Tetrahedron. Vol. 24, pp. 2183 to 2192. Pergamon Press 1968. Printed in Great Britain

PHOTOCHEMICAL REACTIONS OF *trans*-ANETHOLE

H. Nozaki, I. Otani, R. Noyori and M. Kawanisi
Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

(*Received in Japan* 10 *July* 1967; *accepted for publication* 23 *August* 1967)

Abstract—A novel dimer of *trans*-anethole has been obtained photochemically. The dimerization proceeds with strict stereospecificity and the structure of the dimer has been ascertained as 1,*cis*-2-di-*p*-anisyl-*trans*-3,*trans*-4-dimethylcyclobutane. The dimer was transformed into the corresponding diphenol, diacetate and 1,*cis*-2-dimethyl-*trans*-3,*trans*-4-diphenylcyclobutane. The hydrocarbon was independently obtained from β-truxinic acid by reduction. Some dimethyldiphenylcyclobutane isomers have been prepared analogously from cinnamic acid dimers and the NMR spectra have been compared.

Anethole reacts photochemically with benzaldehyde and benzophenone to afford the corresponding oxetanes, some of which decompose spontaneously into stilbenes and acetaldehyde. The anethole dimer was not obtained in the presence of such carbonyl compounds, while isomerization to *cis*-anethole proceeds smoothly. Salicylaldehyde gives another type of 1:1-adduct, which has been shown to be 4-*p*-anisyl-2-hydroxy-3-methylchroman. An analogous hemiacetal was obtained by the reaction of salicylaldehyde and 1,1-diphenylethylene.

Mechanistic implications of anethole photochemistry have been discussed.

PHOTOCHEMICAL transformation of *trans*-anethole (I) into the *cis* isomer (II) has been reported.[1] Previously, it was mentioned that exposure of I to sunlight for a long period caused the precipitation of *photoanethole*, the structure of which was established as 4,4′-dimethoxy-*trans*-stilbene (III).[2] The mechanistic interpretation for the formation of III has not been reported and the photoreaction of I, which constitutes the subject of the present paper, has only been briefly discussed.

Direct irradiation of I *causing dimerization.* Irradiation in cyclohexane solution for 5 hr,* transformed I into II in the ratio of 85:15†, together with formation of a dimer (IV) in 39% yield.‡ Despite all efforts, no trace of III was found among the products.

The homogeneity of IV was ascertained by TLC and by GLC.§ No appreciable change was recognized when IV was heated at 200°, but pyrolysis at 500° afforded I in a 75% yield. Mass spectrometry showed the parent peak at *m/e* 296 and a peak at 240 (dimethoxystilbene).‖ Demethylation of IV with pyridinium chloride[3] gave a diphenol (V) in 87% yield, which was then converted into the diacetate VI. Homogeneity of these crystalline products (V and VI) was checked by TLC. Remethylation

---

* All irradiation experiments were carried out with a 200 W high pressure Hg arc as an external light-source through a Pyrex-filter, unless otherwise stated.

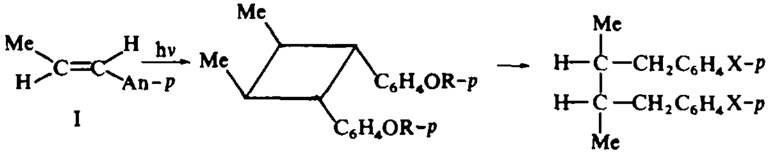
† Prolonged irradiation (> 12 hr) gave a 1:1 mixture.[1]

‡ The dimer IV was originally obtained as an oil. After completion of this work, a sample of IV was found to have crystallized after standing for 18 months in refrigerator. The IR spectrum (CCl_4) of the solid was identical with one of the oily sample.

§ TLC was performed on silicagel G with benzene–CCl_4 (5:8) as an eluant, while GLC on high-vacuum silicone grease (5%), 1 m, at 250° with He carrier.

‖ Mass spectra were operated on HITACHI RMU-6 at an ionizing voltage of 80 eV and a probe temp of 230°.

of V gave a product identical in all respects with IV. The structural and stereochemical uniformity of IV was thus established. Reduction of IV with sodium in liquid ammonia afforded *meso*-1,4-di-*p*-anisyl-2,3-dimethylbutane (VII) in 82% yield. Successive treatment of V with diethyl phosphite and then with sodium in liquid ammonia[4] gave *meso*-2,3-dimethyl-1,4-diphenylbutane (VIII)[5] in 60% yield.



I

IV: R = Me, V: R = H,
VI: R = Ac

VII: X = OMe
VIII: X = H

Three isomers of dimethyldiphenylcyclobutane have been prepared from cinnamic acid dimers, *viz*., α-truxillic, β-truxinic and δ-truxinic acids.* The reactions involved are LAH reduction, tosylation and LAH reduction. A comparison of the NMR spectrum (Fig. 2)† of the hydrocarbon derived from β-truxinic acid with those of

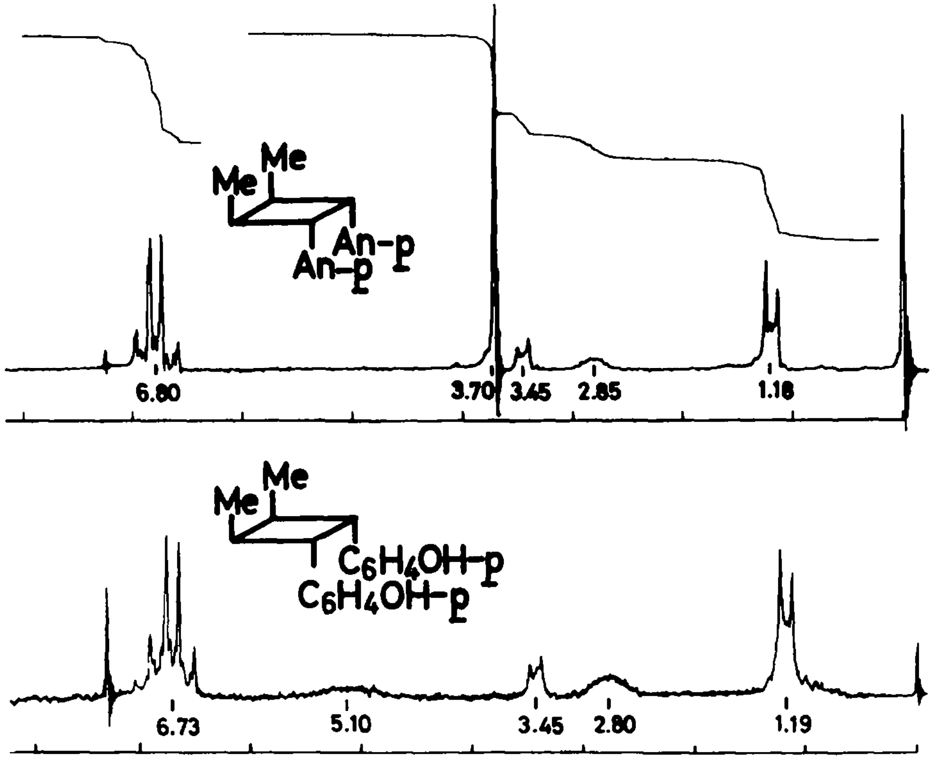


Fig. 1 NMR of anethole photodimer (IV) and the corresponding diphenol (V).

---

* The geometry of these dimers has been established.[6]

† The NMR spectra were taken on JEOLCO C-60-H and Varian A60 in $CDCl_3$ soln. The chemical shifts (δ) are given in ppm from TMS internal standard.

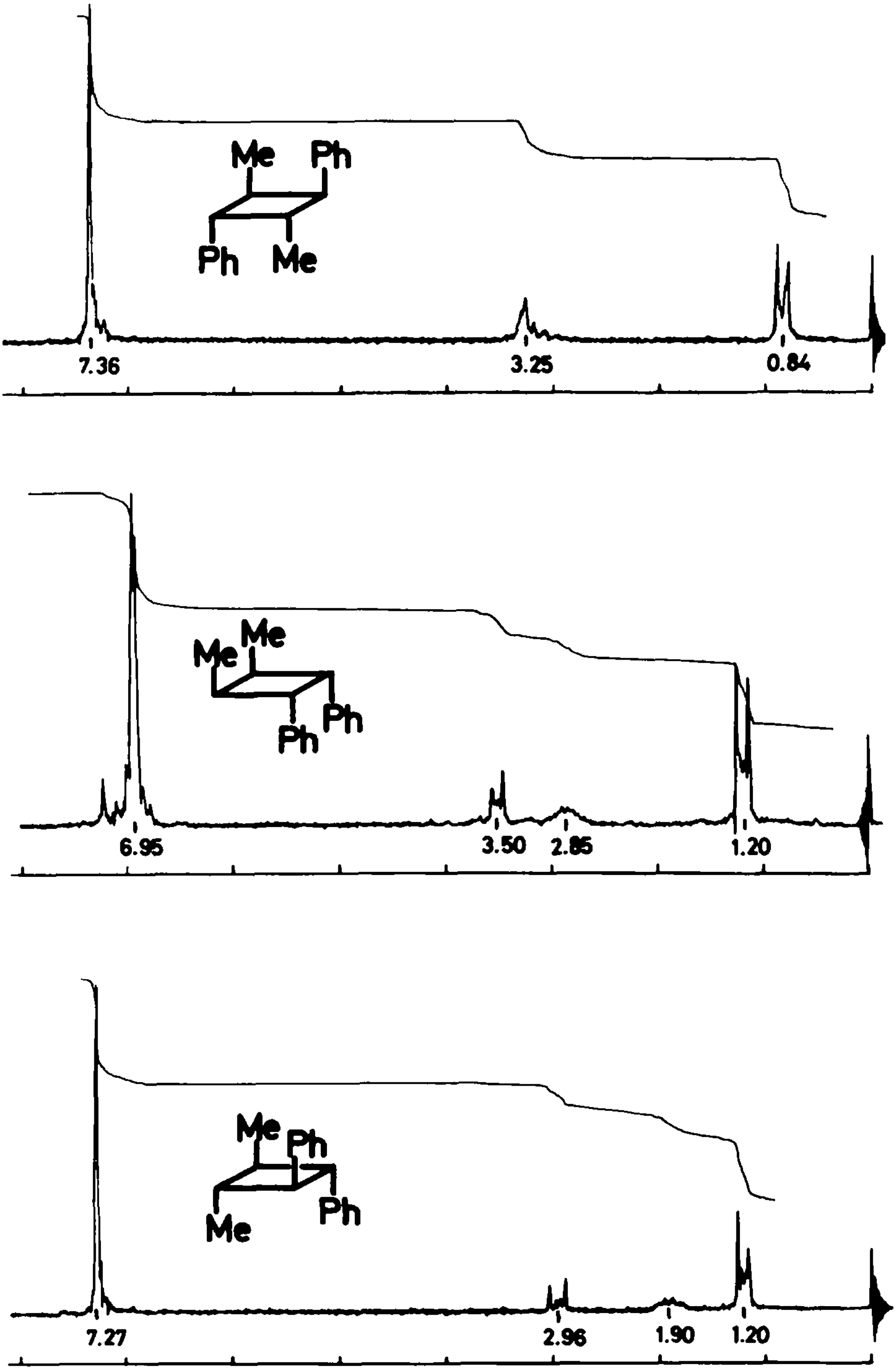
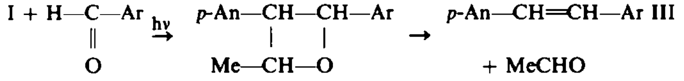


FIG. 2 NMR of dimethyldiphenylcyclobutane isomers.

IV and V (Fig. 1), shows a striking similarity. Final evidence for the *trans-syn-trans* geometry of IV and V was secured by conversion of V into the tosylate which on desulphurization with Raney nickel,[7] yielded a hydrocarbon identical with 1,*cis*-2-dimethyl-*trans*-3,*trans*-4-diphenylcyclobutane.* Prolonged irradiation of I gave less homogeneous IV, which showed some additional NMR peaks possibly arising from dimer(s) produced by the participation of II.

Reaction of trans-*anethole with benzaldehydes.* An equimolar mixture of I and *p*-anisaldehyde was dissolved in benzene and the solution irradiated for a week in a slow stream of nitrogen, from which acetaldehyde was detected as its 2,4-dinitrophenylhydrazone. An isomeric mixture of I and II (47:53) was obtained (80% recovery) and the distillation of the residue gave 4,4'-dimethoxy-*trans*-stilbene (III) in 13% yield after a single recrystallization. A similar reaction:



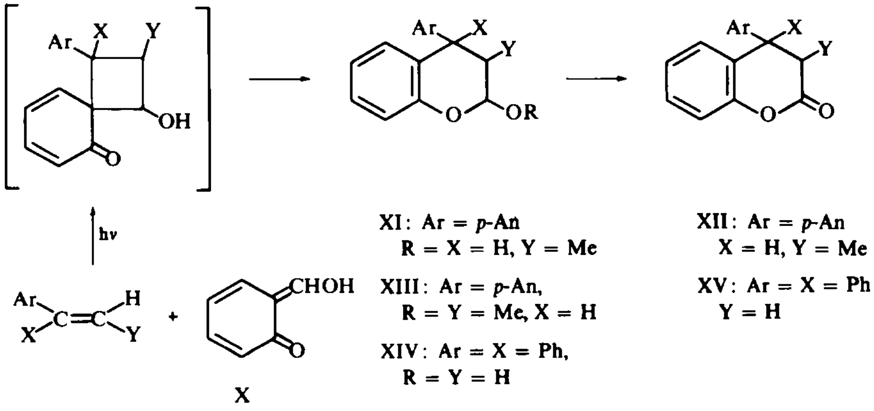
$$\mathrm{I} + \underset{\mathrm{O}}{\underset{\|}{\mathrm{H{-}C{-}Ar}}} \xrightarrow{h\nu} \underset{\mathrm{Me{-}CH{-}O}}{\underset{|\quad\;\; |}{p\text{-}\mathrm{An{-}CH{-}CH{-}Ar}}} \longrightarrow \underset{+\ \mathrm{MeCHO}}{p\text{-}\mathrm{An{-}CH{=}CH{-}Ar\ III}}$$

IX

with 4-chlorobenzaldehyde afforded 4-chloro-4'-methoxy-*trans*-stilbene in 44% yield together with a mixture of I and II (41:59, 37%). In contrast, the reaction of I with benzaldehyde gave an isomeric mixture of I and II (37:63, 52%) and an oily substance (23% yield), which was proved to be an oxetane IX (Ar = Ph). Elemental analyses and IR absorption[8] at 980 cm^{-1} supported the oxetane structure, which was further verified by UV and NMR spectra. Attempted chromatography of IX (Ar = Ph) on an alumina column gave rise to a crystalline product identical with 4-methoxy-*trans*-stilbene.

These findings indicate that *photoanethole* III arises from the photochemical reaction of I with *p*-anisaldehyde which has been produced by oxidation of I.[2] The intermediacy of an oxetane IX (Ar = *p*-An) seems highly probable.

Instead of oxetane or stilbene, salicylaldehyde gave another type of 1:1-adduct with I in 19% yield. The adduct showed an OH band at 3450 cm^{-1} (Nujol) and the



XI: Ar = *p*-An
R = X = H, Y = Me

XII: Ar = *p*-An
X = H, Y = Me

XIII: Ar = *p*-An,
R = Y = Me, X = H

XV: Ar = X = Ph
Y = H

XIV: Ar = X = Ph,
R = Y = H

---

* The stereospecific formation of IV will be discussed in the last section of this paper.

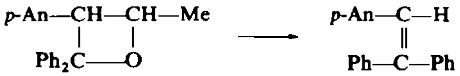
UV spectrum indicated the absence of the stilbene chromophore. Elemental analyses and the NMR spectrum were consistent with the assigned structure XI. Oxidation of XI with chromic acid in pyridine gave a lactone XII which showed an IR absorption at 1765 cm^{-1} (Nujol) and the NMR spectrum supported the structure given. Methylation of XI with dimethyl sulphate yielded a methyl ether XIII. The hemiacetal structure of XI was thus verified, but the stereochemistry has not been determined. The mechanism leading to XI would probably involve cycloaddition of I to photoenolized salicylaldehyde (X)[9] and subsequent rearrangement.

In order to assess the potential value of X in photochemical addition, the reaction was examined with a variety of olefins. 1,1-Diphenylethylene gave an adduct (XIV in 21% yield) which on oxidation gave the known lactone XV[10] in 82% yield. Olefins such as cyclohexene, 1,2-dichloroethylene and propenylbenzene proved to be inactive.

The dimerization of I was not observed in any of these reactions in the presence of the benzaldehydes.

The reaction of I *in the presence of benzophenone*

Mechanistic interpretation of the photochemistry of I. A cyclohexane solution of I was irradiated through cupric sulphate solution as a filter in the presence of added benzophenone. Concentrations of I and the sensitizer were both 1M. The light (>350 mμ) was absorbed almost exclusively by the benzophenone. The isomerization of I to II occurred rapidly and after 3 hr when the maximum I:II ratio of 42:58 was attained. Oxetane formation proceeded slowly and after 115 hr irradiation the product XVI was isolated as an oil in 21% yield. The structure of XVI was supported by elemental analyses and spectrometric data. Attempted chromatography of XVI on a silicagel column afforded 2-*p*-anisyl-1,1-diphenylethylene (XVII).* The dimer IV was not detected among the products. The reactions are formulated as follows, where B denotes benzophenone and excited species are indicated by S_1 or T_1.



$$\begin{array}{l} p\text{-An—CH—CH—Me} \\ \quad\;\;|\qquad\;| \\ \quad Ph_2C\text{——}O \end{array} \longrightarrow \begin{array}{c} p\text{-An—C—H} \\ \| \\ \text{Ph—C—Ph} \end{array}$$

XVI XVII

$$B + h\nu \longrightarrow B(S_1) \longrightarrow B(T_1) \qquad (1)$$

$$B(T_1) + I(\text{or } II) \longrightarrow B + I(\text{or } II)(T_1) \qquad (2)$$

$$I(\text{or } II)(T_1) \longrightarrow II(\text{or } I) \qquad (3)$$

$$B(T_1) + I \xrightarrow{\quad\times\quad} XVI \qquad (4)$$

$$I(\text{or } II)(T_1) + B \longrightarrow XVI \qquad (5)$$

$$I(T_1) + I \xrightarrow{\quad\times\quad} IV \qquad (6)$$

Irradiation of II isolated under similar conditions as I gave a mixture of I and II in the same 42:58 ratio as the isomerization of I. The sensitized isomerization of I to II (or II to I) occurs through the T_1 state of I (or of II) or a phantom triplet[12]

---

* A similar decomposition has been recorded.[11]

and proceeds much faster than the direct irradiation. High energy sensitizers such as 4,4′-dichlorobenzophenone (E_T 68 kcal/mole), acetophenone (74 kcal/mole), and propiophenone (75 kcal/mole) were found as effective as benzophenone (69 kcal/mole), whereas a low energy sensitizer such as fluorenone (53 kcal/mole) was inactive.[13,*] The fast triplet-exchange (Eq 2) accounts for the absence of benzopinacol among the products.

In this particular case, oxetane formation should be formulated by the Eq 5 (Saltiel mechanism)[15] rather than Eq 4 (Arnold mechanism.[8] This assumption was based on the observation that the yield of XVI depended on the concentration of benzophenone, which should be present in the ground state. Practically no XVI was obtained in the presence of less than 10 mole% of benzophenone (based on I), the *cis-trans* isomerization being the sole reaction observed. The T_1 state of I can not attack I to afford the dimer IV (Eq 6), as IV has never been obtained in the presence of carbonyl compounds.

A cyclohexane solution of I was irradiated with Pyrex-filtered light in the presence of added benzophenone. Concentrations of I and the sensitizer were both 1M. After 115 hr reaction the adduct XVI was obtained in 16% yield together with an isomeric mixture of I and II in a ratio of 42:58 and no dimer IV was detected.

The UV spectrum of I shows that it can absorb a considerable fraction of the Pyrex-filtered light. The fluorescence spectrum of I measured in 0·05M ethanol solution indicated a broad band between 310–380 mμ with a max at 335 mμ. Addition of benzophenone (60 mole%) to this solution completely quenched the fluoroescence.†

Accordingly, the Pyrex-filtered light in addition to reactions of Eqs 1, 2, 3 and 5 induces the following

$$\mathrm{I} + h\nu \longrightarrow \mathrm{I}(S_1) \xrightarrow{?} \mathrm{I}(T_1) \qquad (7)$$

$$\mathrm{I}(S_1) + \mathrm{B} \longrightarrow \mathrm{I} + \mathrm{B}(S_1) \qquad (8)$$

With respect to the formation of the dimer IV it may be safe to assume the reaction of Eq 9.

$$\mathrm{I}(S_1) + \mathrm{I} \longrightarrow (\mathrm{I{-}I})^* \longrightarrow \mathrm{IV} \qquad (9)$$

The dimer IV is produced only in the absence of carbonyl compounds as benzaldehydes and benzophenone which effectively quench the S_1 state of I. The remarkable stereospecificity in the dimerization of I can therefore be ascribed to the formation of intermediary excimer (I–I)* derived concertedly[16] from the first excited state (S_1) and the ground state molecule (Eq 9).[17]

The exact nature of the excited state causing direct *cis-trans* isomerization is not clear at present. It should be noted, however, that this transformation accompanying the dimerization was observed also in the presence of azulene (10 mole%) as an efficient triplet quencher. This may imply that the path for direct photoisomerization of I bypasses the triplet state (Eq 10) as suggested by Saltiel.[18]

$$\mathrm{I}(S_1)\ (\text{or phantom singlet}) \longrightarrow \mathrm{II} \qquad (10)$$

---

[*] The E_T of I would probably be less than 62 kcal/mole, which is the value given for styrene.[14]

[†] For singlet quenching by benzophenone, see J. S. Bradshaw and G. S. Hammond, *J. Am. Chem. Soc.* **85**, 3953 (1963).

EXPERIMENTAL

All m.ps and b.ps are uncorrected.

Photodimerization of trans-*anethole* (I). A soln of I (3·70 g, 25 mmoles) in cyclohexane (25 ml) was irradiated under N_2 atmosphere at room temp for 5 hr. Concentration followed by distillation *in vacuo* gave a mixture of I and II (85:15 GLC) and 1,cis-2-*di*-p-*anisyl*-trans-3,trans-4-*dimethylcyclobutane* (IV) as an oil (1·45 g, 39%), b.p. 145–147°/0·07 mm, which crystallized slowly. The solid IV, melted at 53° and no solvent suitable for recrystallization was found. IR absorption bands (neat) were observed at 1245, 1035, 850, 823, 798 and 779 cm^{-1}, while UV (EtOH) at 279 mμ (log ε 3·63). Mass spectrum showed eminent peaks at *m/e* 296 (M^+), 240 and 148 (B^+), (Found: C, 80·8; H, 8·3. $C_{20}H_{24}O_2$ requires: C, 81·0; H, 8·2%.)

A mixture of IV (5·00 g, 17 mmoles) and pyridinium chloride (57 g, 500 mmoles) was heated at 180° with stirring for 2 hr. Work up gave 1,cis-2-*bis*(*4-hydroxyphenyl*)-trans-3,trans-4-*dimethylcyclobutane* (V) as colourless crystals (3·97 g, 87%), m.p. 149–150° (from benzene–hexane). IR max (Nujol) appeared at 3270 cm^{-1} (phenolic OH), while UV (EtOH) at 282 and 299 mμ (log ε, 3·49 and 3·71). (Found: C, 80·9; H, 7·3. $C_{18}H_{20}O_2$ requires: C, 80·6; H, 7·5%.)

To a soln of V (0·54 g, 2·0 mmoles) in 1·6 ml of 2·5N NaOH Me_2SO_4 (1·10 g, 8·7 mmoles) was added gradually at room temp and stirring was continued for an additional 2 hr. Work up gave a dimethyl ether (0·51 g, 86%), b.p. 146–151°/0·1 mm, which was identical with IV in all respects (IR, UV, NMR and MS).

A soln of V (0·80 g, 3 mmoles) and Ac_2O (1·02 g, 10 mmoles) in pyridine (10 ml) was heated on a water bath for 1·5 hr. The *diacetate* (VI) of V formed colourless crystals (1·04 g, 98%), m.p. 87–88° (from EtOH). IR maxima (Nujol) appeared at 1765, 1200 and 860 cm^{-1}. (Found: C, 74·8; H, 7·0. $C_{22}H_{24}O_4$ requires: C, 75·0; H, 6·9%.)

meso-1,4-*Di*-p-*anisyl*-2,3-*dimethylbutane* (VII) *from* IV. A soln of IV (2·40 g, 8·1 mmoles) in ether (10 ml) was added to liq. NH_3 (100 ml) containing metallic Na (2·0 g, 0·087 g-atom) and the mixture was stirred for 0·5 hr. Work up afforded VII as colourless plates (1·97 g, 82%), m.p. 99–100° (from EtOH). IR maxima (Nujol) appeared at 1250, 1031, 832, 810 cm^{-1}. NMR spectrum consisted of signals at δ 0·81 (6H, d, Me), 1·75 (2H, m, CH), 2·50 (4H, AB part of an ABX system, CH_2), 3·75 (6H, s, OMe), 6·85 (8H, qu, aromatic). (Found: C, 80·4; H, 8·8. $C_{20}H_{26}O_2$ requires: C, 80·5; H, 8·8%.)

meso-2,3-*Dimethyl*-1,4-*diphenylbutane* (VIII) *from* V. To a soln of V (3·90 g, 14·5 mmoles) and diethyl phosphite (4·14 g, 30 mmoles) in CCl_4 (15 ml), Et_3N (4·3 ml) was added gradually with stirring at 0°. The temp was maintained for an additional 5 hr. After addition of water the mixture was extracted with ether and this soln was washed (dil HCl), dried ($MgSO_4$) and concentrated to afford the diphosphate of V as an oil (7·27 g, 93%) which was subjected to the following reduction without isolation. The oil (6·55 g, 12 mmoles) was dissolved in liq NH_3 (30 ml) and metallic Na (5·0 g, 0·22 g-atom) was added in portions. After stirring for 1 hr the reaction mixture was treated with MeOH (30 ml) and left overnight. Extraction with benzene and decolourization by passing through an alumina column afforded an oil, distillation of which gave pure VIII (1·70 g, 60%), b.p. 107–109°/0·3 mm (lit.[5] b.p. 108–112°/0·5 mm). NMR consisted of signals at δ 0·80 (6H, d, Me), 1·75 (2H, m, CH), 2·50 (4H, AB part of an ABX system, CH_2), 7·0 (10H, m, aromatic). (Found: C, 90·9; H, 9·4. Calc. for $C_{18}H_{22}$: C, 90·7; H, 9·3%.)

In a test tube (12 × 118 mm) IV was heated at 500° for 30 min. The product was confirmed to be I (ca. 75%) by IR and GLC.

1,cis-2-*Dimethyl*-trans-3,trans-4-*diphenylcyclobutane from* V. To a soln of V (5·36 g, 20 mmoles) in pyridine (20 ml) maintained at 100° *p*-toluenesulphonyl chloride (8·0 g, 42 mmoles) was added in portions in the course of 3 hr. After addition of water, the reaction mixture was extracted with benzene. The benzene soln was washed (dil HCl), dried ($MgSO_4$) and concentrated to afford the tosylate of V as an oil (10·2 g, 89%) which was subjected to the subsequent reaction without isolation. A mixture of this oil (6·46 g, 11 mmoles) and Raney Ni (30 g) in EtOH (100 ml) was heated at reflux for 5 hr. Work up gave the title hydrocarbon, which was purified by alumina column chromatography in hexane soln and then by preparative GLC. The product (0·22 g, ca. 19% based on the consumed tosylate) was proved to be identical in all respects with the hydrocarbon derived from β-truxinic acid (IR, UV, NMR), *vide infra*. From the column 57% of the tosylate was recovered unchanged.

Dimethyldiphenylcyclobutane isomers derived from the cinnamic acid dimers. As the three dimers were subjected to a procedure virtually common to all of them, the experimental details will be given only for α-truxillic acid. To a soln of LAH (1·90 g, 50 mmoles) in THF (30 ml) α-truxillic acid[19] (7·30 g, 25 mmoles) dissolved in THF (100 ml) was added with stirring and the mixture was heated at reflux for 5 hr. Work up gave 1,trans-3-*bis*(*hydroxymethyl*)-cis-2,trans-4-*diphenylcyclobutane* as colourless crystals (6·70 g, ca. 100%), m.p. 103–104° from benzene. (Found: C, 80·2; H, 7·4. $C_{18}H_{20}O_2$ requires: C, 80·6; H, 7·5%.) The product was converted to a tosylate (not isolated) and the crude tosylate (4·59 g) dissolved in THF (70 ml) was treated with a soln of LAH (0·91 g) in THF (50 ml) at reflux. Distillation gave 1,trans-3-*dimethyl*-cis-2,trans-4-*diphenylcyclobutane* (1·62 g, 86%), b.p. 114°/0·1 mm. IR absorptions (neat) appeared at 3050, 2950, 1610, 1500, 1460, 1380, 735, 695 cm^{-1}. (Found: C, 91·7; H, 8·5. $C_{18}H_{20}$ requires: C, 91·5; H, 8·5%.)

β-Truxinic acid[19] gave 1,cis-2-*bis(hydroxymethyl)*-trans-3,trans-4-*diphenylcyclobutane* (93%), m.p. 109–110° (from benzene). IR absorption (Nujol) appeared at 3300 cm^{-1}. (Found: C, 80·3; H, 7·8. $C_{18}H_{20}O_2$ requires: C, 80·6; H, 7·5%.) This was converted to 1,cis-2-*dimethyl*-trans-3,trans-4-*diphenylcyclobutane* (80%), b.p. 110–113°/0·13 mm. IR spectrum (neat) had a broad absorption at 780–740 cm^{-1}. (Found: C, 92·2; H, 8·4. $C_{18}H_{20}$ requires: C, 91·5; H, 8·5%.)

δ-Truxinic acid[20] gave 1,trans-2-*bis(hydroxymethyl)*-cis-3,trans-4-*diphenylcyclobutane* (94%), m.p. 139–140° from benzene. (Found: C, 80·3; H, 7·5. $C_{18}H_{20}O_2$ requires: C, 80·6; H, 7·5%.) This was converted to 1,trans-2-*dimethyl*-cis-3,trans-4-*diphenylcyclobutane* (75%), b.p. 103–104°/0·05 mm. (Found: C, 90·9; H, 8·5. $C_{16}H_{20}$ requires: C, 91·5; H, 8·5%.)

Reaction of I *with benzaldehyde.* A soln of I (5·18 g, 35 mmoles) and benzaldehyde (3·71 g, 35 mmoles) in benzene (35 ml) was irradiated under N_2 atm at room temp. After 168 hr irradiation, distillation *in vacuo* gave 3-p-*anisyl-2-methyl-4-phenyloxetane* (IX, Ar = Ph) as an oil (2·02 g, 23%), b.p. 128–130°/0·1 mm. IR absorptions (neat) were observed at 1100, 980, 835, 750 and 700 cm^{-1}, while UV (EtOH) at 279 and 286 mμ (log ε, 3·48 and 3·50). NMR spectrum consisted of signals at δ 1·50 (3H, d, Me), 3·5 (1H, m, AnCH), 3·71 (3H, s, OMe), 4·9 (1H, m, MeCH), 5·58 (1H, d, PhCH) and 6·6–7·4 (9H, m, aromatic). (Found: C, 79·8; H, 7·2. $C_{17}H_{18}O_2$ requires: C, 80·3; H, 7·1%.)

Treatment of IX (Ar = Ph; 1·55 g, 6·2 mmoles) over a silica-gel column as described before afforded 4-methoxy-*trans*-stilbene (1·06 g, 81%), m.p. and mixed m.p. 135° (lit.[21] m.p. 135°). (Found: C, 85·4; H, 6·7. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%.)

Reaction of I *with* p-*anisaldehyde.* A soln of I (10·37 g, 70 mmoles) and *p*-anisaldehyde (9·53 g, 70 mmoles) in benzene (70 ml) was irradiated under N_2 atm with Pyrex-filtered light at room temp for 168 hr. Work up gave III (2·26 g, 13%), m.p. 209° from benzene (lit.[22] m.p. 214°).

A similar reaction with 4-chlorobenzaldehyde gave 4-chloro-4'-methoxy-*trans*-stilbene (7·59 g, 44%), m.p. and mixed m.p. 174–175° (lit.[21] m.p. 177°).

Reaction of I *with salicylaldehyde.* A soln of I (10·37 g, 70 mmoles) and salicyaldehyde (8·55 g, 70 mmoles) in benzene (70 ml) was irradiated under N_2 atm at room temp for 168 hr. Work up gave 4-p-*anisyl-2-hydroxy-3-methylchroman* (XI; 3·52 g, 19%) as colourless crystals, m.p. 158·5–159° from benzene. IR absorptions (Nujol) occurred at 3450 cm^{-1} and UV (EtOH) at 274 mμ (log ε 3·63). NMR spectrum consisted of signals at δ 0·93 (3H, d, Me), 2·1 (1H, m, MeCH), 3·05 (1H, d, OH), 3·80 (3H, s, OMe), 3·90 (IH, d, AnCH), 5·50 (1H, qu, HOC<u>H</u>), 6·7–7·2 (8H, m, aromatic). (Found: C, 75·3; H, 7·0. $C_{17}H_{18}O_3$ requires: C, 75·5; H, 6·7%.)

A soln of XI (0·30 g, 1·1 mmoles) in pyridine (5 ml) was added to a suspension of CrO_3 (1·0 g) in pyridine (10 ml). Stirring was continued for 15 hr at room temp. Work up afforded 4-p-*anisyl-3-methyl-3,4-dihydrocoumarin* (XII), as colourless crystals (0·25 g, 86%), m.p. 116–117° from EtOH. IR absorption (Nujol) occurred at 1765 cm^{-1}. NMR spectrum consisted of signals at δ 1·21 (3H, d, Me), 2·96 (1H, d of q's, MeCH), 3·83 (3H, s, OMe), 4·00 (1H, d, AnCH) and 6·8–7·3 (8H, m, aromatic). (Found: C, 75·9; H, 6·1. $C_{17}H_{16}O_3$ requires: C, 76·1; H, 6·0%.)

To a soln of XI (175 mg, 0·65 mmole) and NaOH (0·04 g) in 50% EtOH (1 ml), Me_2SO_4 (0·1 ml) was added at room temp with stirring for 4 hr. Work up gave methyl ether of XI, 4-p-*anisyl-2-methoxy-3-methylchroman* (XIII; 182 mg, 97%), m.p. 58° from EtOH, b.p. 154–156°/0·3 mm. Mass spectrum showed the parent peak at *m/e* 284. (Found: C, 75·8; H, 7·4. $C_{18}H_{20}O_3$ requires: C, 76·1; H, 7·1%.)

Reaction of 1,1-*diphenylethylene with salicylaldehyde.* A soln of 1,1-diphenylethylene (11·5 g, 64 mmoles) and salicylaldehyde (7·82 g, 64 mmoles) in benzene (70 ml) was irradiated under N_2 atm at room temp for 240 hr. Work up gave 2-*hydroxy-4,4-diphenylchroman* (XIV) as colourless crystals (4·14 g, 21%), m.p. 217–218° from benzene. IR absorptions (Nujol) occurred at 3250, 1580, 1055, 1030, 745, 690 cm^{-1}. (Found: C, 83·2; H, 6·2. $C_{21}H_{18}O_2$ requires: C, 83·4; H, 6·0%.)

An ice-cold soln of XIV (0·20 g, 0·66 mmole) in acetone (30 ml) was treated with excess Jones reagent[23] (1·0 ml) at 0°. Work up gave XV, m.p. 146–147° (lit.[10] m.p. 150°). IR absorption (Nujol) occurred at 1785 cm^{-1}. NMR spectrum consisted of signals at δ 3·55 (2H, s, CH_2), 6·70–7·50 (14H, m, aromatic). (Found: C, 84·3; H, 5·4. Calc. for $C_{21}H_{16}O_2$: C, 84·0; H, 5·4%.)

Reaction of I *with benzophenone.* A soln of I (2·95 g, 20 mmoles) and benzophenone (3·64 g, 20 mmoles) in cyclohexane (20 ml) was irradiated under N_2 atm through a 10% soln (1·5 cm thick) of $CuSO_4$ as a filter at room temp for 115 hr. The isomeric mixture of I and II was recovered by distillation. GLC showed that the ratio I : II was 42 : 58. The residue was further purified by distillation *in vacuo* to afford 3-p-*anisyl*-4-*methyl*-2,2-*diphenyloxetane* (XVI; 1·41 g, 21%) as a colourless oil, b.p. 153–155°/0·1 mm. IR absorption (neat) occurred at 980 cm^{-1}, while UV (EtOH) at 270 and 285 mμ (log ε, 3·58 and 3·56). NMR spectrum consisted of signals at δ 1·49 (3H, d, MeCH), 3·70 (3H, s, OMe), 4·32 (1H, d, AnCH), 5·0 (1H, d of qu's, MeCH), 6·7–7·5 (14H, m, aromatic). (Found: C, 84·3; H, 6·4. $C_{23}H_{22}O_2$ requires: C, 83·6; H, 6·7%.) Irradiation with Pyrex-filtered light gave XVI (1·04 g, 16%) besides a mixture of I and II (42 : 58). Passing through a silica-gel column with benzene–CCl_4 (2 : 1) as an eluant caused cleavage of XVI (4·01 g) into 2-p-*anisyl*-1,1-*diphenylethylene* (XVII; 3·01 g, 86%), m.p. 77–78° (lit.[24] m.p. 81–82°). (Found: C, 87·9; H, 6·1. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%.)

Reaction of I *in the presence of azulene.* A soln of I (740 mg, 5·0 mmoles) and azulene (6·4 mg, 0·5 mmole) in cyclohexane (10 ml) was irradiated in a Pyrex tube (10 × 40 mm) under N_2 atm at room temp for 30 hr. A mixture of I and II was isolated in a 69% recovery and the ratio I : II was found to be 81 : 19. The higher boiling fraction contained IV (26% yield), which was identified by IR spectrum.

Irradiation of cis-*anethole* (II). A soln of II (1·48 g, 10 mmoles) in cyclohexane (10 ml) was irradiated under N_2 atm at room temp for 5 hr. Concentration followed by distillation *in vacuo* gave a mixture of I and II (5:95, analysis by GLC) and an oil (0·37 g, 25%), b.p. 150–153°/0·1 mm. The oily dimer of II showed IR absorptions (neat) at 1245, 1033, 850, 825, 800, 790 cm^{-1}, while UV (EtOH) at 280 mμ (log ε 3·67). The structure of this dimer was not determined.

Reaction of II *with benzophenone.* A soln of II (148 mg, 1 mmole) and benzophenone (182 mg, 1 mmole) in cyclohexane (1 ml) was placed in a Pyrex tube (10 × 40 mm) under N_2 atm. Irradiation through a 10% soln of $CuSO_4$ as a filter was continued for 5 hr at room temp. GLC of the recovered mixture of I and II showed that the ratio was 42 : 58. The oxetane fraction was not investigated.

Acknowledgement—This work was supported in part by Grant-in-aid (No. 59290) administered by the Ministry of Education, Japanese Government. The authors are grateful to Prof. K. Sisido for help and encouragement and also to Prof. W. Funasaka who gave facilities for determining the fluorescence spectra. Microanalyses were performed by Mrs. K. Fujimoto. Part of NMR spectra were taken by Dr. T. Shingu, Faculty of Pharmaceutical Science, Kyôto University, and all mass spectra by the staff of the Central Research Institute of Toyo Rayon Co. The assistance of these people is gratefully acknowledged.

REFERENCES

[1] Y.-R. Naves, P. Ardizio and C. Favre, *Bull. Soc. Chim. Fr.* 566 (1958).
[2] P. Hoering and K. P. Grälert, *Ber. Deutsch. Chem. Ges.* **42**, 1204 (1909).
[3] E. H. White, F. McCapra and G. F. Field, *J. Am. Chem. Soc.* **85**, 337 (1963).
[4] G. W. Kenner and N. R. Williams, *J. Chem. Soc.* 522 (1955)
[5] J. Shabtai and H. Pines, *J. Org. Chem.* **29**, 2408 (1964).
[6] *Chemistry of Carbon Compounds* (Edited by E. H. Rodd) Vol. II; pp. 62 and 64. Elsevier, Amsterdam (1953).
[7] G. W. Kenner and M. A. Murray, *J. Chem. Soc.* S178 (1949).
[8] D. R. Arnold, R. L. Hinman and A. H. Glick, *Tetrahedron Letters* 1425 (1964).
[9] E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *J. Am. Chem. Soc.* **88**, 2652 (1966) and Refs cited there.
[10] W. H. Starnes, Jr., *Ibid.* **86**, 5608 (1964).
[11] D. J. Patel and D. I. Shuster, *Ibid.* **89**, 184 (1967).
[12] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *Ibid.* **86**, 3197 (1964).
[13] The E_T values were taken from N. J. Turro, *Molecular Photochemistry* p. 132. Benjamin, New York (1965).
[14] D. F. Evans, *J. Chem. Soc.* 1351 (1957); 1735 (1960)).
[15] J. Saltiel, R. M. Coates and W. G. Dauben, *J. Am. Chem. Soc.* **88**, 2745 (1966).
[16] R. Hoffmann and R. B. Woodward, *Ibid.* 2046 (1965).
[17] H. Morrison, H. Curtis and T. McDowell, *Ibid.* **88**, 5415 (1966).
[18] [a] J. Saltiel, E. D. Megarity and K. G. Kneipp, *Ibid.* **88**, 2336 (1966); [b] J. Saltiel, *Ibid.* **89**, 1036 (1967).

[19] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.* 1996 (1964).
[20] R. Stoermer and F. Scholtz, *Ber. Deutsch. Chem. Ges.* **54**, 85 (1921).
[21] R. von Walther and A. Wetzlich, *J. Prakt. Chem.* **61**, 169 (1900).
[22] W. Tadros, L. Ekladius and A. B. Sakla, *J. Chem. Soc.* 2351 (1954).
[23] A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *Ibid.* 2548 (1953).
[24] H. Staudinger and N. Kon, *Liebigs Ann.* **384**, 38 (1911).