (I) readily gives the corresponding ethers. With benzoylacetone and toluene-*p*-sulphinic acid, in acetic acid containing a trace of sulphuric acid at room temperature, it gives the *C*-aralkylated derivative and sulphone respectively. With toluene-*p*-sulphonamide, in acetic acid at room temperature, it gives the *N*-substituted product. This reactivity is shown by xanthhydrol and has been applied to the characterisation of of sulphonamides by Phillips and Frank (*J. Org. Chem.*, 1944, **9**, 9). The acetate reacts similarly with alcohols at room temperature and with sodium toluene-*p*-sulphinate in aqueous dioxan; with aqueous ammonia at 150° it yields di-(2 : 4 : 6-trimethoxydiphenylmethyl)amine; with phenols, thiophenols, and oximes it gives ethers, and with ethyl acetoacetate the *C*-aralkylated derivative. The identity of several of these thio-ethers and sulphones was established by reductive fission, $R{\cdot}SO_2{\cdot}R' \longrightarrow R{\cdot}SO_2H + R'H$.

The alcohol (I) was obtained by reducing 2 : 4 : 6-trimethoxybenzophenone as described by Kostanecki (*Ber.*, 1906, **39**, 4017) but more conveniently by the action of phenylmagnesium bromide on 2 : 4 : 6-trimethoxybenzaldehyde. With the appropriate Grignard reagent, this aldehyde gave excellent yields of 1-(2 : 4 : 6-trimethoxyphenyl)ethanol, α-naphthyl-2 : 4 : 6-trimethoxyphenylmethanol, and 2 : 4 : 6 : 4′-tetramethoxydiphenylmethanol. Attempts to reduce 2 : 4 : 6-trimethoxyacetophenone to the corresponding alcohol were unsuccessful. 2 : 4 : 6-Trimethoxybenzaldehyde was obtained in good yield by application of Dimroth and Zoeppritz's aldehyde synthesis (*Ber.*, 1902, **35**, 995) to phloroglucinol trimethyl ether.

The alcohol (I) is remarkably stable to heat, being recovered unchanged after 12 hours at 200—220°; in 15 minutes at 280—300° it is converted into di-(2 : 4 : 6-trimethoxydiphenylmethyl) ether in 50% yield.

In all attempts to esterify the alcohol (I) with phthalic anhydride, it was quantitatively recovered. Nor would the potassium derivative of the alcohol react with the anhydride in benzene. Succinic anhydride was similarly ineffective. This result may be related with the

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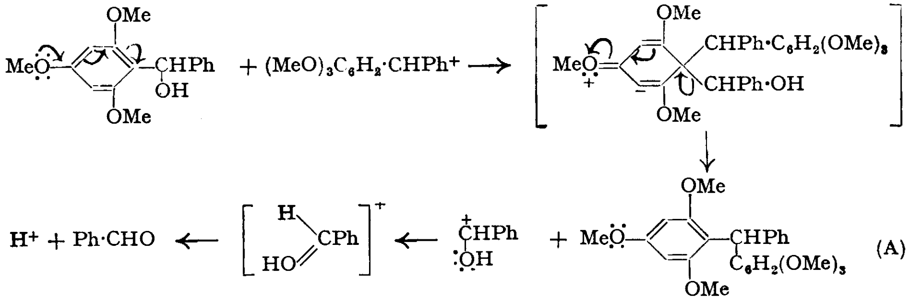
* Part X, *J.*, 1951, 386.

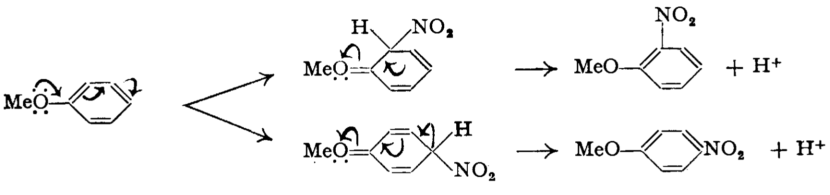
observation that di-*p*-methoxyphenylmethanol does not combine with phthalic anhydride in the presence of pyridine but does so in presence of triethylamine (Balfe, Kenyon, and Thain, *J.*, 1951, 386). In marked contrast, (I) is converted readily into its acetate by acetic anhydride (also by acetic acid at room temperature), both in the presence and the absence of pyridine, thus duplicating the behaviour of di-*p*-methoxyphenylmethanol (Balfe, Kenyon, and Thain, *J.*, 1952, 790).

A solution of (I) in ethanol containing sulphuric acid (1·5%) after several days at room temperature gives rise, not to the expected ethyl ether of (I), but to 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethoxytriphenylmethane (A) and benzaldehyde quantitatively. This triphenylmethane derivative was encountered by Kostanecki (*loc. cit.*) in attempting the methylation of (I) with methyl sulphate and alkali, and he established its constitution. The mechanism of this acid dismutation may involve electrophilic attack by the carbonium cation on the 1-carbon atom of the methoxylated phenyl group of an un-ionised molecule of (I) and may be written :

$$(MeO)_3C_6H_2{\cdot}CHPh{\cdot}OH + H_2SO_4 \longrightarrow (MeO)_3C_6H_2{\cdot}CHPh{\cdot}OH_2^+ + HSO_4^- \longrightarrow (MeO)_3C_6H_2{\cdot}CHPh^+ + H_2O$$


(A)

The stages in the reaction are considered to be : (i) Ionisation of (I) with liberation of a carbonium cation : this proceeds readily on account of the large electron-release of the trimethoxydiphenylmethyl group. (ii) Electrophilic attack by the carbonium cation (which possesses great cationic activity) at the 1-carbon atom (attack occurs at this carbon atom because of the large electron-accession to it brought about by the three methoxyl groups—the effect of one only is indicated in the formulation). (iii) Elimination of protonated benzaldehyde from the transition complex, leading to a sequence of electromeric changes which are the reverse of the initial process. The products are the electrically neutral triphenylmethane derivative and protonated benzaldehyde which gives up its proton. This acid dismutation is formally analogous to nitration of anisole, a reaction which involves electrophilic attack by the nitronium ion, NO_2^+ :



Convincing evidence in support of the mechanism proposed for the dismutation comes from reaction of (I) with 2 : 4 : 6-trimethoxy- and 2 : 4 : 6-triethoxy-benzene. This reaction was carried out in glacial acetic acid by adding a solution of (I) to a solution of the trialkoxylated benzene (two molecular proportions in order to promote the alkylation reaction) containing sulphuric acid. 2 : 4 : 6-Trimethoxybenzene gave a quantitative yield of the expected hexamethoxytriphenylmethane, identical with that obtained from the action of ethanolic sulphuric acid on (I) itself.

p-Tolyl trimethoxydiphenylmethyl sulphide and hydrogen peroxide in acetone or acetic acid gave, not the expected sulphone (a stable compound, readily prepared by the action of sodium toluene-*p*-sulphinate on the methanol), but the bright red 2 : 6-dimethoxy-

1 : 4-benzoquinone encountered by Kostanecki (*loc. cit.*) in an attempt to oxidise (I) with chromic acid to the corresponding ketone. This reaction, which appears complex and of obscure mechanism, is being further examined. The quinone is also obtained by the action of hydrogen peroxide on either (I) or phloroglucinol trimethyl ether.

EXPERIMENTAL

2 : 4 : 6-*Trimethoxybenzaldehyde.*—(*a*) Phosphorus oxychloride (19 g.) was added to a solution of 2 : 4 : 6-trimethoxybenzene (42 g.) and formanilide (30 g.) in dry ether (200 c.c.); next day the solvent was evaporated and the residue decomposed with aqueous sodium hydroxide (900 c.c.; 5%) and steam-distilled. The non-volatile residue, m. p. 112—115° (38 g.), after crystallisation from benzene-ligroin, yielded 2 : 4 : 6-trimethoxybenzaldehyde (31 g., 72%), plates, m. p. 118°. Its oxime, needles (from dioxan or methanol), had m. p. 201—203° (lit., 201—203°). (*b*) The aldehyde was also prepared (62% yield) by application to phloroglucinol trimethyl ether of the method of Wood and Bost (*Org. Synth.*, 1940, **20**, 11).

2 : 4 : 6-*Trimethoxydiphenylmethanol* (α-2 : 4 : 6-*Trimethoxyphenylbenzyl Alcohol*) (I).—2 : 4 : 6-Trimethoxybenzaldehyde (14·5 g.) in hot benzene (150 c.c.) was added slowly to a solution of phenylmagnesium bromide in ether (from bromobenzene, 11·7 g., and magnesium, 1·9 g.) and the mixture heated under reflux for 1½ hours and then decomposed with ice and ammonium chloride. The crude methanol (19 g.; m. p. 124—126°) separated from aqueous alcohol in pale yellow needles (16 g.), m. p. 125° alone or when mixed with a specimen prepared by Kostanecki's method (*Ber.*, 1906, **39**, 4017).

1-(2 : 4 : 6-*Trimethoxyphenyl*)*ethanol*, prepared in a similar way, separated from ligroin in pale yellow needles, m. p. 76—77° (Found : C, 62·0; H, 7·5. $C_{11}H_{16}O_4$ requires C, 62·2; H, 7·6%).

α-*Napthhyl*-2 : 4 : 6-*trimethoxyphenylmethanol*, prepared similarly in 90% yield, separated from methanol in lustrous plates, m. p. 142·5—143·5° (Found : C, 73·9; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

2 : 4 : 6 : 4′-Tetramethoxydiphenylmethanol, prepared from *p*-methoxyphenylmagnesium bromide in 95% yield, separated from aqueous methanol in prismatic rods, m. p. 103° Kostanecki (*loc. cit.*) gives m. p. 103°.

Condensation with Thiols.—The following were smoothly prepared in excellent yield by heating chloroform solutions of the appropriate methanol and thiol under reflux for several hours: *benzyl*, rods (from ethanol), m. p. 90—91° (Found : C, 72·8; H, 6·5; S, 8·1. $C_{23}H_{24}O_3S$ requires C, 72·6; H, 6·4; S, 8·4%), *phenyl*, rods (from methanol), m. p. 127—128° (Found : C, 72·2; H, 6·0. $C_{22}H_{22}O_3S$ requires C, 72·1; H, 6·0%), and p-*tolyl* 2 : 4 : 6-*trimethoxydiphenylmethyl sulphide*, rods (from ethanol), m. p. 143—144° (Found : C, 72·3; H, 6·2; S, 8·6. $C_{23}H_{24}O_3S$ requires C, 72·6; H, 6·4; S, 8·4%); α-*naphthyl*-2 : 4 : 6-*trimethoxyphenylmethyl*, rods (from butanol), m. p. 170—171° (Found : C, 75·3; H, 6·4; S, 7·0. $C_{27}H_{26}O_3S$ requires C, 75·4; H, 6·1; S, 7·5%), and 2 : 4 : 6 : 4′-*tetramethoxydiphenylmethyl* p-*tolyl sulphide*, rods (from ethanol), m. p. 119—120° (Found : C, 70·3; H, 6·2. $C_{24}H_{26}O_4S$ requires C, 70·2; H, 6·4%).

(2 : 4 : 6-*Trimethoxydiphenylmethylthio*)*acetic acid*, formed from (I) and mercaptoacetic acid, separated from aqueous alcohol in plates, m. p. 155—157° (decomp.) (Found : C, 61·9; H, 5·3. $C_{18}H_{20}O_5S$ requires C, 62·1; H, 5·8%).

The *thioacetate* of (I), formed by the interaction of thioacetic acid and (I), separates from alcohol in plates, m. p. 135·5—137° (Found : C, 64·8; H, 6·2; S, 9·6. $C_{18}H_{20}O_4S$ requires C, 65·1; H, 6·1; S, 9·6%). After being heated under reflux with methanol for 10 hours it was quantitatively recovered unchanged.

Hydrogenolysis of the Sulphides.—(*a*) The *p*-tolyl sulphide (1 g.) from (I) when heated under reflux with Raney nickel (2 teaspoonsful of settled material; Mozingo, *Org. Synth.*, **21**, 15; *J. Amer. Chem. Soc.*, 1943, **65**, 1013) in ethanol (35 c.c.) for 7 hours, gave 2 : 4 : 6-*trimethoxydiphenylmethane* (0·55 g.), rods, m. p. 93—94° (from ethanol) (Found : C, 74·0; H, 6·9. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%). This does not form a picrate. (*b*) The *p*-tolyl derivative of the naphthyl compound by similar treatment gave α-*naphthyl* 2 : 4 : 6-*trimethoxyphenylmethane*, m. p. 149—150° (rapid heating), plates from ethanol (Found : C, 77·4; H, 6·4. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5%).

Basic Reductive Fission of the Sulphones.—(*a*) The *p*-tolyl 2 : 4 : 6-trimethoxydiphenylmethyl sulphone (1 g.) in ethanol (25 c.c.) was heated 4 hours under reflux with sodium amalgam (25 g.; 6%). The decanted solution yielded rods (0·55 g.; 88%) of 2 : 4 : 6-trimethoxydiphenylmethane, m. p. 93—94° alone or mixed with the specimen from the hydrogenolysis of the corresponding sulphide. The filtrate contained sodium toluene-*p*-sulphinate which was characterised as benzyl *p*-tolyl sulphone (0·3 g.), m. p. 145—146° alone or mixed with authentic material. (*b*) The *p*-tolyl sulphone from the naphthyl derivative by similar treatment gave α-naphthyl-2 : 4 : 6-trimethoxyphenylmethane, m. p. 150° alone or mixed with the specimen from the hydrogenolysis of the sulphide.

Oxidations with Hydrogen Peroxide.—(*a*) *p*-Tolyl 2 : 4 : 6-trimethoxydiphenylmethyl sulphide (1·3 g.) in acetic acid (40 c.c.) containing hydrogen peroxide (1 c.c. of 30%), when kept at room temperature for 8 days, deposited 2 : 6-dimethoxy-1 : 4-benzoquinone (0·13 g.), red needles, m. p. 252° (decomp.) unchanged after recrystallisation from water (Found : C, 56·9; H, 4·7. Calc. for $C_8H_8O_4$: C, 57·2; H, 4·8%). Ciamician and Silber (*Ber.*, 1893, **26**, 786) give m. p. 249°. A similar result was obtained with acetone as solvent, and in this case also careful search for other products of oxidation was fruitless.

(*b*) 2 : 4 : 6-Trimethoxydiphenylmethanol, by a similar procedure, yielded (0·14 g. from 1 g.) 2 : 6-dimethoxybenzoquinone, m. p. 252° (decomp.), along with benzaldehyde and benzoic acid in varying amounts.

(*c*) 2 : 4 : 6-Trimethoxybenzene (2 g.) in acetic acid (15 c.c.) containing hydrogen peroxide (4 c.c.) gave, after several days, 2 : 6-dimethoxybenzoquinone (0·5 g.), m. p. 251° (decomp.).

Formation of Sulphones and Sulphonamides.—A solution of (I) (0·55 g.) in acetic acid (4 c.c.) was mixed with sodium toluene-*p*-sulphinate (0·4 g.) and sulphuric acid (0·15 c.c.) in acetic acid (2 c.c.). After 2 hours the mixture was poured into ice water and the precipitate crystallised from methanol : the resulting p-*tolyl* 2 : 4 : 6-*trimethoxydiphenylmethyl sulphone* (0·4 g.) formed tablets, m. p. 139—140° (Found : C, 66·5; H, 5·6. $C_{23}H_{24}O_5S$ requires C, 66·9; H, 5·9%). In a similar manner were obtained p-*tolyl* 1-(2 : 4 : 6-*trimethoxyphenyl*)*ethyl sulphone*, yellow tablets (from ethanol), m. p. 141—142° (Found : C, 61·9; H, 6·4; S, 7·7. $C_{18}H_{22}O_5S$ requires C, 61·7; H, 6·3; S, 7·3%), and α-*naphthyl*-2 : 4 : 6-*trimethoxyphenylmethyl* p-*tolyl sulphone*, rods (from ethanol), m. p. 157—158° (to a red liquid) (Found : C, 70·2; H, 6·0. $C_{27}H_{26}O_5S$ requires C, 70·1; H, 5·7%). The sulphone from (I) was recovered unchanged after 7 hours in hot ethanolic sulphuric acid (5%).

N-(2 : 4 : 6-*Trimethoxydiphenylmethyl*)*toluene*-p-*sulphonamide.*—A solution of (I) (0·55 g.) and toluene-*p*-sulphonamide (0·35 g.) in warm acetic acid (10 c.c.) containing a trace of sulphuric acid, after 2 days at room temperature, was poured into ice-water. The precipitated *amide* separated from butanol in plates (0·6 g.), m. p. 188° (Found : C, 64·5; H, 6·0; N, 3·1; S, 7·0. $C_{23}H_{25}O_5NS$ requires C, 64·6; H, 5·9; N, 3·3; S, 7·5%).

N-(α-*Naphthyl*-2 : 4 : 6-*trimethoxyphenylmethyl*)*toluene*-p-*sulphonamide*, prepared similarly, had m. p. 215—217°, tablets from acetic acid (Found : C, 67·4; H, 5·7; N, 2·4; S, 6·7. $C_{27}H_{27}O_5NS$ requires C, 67·9%; H, 5·7; N, 2·9; S, 6·7%).

Formation of Substituted Benzoylacetones.—The components were mixed at ordinary temperature in acetic acid containing a trace of sulphuric acid, giving the following. (i) 1-*Phenyl*-2-(2 : 4 : 6-*trimethoxydiphenylmethyl*)*butane*-1 : 3-*dione*, from benzoylacetone and (I), prismatic needles (from propanol), m. p. 149·5—150·5° (Found : C, 74·6; H, 6·3. $C_{26}H_{26}O_5$ requires C, 74·6; H, 6·3%). This ketone condenses with (*a*) phenylhydrazine in boiling acetic acid to yield 3-*methyl*-1 : 5-*diphenyl*-4-(2 : 4 : 6-*trimethoxydiphenylmethyl*)*pyrazole*, plates (from ethanol), m. p. 177—178° (Found : C, 78·0; H, 6·2; N, 5·6. $C_{32}H_{30}O_3N_2$ requires C, 78·3; H, 6·2; N, 5·7%), (*b*) *p*-nitrophenylhydrazine to yield 3-*methyl*-1-p-*nitrophenyl*-5-*phenyl*-4-(2 : 4 : 6-*trimethoxydiphenylmethyl*)*pyrazole*, yellow rhombs (from propanol), m. p. 179—180° (Found : C, 71·6; H, 5·5; N, 7·5. $C_{32}H_{29}O_5N_3$ requires C, 71·7; H, 5·5; N, 7·8%), (*c*) toluene-*p*-sulphonylhydrazine to yield 3-*methyl*-5-*phenyl*-1-*toluene*-p-*sulphonyl*-4-(2 : 4 : 6-*trimethoxydiphenylmethyl*)*pyrazole*, rods (from propanol), m. p. 211—212° (Found : C, 69·9; H, 6·0; N, 4·9; S, 5·7. $C_{33}H_{32}O_5N_2S$ requires C, 69·7; H, 5·7; N, 4·9; S, 5·6%), and (*d*) hydroxylamine hydrochloride in pyridine–ethanol to yield 3-*methyl*-5-*phenyl*-4-(2 : 4 : 6-*trimethoxydiphenylmethyl*)isooxazole, rods, m. p. 166·5—167·5° (from *n*-propanol) (Found : C, 75·3; H, 6·1; N, 3·2. $C_{26}H_{25}O_4N$ requires C, 75·2; H, 6·1; N, 3·4%). (ii) 2-(α-*Naphthyl*-2 : 4 : 6-*trimethoxyphenylmethyl*)-1-*phenylbutane*-1 : 3-*dione*, rods (from ethanol), m. p. 162° (Found : C, 76·9; H, 6·0. $C_{30}H_{28}O_5$ requires C, 76·9; H, 6·0%).

2 : 4 : 6-*Trimethoxydiphenylmethyl Acetate.*—Acetic anhydride (1 g.) and (I) (0·55 g.) were heated at 100° for 2 hours and the excess of anhydride removed. Crystallisation of the residual ester from *cyclo*hexane yielded the *acetate* as needles (0·45 g.), m. p. 111·5—112·5° (Found : C, 68·8; H, 6·2. $C_{18}H_{20}O_5$ requires C, 68·4; H, 6·4%). This was also obtained from acetic anhydride and pyridine in the normal manner, and from (I) (0·5 g.) in acetic acid (3 c.c.) after several hours at room temperature; yields were quantitative.

α-*Naphthyl*-2 : 4 : 6-*trimethoxyphenylmethyl acetate* formed prisms, m. p. 153—154°, from ether–light petroleum (Found : C, 72·4; H, 6·2. $C_{22}H_{22}O_5$ requires C, 72·1; H, 6·1%).

Reactions of the Acetates with Alcohols and Phenols.—(*a*) *With ethanol.* (i) The acetate of (I) (0·5 g.) in 99% ethanol (5 c.c.) was heated for several minutes and left overnight; the solution deposited the *ethyl ether* of (I) as needles, m. p. 72—74° after recrystallisation (Found: C, 71·2; H, 7·2. Calc. for $C_{18}H_{22}O_4$: C, 71·5; H, 7·3%). Kostanecki (*loc. cit.*) gives m. p. 72—73°.. (ii) The acetate of the naphthyl derivative yielded the corresponding *ethvl ether*, rods (from *cyclo*hexane), m. p. 105—106° (Found: C, 74·7; H, 6·8. $C_{22}H_{24}O_4$ requires C, 75·0; H, 6·9%).

(*b*) *With* sec.-*butyl alcohol.* A solution of the acetate of (I) (0·6 g.) in this alcohol (5 c.c.) was allowed to evaporate at room temperature. The crystalline residue of the sec.-*butyl ether* separated from aqueous methanol in rods, m. p. 89—90° (Found: C, 72·2; H, 7·7. $C_{20}H_{26}O_4$ requires C, 72·6; H, 7·9%).

(*c*) *With benzyl alcohol.* A solution of the acetate of (I) (0·63) g. and benzyl alcohol (0·22 g.) in chloroform was heated for several hours. The resulting *benzyl ether* separated from methanol in hexagonal plates (0·38 g.), m. p. 108—109° (Found: C, 76·1; H, 6·6. $C_{23}H_{24}O_4$ requires C, 75·8; H, 6·6%).

The following derivatives of (I) were prepared similarly in chloroform solution: p-*tolyl ether*, rods (from methanol), m. p. 128·5—129·5° (Found: C, 75·8; H, 6·4. $C_{23}H_{24}O_4$ requires C, 75·8; H, 6·6%); β-*naphthyl ether*, rhombs (from ethanol), m. p. 153—154° (Found: C, 78·0; H, 6·2. $C_{26}H_{24}O_4$ requires C, 78·0; H, 6·0%) (both these were similarly formed from the alcohol in 10 hours); 8-*quinolyl ether*, yellow rhombs (from butanol), m. p. 206—208° (Found: C, 74·4; H, 5·7; N, 3·5. $C_{25}H_{23}O_4N$ requires C, 74·8; H, 5·8; N, 3·4%); *p*-tolyl sulphide, m. p. 143—144° alone or when mixed with a specimen obtained from (I).

p-*Nitrobenzaldoxime* O-(2 : 4 : 6-*trimethoxydiphenylmethyl*) *ether* was prepared from α-*p*-nitrobenzaldoxime (cf. Balfe, Kenyon, and Wicks, *J.*, 1946, 807) and the acetate of (I); it had m. p. 157—158°, forming rods from ethanol (Found: C, 65·4; H, 5·3; N, 6·6. $C_{23}H_{22}O_6N_2$ requires C, 65·4; H, 5·3; N, 6·6%). p-*Nitrobenzaldoxime* O-(α-*naphthyl*-2 : 4 : 6-*trimethoxyphenylmethyl*) *ether* formed yellow rods, m. p. 193·5—194·5°, from *n*-propanol (Found: C, 68·4; H, 5·2; N, 5·9. $C_{27}H_{24}O_6N_2$ requires C, 68·6; H, 5·1; N, 5·9%). o-*Methoxybenzaldoxime* O-(2 : 4 : 6-*trimethoxydiphenylmethyl*) *ether* formed tablets, m. p. 137·5—138·5°, from methanol (Found: C, 71·1; H, 6·4; N, 3·0. $C_{24}H_{25}O_5N$ requires C, 70·7; H, 6·2; N, 3·4%). *Benzophenone oxime* 2 : 4 : 6-*trimethoxydiphenylmethyl ether* formed rods, m. p. 123—124°, from ethanol (Found: C, 77·1; H, 6·0; N, 3·3. $C_{29}H_{27}O_4N$ requires C, 76·8; H, 6·0; N, 3·1%) (this may be the *O*-ether, since the *O*-ethers of benzophenone oxime are more stable than the *N*-ethers; cf. Semper and Lichtenstadt, *Ber.*, 1918, **51**, 928).

Ethyl C-2 : 4 : 6-*trimethoxydiphenylmethylacetoacetate*, from acetoacetic ester and the acetate of (I), rhombs, had m. p. 83·5—84·5°, from ligroin (Found: C, 68·3; H, 6·7. $C_{22}H_{26}O_6$ requires C, 68·4; H, 6·8%).

Di-(2 : 4 : 6-*trimethoxydiphenylmethyl*)*amine* was obtained when the acetate (1 g.) of (I) was heated (8 hours) at 150° with aqueous ammonia (12 c.c.; *d* 0·88). Crystallisation of the residue (1 g.) from propanol yielded plates, or needles (from a small amount of solvent), m. p. 165·5—166·5° (Found: C, 72·5; H, 6·7; N, 2·7. $C_{32}H_{35}O_6N$ requires C, 72·5; H, 6·7; N, 2·6%).

The o-*bromobenzoate* of (I) was formed when the acetate (0·63 g.) and *o*-bromobenzoic acid (0·8 g., 2 mol.) were heated under reflux (17 hours) in chloroform (10 c.c.). After removal of the solvent, the residue was washed with dilute sodium carbonate solution. Seven crystallisations from benzene–*cyclo*hexane yielded cubes (0·2 g.), m. p. 111° (Found: C, 60·4; H, 4·8; Br, 17·7. $C_{23}H_{21}O_5Br$ requires C, 60·4; H, 4·6; Br, 17·5%).

The p-*tolyl sulphone*, obtained from the acetate of (I) and sodium toluene-*p*-sulphinate in aqueous dioxan (12 hours), had m. p. 139° alone or when mixed with a specimen obtained from (I).

Action of Heat on (I).—After being kept at 200—220° for 12 hours, (I) was unchanged; at 280—300° for 15 minutes, (I) (1 g.) gave *di*-(2 : 4 : 6-*trimethoxydiphenylmethyl*) *ether* (0·5 g.), needles (from butanol), m. p. 194—195° (Found: C, 72·5; H, 6·7. $C_{32}H_{34}O_7$ requires C, 72·4; H, 6·5%).

Dismutations by Mineral Acid.—Ethanolic sulphuric acid (2 c.c.; 20%) was added to a solution of (I) (0·75 g.) in ethanol (25 c.c.); next day crystals (0·43 g.; m. p. 182—183°) had separated, which by recrystallisation from benzene–*cyclo*hexane yielded 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethoxytriphenylmethane, m. p. 185—186° alone or mixed with a specimen prepared by Kostanecki's method (*loc. cit.*) (Found: C, 71·2; H, 6·6. Calc. for $C_{25}H_{28}O_6$: C, 70·7; H, 6·6%). Addition of Brady's reagent to the acid filtrate yielded benzaldehyde 2 : 4-dinitrophenylhydrazone (0·25 g.), m. p. 237—238°, alone or mixed with an authentic specimen.

By similar treatment 2 : 4 : 6 : 4′-tetramethoxydiphenylmethanol (1 g.) yielded 2 : 4 : 6 : 2′ : 4′ : 6′ : 4″-*heptamethoxytriphenylmethane* (0·6 g.), rods (from ethanol), m. p. 144—145° (Found: C, 68·4; H, 6·6. $C_{26}H_{30}O_7$ requires C, 68·7; H, 6·7%), identical with the compound obtained by condensing *p*-methoxybenzaldehyde with 2 : 4 : 6-trimethoxybenzene; the filtrate from the dismutation reaction yielded *p*-methoxybenzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 258° alone or mixed with an authentic specimen.

Subjected to dismutation the naphthyl alcohol yielded 2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethoxydiphenyl-α-naphthylmethane*, rods (from benzene–*cyclo*hexane) or needles (from butanol), m. p. 205·5—206·5° (Found: C, 72·9; H, 6·2. $C_{29}H_{30}O_6$ requires C, 73·3; H, 6·4%).

Condensation of (I) *with* 2 : 4 : 6-*Trimethoxybenzene and with* 2 : 4 : 6-*Triethoxybenzene.*—A solution of (I) (0·6 g.) in acetic acid (10 c.c.) was added to a vigorously stirred solution of 2 : 4 : 6-trimethoxybenzene (0·7 g., 2 mols.) in acetic acid (15 c.c.) containing 5 drops of sulphuric acid. Next day water (15 c.c.) was added and the precipitate crystallised from butanol (20 c.c.). The resulting 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethoxytriphenylmethane (0·85 g.) had m. p. 185—186° alone or mixed with the foregoing specimen. 2 : 4 : 6-*Triethoxy*-2′ : 4′ : 6′-*trimethoxytriphenylmethane*, prepared similarly, formed rods (from ethanol), m. p. 113·5—114·5° (Found: C, 72·5; H, 7·8. $C_{28}H_{34}O_6$ requires C, 72·1; H, 7·4%).

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