Photo-oxidation of Aryldihydropyrans

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6-*p*-Methoxyphenyl-3,4-dihydro-2*H*-pyran (III) and its 4,4-dimethyl analogue (IV) have been prepared and photo-oxidised. The mechanism of formation of the products, 4-*p*-anisoyloxybutyraldehyde (XVII) and 4-*p*-anisoyloxy-2,2-dimethylbutyraldehyde (XVIII), is considered.

SENSITISED photo-oxidation of olefins commonly leads to allylic peroxides.[1,2] The accepted mechanism of this reaction, involving singlet oxygen in a six-membered transition state, has recently been challenged by Fenical, Kearns, and Radlick who have shown[3] that an intermediate is involved which can be diverted by attack with azide ion. This intermediate they believe to be a perepoxide (I). A less common reaction of olefins in

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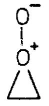
[1] 'Oxidation of Organic Compounds,' vol. III, Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D.C., 1968.

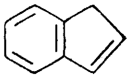
[2] K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

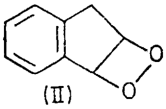
[3] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 7771.

photosensitised oxidations results in carbonyl fragments, exemplified by the conversion of indene to *o*-formylphenylacetaldehyde.

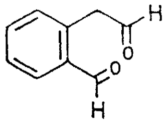


(I)



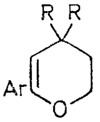


(II)

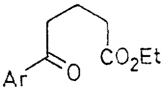


Fenical *et al.* have shown that in this particular case,[4] an independent photo-oxidative mechanism is operating and the products are not formed by decomposition of an intermediate hydroperoxide.[5] A dioxetan (II) was suggested as the precursor of the homophthaldehyde and is supported by the work of Kopecky [6] who has prepared alkyl dioxetans and shown that they decompose thermally to yield carbonyl fragments.[7]

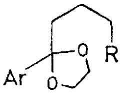
This paper reports the behaviour of the dihydropyrans (III) and (IV) towards singlet oxygen.[8]



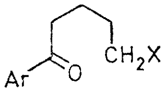
(III) R = H
(IV) R = Me



(V)



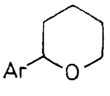
(VI) R = CO_2Et
(VII) R = $CH_2 \cdot OH$



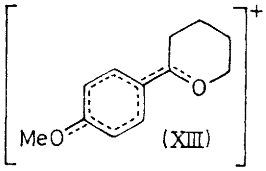
(VIII) X = OH
(IX) X = OAc
(X) X = OTos
(XI) X = OEt

Ar = *p*-MeO·C_6H_4-

The synthesis of the dihydropyran (III) is outlined above. Even prolonged acetalisation of the ester (V) went only *ca.* 90% to completion judging from a small residual benzylic carbonyl band in the i.r. spectrum of the acetal (VI). The keto-ester remaining appeared, after reduction with lithium aluminium hydride and deacetalisation, as the tetrahydropyran (XII), m.p. 43·5—45°, easily separable from the crystalline keto-alcohol (VIII). Attempted deacetalisation of crude (VII) by heating it with aqueous acetic acid gave a 5 : 3 mixture of acetate (IX) and the required keto-alcohol (VIII). Partial acetylation of the latter also occurred in hot aqueous acetic acid. The intervention of the protonated form of the dihydropyran (XIII) and its subsequent attack by acetic acid or water probably assists in this behaviour.[9] Deacetalisation to give the keto-alcohol (VIII) was better carried out with acetone and sulphuric acid.



(XII)

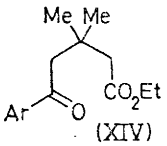


(XIII)

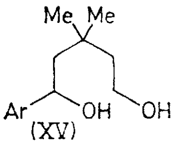
Ar = *p*-MeO·C_6H_4

Attempts to prepare the dihydropyran (III) by acid cyclisation of the keto-alcohol (VIII) failed. However, a crystalline tosylate (X) was prepared and, although sodium ethoxide in ethanol gave only the ether (XI), potassium t-butoxide in t-butyl alcohol gave a good yield of the required dihydropyran (III) as an oil which crystallised at low temperature. Its structure follows from its i.r. (1652 cm.$^{-1}$; enol-ether) and n.m.r. spectra.

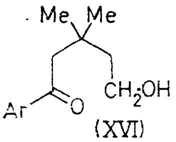
An attempt to prepare the dimethyldihydropyran (IV) by an analogous route foundered because acetalisation of keto-ester (XIV) (prepared by acylation of anisole with 3,3-dimethylglutaric anhydride and aluminium chloride followed by esterification) was unsuccessful.



(XIV)



(XV)



(XVI)

Ar = *p*- MeO·C_6H_4

However, reduction of the keto-ester (XIV) with an excess of lithium aluminium hydride gave the diol (XV) which was converted into the dimethyldihydropyran (IV) by oxidation with manganese dioxide in acetone followed by cyclisation with toluene-*p*-sulphonic acid in benzene. The ring closure of (XVI) with acid is in contrast to the behaviour of (VIII) and is characteristic of the gem-dialkyl effect.[10]

Photo-oxidation of Compounds (III) *and* (IV).—The dihydropyran (III) is sensitive to oxygen and when the compound was set aside a band at 1705 cm.$^{-1}$ in the i.r. spectrum slowly developed and the material gradually became more viscous. It was also sensitive to moisture (in the absence of base) with the formation of the keto-alcohol (VIII). Preliminary experiments showed that oxidation of (III) occurred when oxygen was passed into a pyridine solution of the compound in the absence of light, but that photo-oxidation in the presence of haematoporphyrin as sensitiser and with illumination from a tungsten bulb proceeded at a greatly accelerated rate. The progress of the reaction was monitored by observing the disappearance of the band at 1652 cm.$^{-1}$ and the appearance of a broad carbonyl band in the i.r. spectrum of withdrawn samples. Consumption of (III) was complete within 1 hr. and the formyl-ester (XVII) was obtained in 76% yield after evaporation of the pyridine and removal of haematoporphyrin by chromatography through a short silica column.

The dimethyldihydropyran (IV) is significantly more stable than (III) towards aerial oxidation and complete

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[4] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 3396.

[5] For an example of a hydroperoxide which readily yields carbonyl fragments, C. Dufraisse, *Compt. rend.*, 1957, **244**, 970; J. Sonnenberg and D. M. White, *J. Amer. Chem. Soc.*, 1964, **86**, 5685; E. H. White and M. J. C. Harding, *ibid.*, 1964, **86**, 5686.

[6] K. R. Kopecky and C. Mumford, *Canad. J. Chem.*, 1969, **47**, 709.

[7] Dioxetans have also been postulated intermediates in chemiluminescent reactions: F. McCapra, *Quart. Rev.*, 1966, **20**, 485; T. Goto and and Y. Kishi, *Angew. Chem. Internat. Edn.*, 1968, **7**, 407; P. D. Bartlett and A. P. Schaaf, *J. Amer. Chem. Soc.*, 1970, **92**, 3223; S. Mazur and C. S. Foote, *ibid.*, 1970, **92**, 3225.

[8] Preliminary Communication: *Chem. Comm.*, 1970, 177.

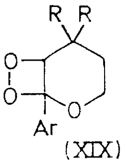
[9] H. R. Ward and P. D. Sherman, *J. Amer. Chem. Soc.*, 1968, **90**, 3812.

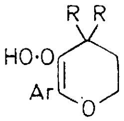
[10] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Interscience, New York, 1965, p. 191.

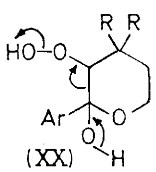
photo-oxidation required 5 hr. where (III) required 1 hr. After 4 hr. the intensity of the carbonyl band reached a maximum although 10% of (IV) still remained. The formyl-ester (XVIII) was isolated after a similar work-up to that required for (XVII). Further oxidation of the formyl-ester (XVIII)[11] probably accounts for the maximum observed after 4 hr. and both aldehydes (XVIII) and (XVII) were extensively decomposed when exposed to the atmosphere overnight. Both formyl-esters were identified by spectroscopy and by conversion into 2,4-dinitrophenylhydrazones.

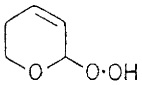
$$p\text{-MeO}\cdot C_6H_4\cdot CO\cdot O\cdot[CH_2]_2\cdot CR_2\cdot CHO \qquad \begin{array}{l}\text{(XVII) } R = H\\ \text{(XVIII) } R = Me\end{array}$$

Mechanism of Photo-oxidation.—The fact that (IV) is photo-oxidised suggests that the formyl-esters (XVII) and (XVIII) do not arise by decomposition of intermediate allylic peroxides, and an intermediate dioxetan (XIX) is the most obvious precursor.


(XIX)

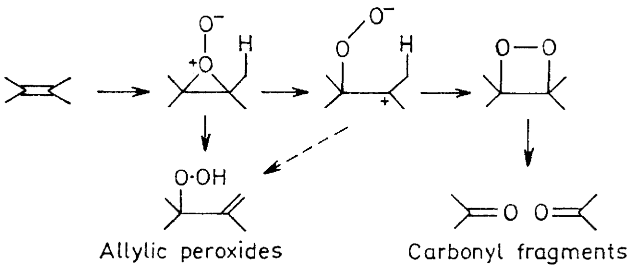



(XX)


(XXI)

Ar = p-MeO·C_6H_4 R = H,Me

Another possible mechanism, the addition of adventitious water to a hydroperoxide with subsequent fragmentation, (XX), is less likely since there was no uptake of deuterium as judged from n.m.r. and mass spectral analysis, when the photo-oxidation was conducted in the presence of added deuterium oxide. Whether the dioxetan is the first formed intermediate or is itself derived by decomposition of an initially formed perepoxide (Scheme) is difficult to prove. This would unify the first photo-oxidation step of olefins with subsequent decomposition of the perepoxide, either to form allylic hydroperoxides or by rearrangement to dioxetans.



SCHEME

This idea is supported by the fact that it is those olefins (enamines, styrenes, and polyenes)[12] where there would be stabilisation of the carbonium ion (formed by ring fission of the perepoxide), which give carbonyl fragments.* In these cases, formation of the dioxetan and its subsequent cleavage to carbonyl compounds may become competitive with proton abstraction and formation of the allylic peroxide. There is also a statistical effect possible in that an olefin which bears electron-donating substituents has, *per se*, less available hydrogens for abstraction. However, Kearns[13] has calculated that these (low-ionisation potential) olefins may add singlet oxygen directly to form dioxetans in contrast to the combination of two ground-state olefins.

The importance of the aromatic ring in dihydropyrans (III) and (IV) in determining the photo-oxidative path is shown by comparison with dihydropyran itself which is reported to yield the hydroperoxide (XXI).[14]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra were determined as Nujol mulls. N.m.r. spectra were measured with a Varian A60A and mass spectra with an A.E.I. MS902 spectrometer. The alumina used was Spence type 'H.' The *para*-substituted aromatic AA′BB′ signals in the n.m.r. spectra are denoted by the position of the four main peaks.

Synthesis of the Dihydropyran (III).—Ethyl 4-*p*-anisoylbutyrate, m.p. 58—59° (lit.,[15] 57—59°) (11·8 g.) was heated with toluene-*p*-sulphonic acid (700 mg.) and ethylene glycol (4·38 g., 1·5 mole) in benzene (200 ml.) using a Dean-Stark trap. The benzene was extracted with sodium hydrogen carbonate and water, and then dried and evaporated. I.r. examination (film) of the oil obtained showed the presence of 10% of residual ketone ($\nu_{max.}$ 1676 cm.$^{-1}$) which was unaffected when heated further with ethylene glycol, toluene-*p*-sulphonic acid, and benzene.

The oily acetal obtained (13 g.) was dissolved in ether (100 ml.) and added dropwise with stirring to lithium aluminium hydride (1·8 g.) in ether (150 ml.). After addition, the solution was stirred for a further 1 hr. and then excess of hydride was decomposed with ethyl acetate; water was added and the ether was separated, dried, and evaporated. I.r. examination of the residual oil (10 g.) showed the disappearance of the ester carbonyl band and the appearance of a broad OH band at 3520 cm.$^{-1}$ (film).

Deacetalisation of Compound (VII) *with Aqueous Acetic Acid.*—The crude ethylene acetal obtained above (1 g.) was heated on a steam-bath for 1 hr. with acetic acid–water (20 ml.; 4 : 1). The bulk of the acetic acid was removed under reduced pressure and the residue was extracted into chloroform. After being washed with sodium hydrogen carbonate and water, the chloroform solution was dried and evaporated. Crystallisation of the residue gave 4-p-*anisoylbutyl acetate* (IX) (250 mg.) as plates (from ethanol), m.p. 93—94° (Found: C, 67·2; H, 7·35. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·25%), $\nu_{max.}$ 1728s, 1668s, and 1603s cm.$^{-1}$; τ ($CDCl_3$) 8·5—8·0 (2-CH_2 and 3-CH_2, m), 7·98 ($COCH_3$, s), 7·05 (4-CH_2, t, J 7 Hz, with further splitting), 6·14 (OCH_3, s), 5·89 (1-CH_2, t, J 6 Hz, with further splitting), 3·16, 3·01, 2·15, 1·99 (ArH).

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* An apparent exception is ethyl sorbate which gives (ref. 2) acetaldehyde and β-formyl ethyl acrylate.

[11] G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Canad. J. Chem.*, 1969, **47**, 3017.

[12] A. Gilbert in 'Photochemistry,' Specialist Periodical Reports The Chemical Society, London, 1970, vol. 1; see also ref. 2.

[13] D. R. Kearns, *J. Amer. Chem. Soc.*, 1969, **91**, 6554.

[14] G. O. Schenck, *Angew. Chem.*, 1952, **64**, 12.

[15] W. S. Johnson, A. R. Jones, and W. P. Schneider, *J. Amer. Chem. Soc.*, 1950, **72**, 2395.

After removal of the above acetate, the residue was chromatographed on alumina. Elution with benzene gave 2-p-*methoxyphenyltetrahydropyran* (XII) (100 mg.) as plates (from hexane), m.p. 43·5—45° (Found: C, 74·8; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%), τ (CCl_4) 8·64—7·96 (3-CH_2, 4-CH_2, and 5-CH_2, m), 6·26 (OCH_3, s), 6·18—5·71 (2-H and 6-CH_2, m), 3·36, 3·22, 2·94, 2·80 (ArH).

This compound showed a very characteristic red spot (R_F 0·25 in benzene) fading to grey-green on t.l.c. (developed with H_2SO_4 and heat).

Further elution with benzene yielded more of the acetate (IX) (80 mg., total 330 mg.) and finally elution with ethanol–ethyl acetate (1 : 1) yielded 4-p-*anisoylbutanol* (VIII) (480 mg.) which crystallised as needles (from benzene–light petroleum), m.p. 49—53·5° (Found: C, 69·3; H, 7·75. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·75%), $\nu_{max.}$ 3470m,br, 1672s, and 1603s cm.$^{-1}$; τ ($CDCl_3$) 8·5—7·97 (2-CH_2, 3-CH_2, and OH, m), 7·04 (4-CH_2, t, *J* 6·5 Hz, with further splitting), 6·48—6·2 (1-CH_2, m), 6·15 (OCH_3, s), 3·15, 3·00, 2·14, 1·98 (ArH).

Deacetalisation of Compound (VII) *with Acetone–Sulphuric Acid.*—The crude acetal (VII) (10 g.) was heated under reflux for 3 hr. with acetone (150 ml.), water (15 ml.), and conc. sulphuric acid (15 drops).[16] Sodium hydrogen carbonate was added and the bulk of the acetone was removed. Chloroform was added, and the organic layer was separated washed with water, dried, and evaporated to yield an oil (8·5 g.) which crystallised when set aside. This product (VIII) was used directly in the tosylation below.

4-p-*Anisoylbutyl Toluene*-p-*sulphonate* (X).—To the alcohol (VIII) (2·6 g.) in ice-cold pyridine (20 ml.) was added toluene-*p*-sulphonyl chloride (2·9 g.); the resulting solution was stirred at 0° for 5 hr. The mixture was poured into ice-water to give an oil which solidified. Crystallisation from ethanol gave the *toluene*-p-*sulphonate* (X) (3·35 g., 74%) as needles, m.p. 72·5—73° (Found: C, 62·9; H, 6·05. $C_{19}N_{22}O_5S$ requires C, 63·0; H, 6·1%), τ ($CDCl_3$) 8·43—8·10 (2-CH_2 and 3-CH_2, m), 7·59 (CH_3, s), 7·27—6·96 (4-CH_2, m), 6·16 (OCH_3, s), 6·05—5·80 (1-CH_2, m), 3·16, 3·02, 2·75, 2·61, 2·28, 2·18, 2·14, 2·03 (2 AA′BB′ systems).

6-p-*Methoxyphenyl*-3,4-*dihydro*-2H-*pyran* (III).—The toluene-*p*-sulphonate (X) (500 mg.) was added in one portion to a solution prepared from potassium (150 mg.) in dry t-butyl alcohol (18 ml.). The solution was gently brought to boil, with occasional swirling; it was then cooled, diluted with benzene, and poured into water. The organic layer was washed with sodium hydrogen carbonate, separated, dried (Na_2CO_3), and evaporated to yield an oil (220 mg., 84%). An n.m.r. sample was prepared by bulb-tube distillation (b.p. 142—147°/2 mm., bath temp.) which crystallised at low temperature; $\nu_{max.}$ (film) 1652m, 1610s, and 1517s cm.$^{-1}$; τ (CCl_4) 8·53—7·64 (3-CH_2 and 4-CH_2, m), 6·29 (OCH_3, s), 5·91 (2-CH_2, t, *J* 5 Hz), 5·05—4·81 (5-H, m), 3·35, 3·20, 2·67, 2·53 (ArH).

Exposure of this material to air caused fairly rapid deterioration (less than 1 hr.) with the appearance of a band at 1705 cm.$^{-1}$ in the i.r. spectrum.

Reaction of 4-p-*Anisoylbutyl Toluene*-p-*sulphonate* (X) *with Sodium Ethoxide.*—The toluene-*p*-sulphonate (1·67 g.) was added to a solution prepared by dissolving sodium (120 mg.) in ethanol (10 ml.); the solution was heated under reflux for 10 min and was then cooled. The bulk of the ethanol was removed under reduced pressure, chloroform was added and the organic layer was washed with water, dried, and evaporated. Crystallisation from light petroleum gave 4-p-*anisoylbutyl ethyl ether* (XI) (0·95 g., 87%) as plates, m.p. 46—47° (Found: C, 71·4; H, 8·5. $C_{14}H_{20}O_3$ requires C, 71·15; H, 8·5%), $\nu_{max.}$ 1673s,br and 1603s cm.$^{-1}$; τ ($CDCl_3$) 8·82 (*CH_3*CH_2O, t, *J* 7 Hz), 8·50—8·02 (2-CH_2 and 3-CH_2, m), 7·06 (4-CH_2, t, *J* 6·5 Hz, with further splitting), 6·54 (1-CH_2, t, *J* 6·5 Hz), 6·53 (CH_3*CH_2*O, q, *J* 7 Hz), 6·13 (OCH_3, s), 3·16, 3·00, 2·13, 1·98 (ArH).

Synthesis of the Dihydropyran (IV). 4-*p*-Anisoyl-3,3-dimethylbutyric acid was prepared from 3,3-dimethylglutaric anhydride (30 g.), aluminium chloride (56 g.), and anisole (21·6 g.) in nitrobenzene (250 ml.) by the method used for preparation of 4-*p*-anisoylbutyric acid[16] except that the mixture was kept for 3 weeks at 0°. The product was an oil (50·2 g., 95%) which was shown to be pure by n.m.r. spectroscopy; $\nu_{max.}$ (film) 1713s,br, 1683s,br and 1608s cm.$^{-1}$; τ ($CDCl_3$) 8·83 (2 × 3-CH_3, s), 7·43 (2-CH_2, s), 6·94 (4-CH_2, s), 6·12 (OCH_3, s), 3·14, 2·98, 2·11, 1·95 (ArH), 1·67 (CO_2H, br, s).

The product gave a 2,4-*dinitrophenylhydrazone*, m.p. 177·5—180° (from ethanol) (Found: C, 55·35; H, 5·2; N, 12·55. $C_{20}H_{22}N_4O_7$ requires C, 55·8; H, 5·15; N, 13·0%).

Esterification of 4-(p-*Anisoyl*)-3,3-*dimethylbutyric Acid.*—This procedure was carried out using 4-*p*-anisoyl-3,3-dimethylbutyric acid (10·5 g.), ethanol, and hydrogen chloride gas. N.m.r. examination of the crude product (12·7 g.) showed only those signals expected for the ethyl ester (XIV) at τ (CCl_4) 8·86 (2 × 3-CH_3, s), 8·83 (*CH_3*CH_2O, t, *J* 7 Hz), 7·57 (2-CH_2, s), 7·02 (4-CH_2, s), 6·17 (OCH_3, s), 5·97 (CH_3*CH_2*O, q, *J* 7 Hz), 3·25, 3·10, 2·22, 2·07 (ArH).

Lithium Aluminium Hydride Reduction of the Ester (XIV).—The crude ester above (12·7 g.) was reduced in ether with an excess of lithium aluminium hydride. I.r. examination (film) of the product oily diol (XV) (10 g.) showed the disappearance of ester and ketone bands and the appearance of a broad band at 3435 cm.$^{-1}$; τ ($CDCl_3$) 9·07 and 8·98 (2 × 3-CH_3, 2 × s), 8·83—7·82 (2-CH_2 and 3-CH_2, m), 7·06 (2 × OH, br, s), 6·32 (1-CH_2, t, *J* 6·5 Hz), 6·23 (OCH_3, s), 5·26 (5-CH, dd, *J* 6 × 3 Hz), 3·27, 3·13, 2·86, 2·72 (ArH).

Oxidation of the Diol (XV) *and Cyclisation to Compound* (IV).—The diol (IV) (1·65 g.) was vigorously stirred with powdered manganese dioxide (17 g.) in acetone (50 ml.)[17] for 9 hr. at room temperature. Manganese dioxide was separated off, the acetone was evaporated, and the residue was heated with toluene-*p*-sulphonic acid (100 mg.) and benzene (20 ml.) in a Dean–Stark trap for 15 min. The cooled solution was washed with sodium hydrogen carbonate and water, dried (Na_2CO_3), evaporated and the residual oil chromatographed over alumina. Elution with benzene gave 6-p-*methoxyphenyl*-3,4-*dihydro*-4,4-*dimethyl*-2H-*pyran* (IV) (1·13 g., 74%) which crystallised as plates (from hexane at −40°), m.p. 29—30° (Found: C, 76·65; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·05; H, 8·3%), $\nu_{max.}$ (film) 1648w, 1611m, and 1516s cm.$^{-1}$; τ (CCl_4) 8·91 (2 × 4-CH_3, s), 8·38 (3-CH_2, unsym. t, *J* 5 Hz), 6·30 (OCH_3, s), 6·04—5·81 (2-CH_2, m), 5·10 (5-H, s), 3·38, 3·23, 2·71, 2·56 (ArH).

Photo-oxidation of 6-p-*methoxyphenyl*-3,4-*dihydro*-2H-*pyran* (III).—Freshly prepared dihydropyran (III) (320 mg.) was dissolved in pyridine (40 ml.) containing haematoporphyrin (3 mg.) and oxygen was bubbled through the solution by way of a sintered disc; the mixture was illuminated with

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[16] B. J. Magerlein and R. H. Levin, *J. Amer. Chem. Soc.*, 1955, **77**, 1904.

[17] E. Adler and H. D. Becker, *Acta Chem. Scand.*, 1961, **15**, 849.

a 240 W tungsten bulb at a distance of 0·5 cm. The solution was stirred vigorously while ice-water was passed through a cooling coil in the solution to maintain an equilibrium temperature of 18°. After 50 min., consumption of starting material was complete as indicated by the disappearance of the i.r. band at 1652 cm.$^{-1}$ and the appearance of a carbonyl band at 1712 cm.$^{-1}$. Pyridine was removed under reduced pressure and the residue was chromatographed through a short silica column with benzene–ethyl acetate (5 : 1) as eluant. 4-*p*-Anisoyloxybutyraldehyde (XVII) (280 mg., 76%) was obtained as an oil, b.p. (bulb–tube; bath-temp.) 165—170°/2 mm., $\nu_{max.}$ (film) 2770w, 1712s,br, and 1610s cm.$^{-1}$; τ (CCl_4) 8·25—7·32 (2-CH_2 and 3-CH_2, m), 6·18 (OCH_3, s), 5·76 (4-CH_2, t, *J* 6·5 Hz), 3·26, 3·11, 2·21, 2·06 (ArH), 0·27 (CHO, t, *J* 1·2 Hz). The 2,4-*dinitrophenylhydrazone* had m.p. 141—142° (from chloroform–light petroleum) (Found: C, 53·75; H, 4·55; N, 13·95. $C_{18}H_{18}N_4O_7$ requires C, 53·75; H, 4·5; N, 13·95%).

Photo-oxidation of 6-(p-*methoxyphenyl*-3,4-*dihydro*-4,4-*dimethyl*-2H-*pyran* (IV).—The photo-oxidation was carried out as above with dihydropyran (IV) (370 mg.), pyridine (40 ml.), and haematoporphyrin (3 mg.). Photo-oxidation was continued for 4 hr., following the reaction by i.r. examination of withdrawn samples. Chromatography of the residue, obtained after evaporation of the pyridine, on silica with benzene–ethyl acetate (10 : 1) as eluant gave 4-*p*-anisoyloxy-2,2-dimethylbutyraldehyde (XVIII) (280 mg., 66%) as an oil, b.p. (bulb–tube; bath-temp.) 175—180°/2 mm., $\nu_{max.}$ (film) 2770w, 1713s,br and 1609s cm.$^{-1}$; τ(CCl_4) 8·87 (2 × 2-CH_3, s), 8·09 (3-CH_2, t, *J* 6·5 Hz), 6·17 (OCH_3, s), 5·74 (4-CH_2, t, *J* 6·5 Hz), 3·22, 3·07, 2·20, 2·05 (ArH), 0·52 (CHO, s). The 2,4-*dinitrophenylhydrazone*, had m.p. 145—148° (from ethanol) (Found: C, 55·75; H, 5·15; N, 13·1. $C_{20}H_{22}N_4O_7$ requires C, 55·81; H, 5·15; N, 13·1%).

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