Configuration and Stereochemistry of Photoproducts by Application of the Nuclear Overhauser Effect. Adducts of Benzophenone with Methyl-substituted Furans and 2,5-Dimethylthiophen, and of Methyl-substituted Maleic Anhydrides with Thiophen and Its Methyl Derivatives, and Benzo[*b*]thiophen

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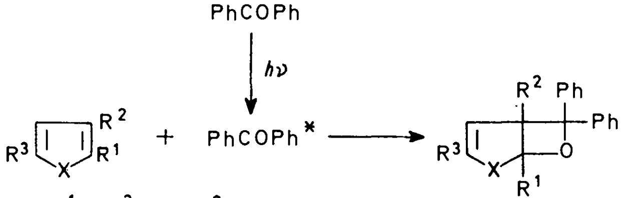
The configurations and the stereochemistry of two series of photocycloaddition products have been elucidated by means of ^{1}H n.m.r. spectroscopy including intramolecular internuclear Overhauser effect measurements. The first series consists of the oxetans (3)—(6) obtained by photoreactions of benzophenone with 3- and 2-methylfuran (1a and b), furfuryl alcohol (1c), 2,3-dimethylfuran (1d), and 2,5-dimethylthiophen (1e). The second series includes photocycloaddition products (9)—(18) formed in reactions of methyl-substituted maleic anhydrides (8a and b) with thiophen (7a), methylthiophens (7b—d), and benzo[*b*]thiophen (15).

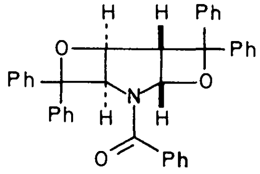
THE intramolecular internuclear Overhauser effect[1] (NOE) has been applied successfully in many configurational and conformational studies of organic molecules in recent years.[1]

It is well known that photoreactions of benzophenone with furan[2] and its methyl derivatives[3-5] lead to oxetans. The reaction presumably involves $n \longrightarrow \pi^*$ excitation of benzophenone *via* a singlet to a low lying triplet state[6]



(1) a; $R^1 = R^3 = H, R^2 = Me, X = O$
b; $R^1 = Me, R^2 = R^3 = H, X = O$
c; $R^1 = CH_2{\cdot}OH, R^2 = R^3 = H, X = O$
d; $R^1 = R^2 = Me, R^3 = H, X = O$
e; $R^1 = R^3 = Me, R^2 = H, X = S$

(3)-(6)



(2)

and subsequent addition of the diradical species to the most labile double bond in the heterocycle. In contrast to the furans, the thiophen and pyrrole analogues do not undergo this type of photoaddition. Nevertheless, it has proved possible to prepare an oxetan (6) from benzophenone and 2,5-dimethylthiophen (1e)[7] and an adduct (2) from *N*-benzoylpyrrole.[8]

We have previously reported the synthesis of the oxetans (3), (4a), and (4b) by photoaddition[3] of benzophenone to 3-methylfuran (1a), 2-methylfuran (1b), and furfuryl alcohol (1c). It appears that benzophenone always adds specifically to the double bond bearing alkyl substituents in the furan series under the conditions of these irradiations (—10°; Hanovia 450 W lamp). In accord with this observation, the oxetan (5) was obtained from benzophenone and 2,3-dimethylfuran (1d) in virtually quantitative yield. The structures of the oxetans (3)—(6) were previously inferred by simple inspection of their ^{1}H n.m.r. spectra, and their configurations and the stereochemistry were not determined on a firm basis. We now demonstrate by the use of NOE data that the oxetans have the configurations shown in Table 1.

The ^{1}H n.m.r. spectra of the products (3)—(6) exhibit two mutually coupled olefinic proton signals. Therefore, the benzophenone must have added to the methylfuran C(1)=C(4) double-bond bearing the methyl substituent(s). That these cycloadditions occurred in a *cis* manner was demonstrated by observing the NOE interactions between the 1-H and the 4-Me [see formula (3)] and between the 4-H and 1-Me (or 1-$CH_2{\cdot}OH$) signals [see formulae (4) and (6)]. Enhancement in the intensities of the 5-H signals was clearly observed in all the spectra when second rf fields were applied at appropriate positions within the humps of the phenyl proton signals [see formulae (3)—(6)]. Similar phenomena were observed for the 4-H signals in the spectra of (4) and (6). These observations rule out the possibility that the positions of the carbon atom carrying the two phenyl groups and the adjacent oxygen atom are reversed.

The data obtained are summarised in Table 1.

It is well known that, if, in addition to the heterocyclic substrate, the reaction medium contains a compound the

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[1] (*a*) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5250; (*b*) J. H. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect; Chemical Applications,' Academic Press, New York, 1971; (*c*) G. E. Bachers and T. Schaefer, *Chem. Rev.*, 1971, **71**, 617; (*d*) R. A. Bell and J. K. Saunders, *Topics Stereochem.*, 1973, **7**, 1.

[2] G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.* 1963, **96**, 498; G. S. Hammond and N. J. Turro, *Science*, 1963, **142**, 1541; S. Toki and K. Sakurai, *Tetrahedron Letters*, 1967, 4119; J. Leitich, *ibid.*, p. 1937.

[3] C. Rivas and E. Payo, *J. Org. Chem.*, 1967, **32**, 2918.

[4] M. Ogata, H. Watanabe, and H. Kano, *Tetrahedron Letters*, 1967, 533.

[5] G. R. Evanega and E. B. Whipple, *Tetrahedron Letters*, 1967, 2163; E. B. Whipple and G. R. Evanega, *Tetrahedron*, 1968, **24**, 1299.

[6] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, 1961, **83**, 2789, and related papers.

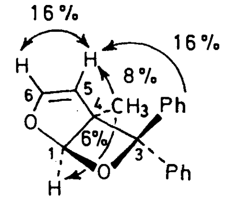
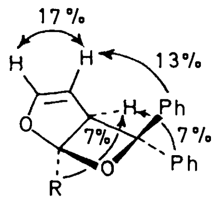
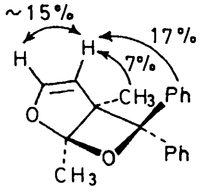
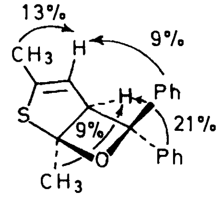
[7] C. Rivas, M. Velez, and O. Crescente, *Chem. Comm.*, 1970, 1474.

[8] C. Rivas, M. Velez, M. Cucarella, R. A. Bolivar, and S. E. Flores, *Acta cient. Venezolana*, 1971, **22**, 145.

lowest triplet level of which is lower in energy than the lowest triplet state of benzophenone, a triplet energy transfer may occur from the latter for the former.[9] Citraconic and 2,3-dimethylmaleic anhydrides are easily photosensitised by benzophenone in this manner, and they have been used in a series of reactions with thiophen derivatives in order to prepare a series of cycloaddition products containing a cyclobutane ring. Thus, in a previous paper [10] we reported the photoreactions of thiophen (7a), 2-methylthiophen (7b), and 3-methylthiophen (7c) with citraconic anhydride (8a), and those of (7b), (7c), and 2,5-dimethylthiophen (7d) with 2,3-dimethylmaleic anhydride (8b), in the presence of benzophenone as sensitiser. However, the structures and especially the stereochemistry of the addition products were not firmly defined. The application of ^{1}H n.m.r. spectroscopy, including NOE measurements has now established the configurations and the stereochemistry of these products as shown in Table 2. In most of these cases, the products isolated were diacids,* instead of the expected anhydrides, as revealed by mass spectrometric molecular-weight determinations.

TABLE 1

^{1}H N.m.r. spectral data for compounds (3)—(6) in [^{2}H]chloroform

Formula† and NOE‡ (increase in integrated area)		J/Hz	δ	
(3)		$J_{1.6}$ 0·9 $J_{5.6}$ 2·8 $J_{6.4-Me}$ 0·1	1-H 4-CH_3 5-H 6-H	6·08(d) 1·09(s) 5·13(d) 6·28(dd)
(4a) (R = Me)		$J_{4.5}$ 2·8 $J_{4.6}$ 1·2 $J_{5.6}$ 3·0 $J_{5.1-Me}$ 0·2$_5$	1-CH_3 4-H 5-H 6-H	1·56(m) 4·14(dd) 4·87(dd) 6·37(dd)
(4b) (R = CH_2·OH)		$J_{4.5}$ 2·8 $J_{4.6}$ 1·2 $J_{5.6}$ 3·0	1-CH_2 4-H 5-H 6-H	3·69(m) 4·46(dd) 4·90(dd) 6·24(dd)
(5)		$J_{5.6}$ 3·0 $J_{5.1-Me}$ 0·2$_5$ $J_{6.1-Me}$ 0·1	1-CH_3 4-CH_3 5-H 6-H	1·57(s) 1·14(s) 5·05(d) 6·24(d)
(6)		$J_{1.6-Me}$ 0·1 $J_{4.5}$ 3·1 $J_{4.6-Me}$ 1·5 $J_{5,6-Me}$ 0·1	1-CH_3 4-H 5-H 6-CH_3	1·81(s) 4·44(dq) 4·82(dq) 1·79(t)

† Here and in the other Tables all products are racemic modifications; only one enantiomer is depicted in each case. ‡ Here and in the other Tables the positive NOE values observed are indicated by arrows in the formulae. i-H$\rightarrow$$j$-H indicates that an NOE was observed on the j-H signal when the i-H frequency was saturated. i-H$\leftrightarrow$$j$-H denotes both i-H$\rightarrow$$j$-H and j-H$\rightarrow$$i$-H.

The ^{1}H n.m.r. signals of all the products in [$^2H_6$]-acetone were assigned on the bases of double- and triple-resonance studies and comparison of chemical shifts. The data obtained are listed in Table 2. Intramolecular NOE data were obtained for all possible two-signal combinations in each product, and positive NOE values obtained are shown in the formulae.

Maleic anhydride derivatives added in a *cis*-manner to

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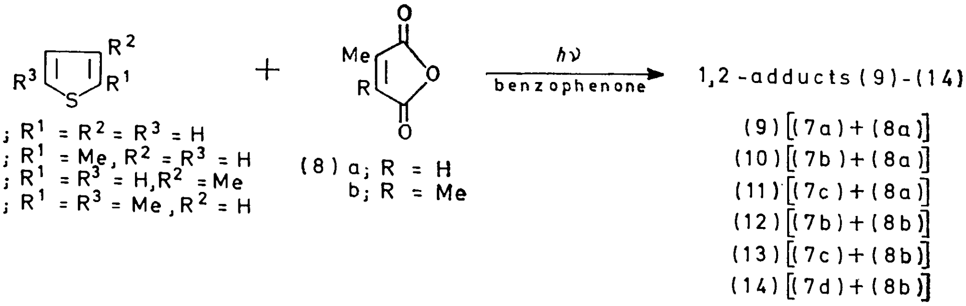
* It is not certain whether the ring opening of the product occurred during the irradiation or during the isolation procedure. Precautions were taken in some experiments to avoid moisture inside the irradiation apparatus; however, the end product was the diacid.

[9] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J Amer. Chem. Soc.*, 1961, **83**, 2395, 2396, 2397.

[10] C. Rivas, M. Velez, O. Crescente, and S. E. Flores, *Revista Latinoamericana de Química*, 1971, **2**, 9.

either the substituted or the unsubstituted double bond of thiophen, depending on the position of the methyl substituent. Cycloaddition of (8a) and (8b) to (7b) occurred at the unsubstituted double bond; the spectra of the products (10) and (12a) show MeC= signals at δ 2·00 and olefinic proton signals at δ 5·30 [see formulae (10) and (12a)]. On the other hand, the spectra of the products (11) and (13) prepared from reactions of (8a) and (8b) with (7c), two mutually coupled olefinic proton signals (J 6·0 Hz) appear at lower field [see formulae (11) and (13)]; this indicates that (8a) and (8b) add to the substituted double bond of (7c).



The *cis*-configuration of the C(1)–C(4) ring junction was inferred from the values of the coupling constants[11] between 1-H and 4-H [J 8·7 in (9) and (10), 8·8 in (12a), and 9·5 Hz in (12b), which was derived from (12a)], and confirmed by observing the NOE interactions between the 1-H and the 4-H [see formulae (9), (10), and (12)], between the 1-H and the 4-Me signals [formulae (11) and (13)], and between the 1-Me and the 4-H signals [formula (14)]. The configurations of the C(2)-H (or Me) and the C(3)-Me, and also their location were unequivocally determined as follows. These groups must be *cis* to each other because NOE enhancements were clearly observed for the 2-H signals on saturating the 3-Me signals [see formulae (9)—(11)]. The values of the coupling constants involving 1-H, 2-H, and 4-H (see Table 2) and the absence of NOE interaction between 1-H and 2-H in (9)—(11), between 4-H and 3-Me in (9), (10), (12), and (14), and between 1-H and 2-Me in (12) and (13) suggest that both 2-H (or 2-Me) and 3-Me should be *trans* to the *cis*-protons (or the proton and methyl group) at C-1 and C-4. The presence of NOE interaction between the 5-H and the 3-Me signals for all the products provides conclusive evidence that the methyl group is at C-3, not at C-2, and also that the 3-Me is *trans* to the *cis*-protons (or the proton and methyl group) at C-1 and C-4.

In a previous paper[10] we also reported the photosensitised cycloadditions of citraconic anhydride (8a) and 2,3-dimethylmaleic anhydride (8b) to benzo[*b*]thiophen (15). However, again the configurations and the stereochemistry of the products were not established unambiguously. We now report that the products have the configurations shown in formulae (16)—(18), determined by the same technique as applied to the oxetans and the other thiophen derivatives.

The ^{1}H n.m.r. signals of the products (16)—(18) were assigned by spin-decoupling experiments and by chemical shift comparisons. On double irradiation at appropriate positions within the complex multiplets due to the benzene ring protons, the signals at δ 4·60, 4·84, and 4·41 were changed into a distinct doublet ($J_{1,4}$ 8·6 Hz), a doublet of doublets ($J_{1,4}$ 8·2, $J_{2,4}$ 1·1 Hz), and a doublet of doublets ($J_{1,4}$ 9·0, $J_{3,4}$ 6·0 Hz) in the spectra of (16), (17a), and (18), respectively. These results must be due to spin-decoupling of the benzylic coupling[12] between 4-H and 5-H; hence they confirm the assignment of the 4-H signals. Other signals were easily assigned. The data obtained are summarised in Table 3. The results from the NOE measurements described later are also compatible with the assignments.

The additions of the anhydrides to compound (15) were inferred to occur in a *cis*-manner from the $J_{1,4}$ values obtained.[11] However, the 1-H and 4-H signals are too close to each other in all of the spectra to confirm the presence of NOE interactions between them. On successive saturation of the 2-Me and the 3-Me frequencies in the spectra of the product (16) obtained by the addition of (8b) to (15) no enhancement in intensities of the 1-H and the 4-H signals was observed; but very weak couplings between the 2-Me and the 1-H, and between the 3-Me and the 4-H were revealed. These facts strongly suggested that the two methyl groups are in a *trans*-relationship to the *cis*-protons at C-1 and C-4, and hence, *cis* to each other [see formula (16)]. On saturation of the methyl frequency at δ 1·05, apparent enhancement, though the amounts were not determined, was observed in the intensities of several peaks in multiplets arising from the benzene ring protons (probably from the 5-H), whereas on saturation of the other methyl frequency (δ 1·37) no changes were observed in the multiplets. These results supported the assignment of the methyl signals and confirmed the *trans*-relationship between 4-H and 3-Me [see formula (16)].

In the case of the addition of (8a) to (15), two kinds of adducts were obtained as shown in formulae (17a) and (18). When the product (17a) was treated with, for example, [$^2H_6$]acetone, a diacid (17b) was easily formed by opening of the anhydride ring. The anhydride (17a) exhibits a $J_{1,2}$ value (2·6 Hz) which is small compared

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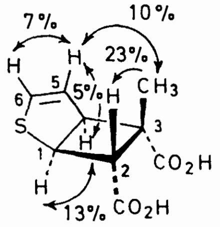
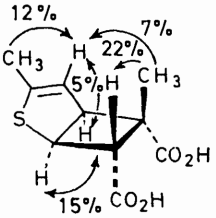
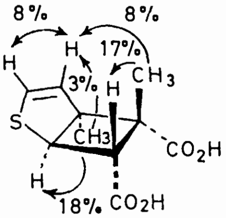
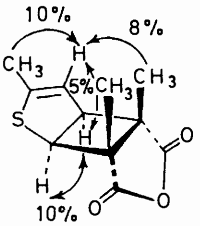
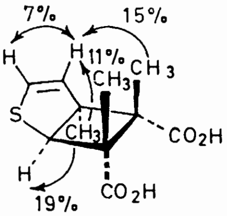
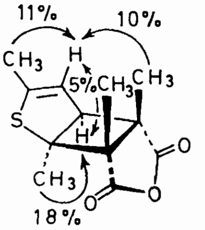
[11] I. Fleming and D. H. Williams, *Tetrahedron*, 1967, **23**, 2747; D. Wendisch and W. Metzner, *Chem. Ber.*, 1968, **101**, 4106; however, see also E. B. Whipple and G. R. Evanega, *Org. Magnetic Resonance*, 1970, **2**, 1, and references therein.

[12] S. Sternhell, *Rev. Pure Appl. Chem.*, 1964, **14**, 15.

TABLE 2

^{1}H N.m.r. spectral data for compounds (9)—(14) in [^{2}H]chloroform

	Formula and NOE (increase in integrated area)	J/Hz		(δ)
(9)		$J_{1,2}$ 8·0 $J_{1,4}$ 8·7 $J_{1,5}$ 0·1 $J_{1,6}$ 1·2 $J_{2,4}$ 1·3 $J_{4,5}$ 2·8 $J_{4,6}$ 2·0 $J_{4,3\text{-Me}}$ 0·1 $J_{5,6}$ 6·0	1-H 2-H 3-CH_3 4-H 5-H 6-H	4·52(ddd) 3·15(dd) 1·43(s) 3·91(dm) 5·63(dd) 6·45(dd)
(10)		$J_{1,2}$ 8·0 $J_{1,4}$ 8·7 $J_{1,5}$ 0·1 $J_{1,6\text{-Me}}$ 0·2 $J_{2,4}$ 1·3 $J_{4,5}$ 2·8 $J_{4,3\text{-Me}}$ 0·1 $J_{4,6\text{-Me}}$ 2·0 $J_{5,6\text{-Me}}$ 1·5	1-H 2-H 3-CH_3 4-H 5-H 6-CH_3	4·49(dd) 3·20(dd) 1·42(s) 3·89(dm) 5·30(dq) 2·00(dd)
(11)		$J_{1,2}$ 8·4 $J_{1,5}$ 0·4 $J_{1,6}$ 1·2 $J_{1,4\text{-Mc}}$ 0·1 $J_{5,6}$ 6·0 $J_{5,4\text{-Me}}$ 0·1	1-H 2-H 3-CH_3 4-CH_3 5-H 6-H	4·19(dm) 2·92(d) 1·44(s) 1·12(s) 5·58(d) 6·31(dd)
(12a) (anhydride)		$J_{1,4}$ 8·8 $J_{1,5}$ 0·1 $J_{1,6\text{-Me}}$ 0·2 $J_{4,5}$ 3·0 $J_{4,3\text{-Me}}$ 0·2 $J_{4,6\text{-Me}}$ 1·8 $J_{5,6\text{-Me}}$ 1·5	1-H 2-CH_3 3-CH_3 4-H 5-H 6-CH_3	4·73(d) 1·40(s) 1·30(s) 4·17(dm) 5·30(dq) 2·00(dd)
(12b) (diacid)		$J_{1,4}$ 9·5 $J_{1,5}$ 0·1 $J_{1,6\text{-Me}}$ 0·2 $J_{4,5}$ 2·8 $J_{4,3\text{-Me}}$ 0·2 $J_{4,6\text{-Me}}$ 2·1 $J_{5,6\text{-Me}}$ 1·5	1-H 2-CH_3 3-CH_3 4-H 5-H 6-CH_3	4·94(d) 1·44(s) 1·27(s) 3·91(dm) 5·24(dq) 1·95(dd)
(13)		$J_{1,5}$ 0·4 $J_{1,6}$ 1·0 $J_{1,4\text{-Me}}$ 0·1 $J_{5,6}$ 6·0 $J_{5,4\text{-Me}}$ 0·1	1-H 2-CH_3 3-CH_3 4-CH_3 5-H 6-H	4·54(m) 1·41(s) 1·28(s) 1·11(s) 5·54(d) 6·22(dd)
(14)		$J_{4,5}$ 3·5 $J_{4,1\text{-Me}}$ 0·1 $J_{4,3\text{-Me}}$ 0·1 $J_{4,6\text{-Me}}$ 1·5 $J_{5,1\text{-Me}}$ 0·2 $J_{5\ 6\text{-Me}}$ 1·6	1-CH_3 2-CH_3 3-CH_3 4-H 5-H 6-CH_3	1·61(s) 1·44(s) 1·27(s) 3·67(dq) 5·17(dq) 2·00(dd)

with those (*ca.* 8 Hz) observed for similar four-membered compounds obtained from the methylthiophens. This fact can be explained as follows: when the anhydride is converted into the diacid, the ring strain imposed on it by the two almost coplanar carbonyl groups is released, causing a change in conformation of the cyclobutane ring, and hence also in the dihedral angle between 1-H and 2-H. The $J_{1,2}$ value for the diacid (17b) was 7·4 Hz, which is at C-2, or *cis* to the 4-H, no NOE would be expected between this methyl group and any benzene ring proton.

The second product from the same photoreaction was obtained as a diacid (18).§ Its structure and the configuration were established as follows. The *cis*-orientation of 2-Me and 3-H was inferred from their NOE [see formula (18)]. That the 2-Me and 3-H are *trans* to the *cis*-protons at C-1 and C-4 was confirmed by the $J_{3,4}$ value of 6·0 Hz compatible with the J_{trans} values between these protons in similar four-membered ring compounds from the methylthiophens. The NOE observed between the 2-H and the 3-Me established that they are *cis*. That the 3-Me is *trans* to 4-H was suggested by the absence of NOE interaction between their signals. The fact that intensities of several peaks, probably those due to 5-H, in the benzene-ring multiplets were enhanced by about 10% in height on saturation of the 3-Me frequency, confirmed the assignment of the methyl group to C-3, and also the *trans*-relationship between the methyl and the 4-H [see formula (17a)]. If the methyl group were either situated and also by the absence of NOE between the 1-H and the 2-Me.

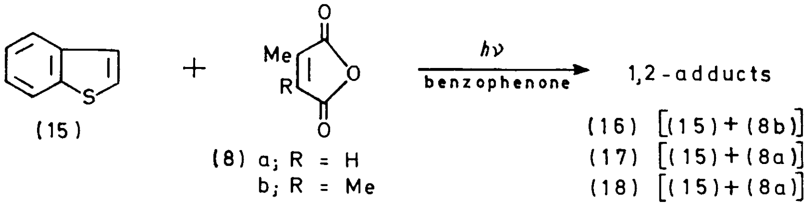
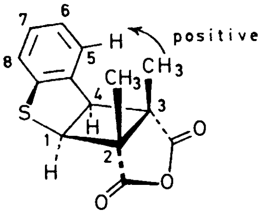
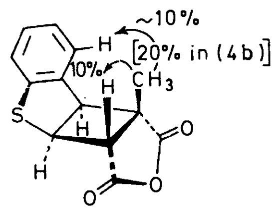
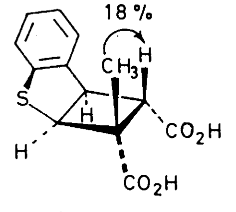


TABLE 3

^{1}H N.m.r. spectral data for compounds (16)—(18)

Formula and NOE (increase in integrated area)		*J*/Hz	δ	
(16)[a]		$J_{1,4}$ 8·6 (8·4) $J_{1,2\text{-Me}}$ 0·1 $J_{4,5}$ *ca.* 0·4	1-H 2-CH$_3$ 3-CH$_3$ 4-H	4·65(d) (4·88) 1·37(s) (1·38) 1·05(s) (1·07) 4·60(dm) (4·72)
(17a)[b] (anhydride)		$J_{1,2}$ 2·6 $J_{1,4}$ 8·2 $J_{2,4}$ 1·1 $J_{4,5}$ *ca.* 0·4	1-H 2-H 3-CH$_3$ 4-H	4·67(dd) 3·46(dd) 1·18(s) 4·84(ddm)
(17b)[b] (diacid)		$J_{1,2}$ 7·4 $J_{1,4}$ 8·6 $J_{2,4}$ 0·9 $J_{4,5}$ *ca.* 0·4	1-H 2-H 3-CH$_3$ 4-H	4·66(dd) 3·12(dd) 1·29(s) 4·47(ddm)
(18)[c]		$J_{1,3}$ 0·8 $J_{1,4}$ 9·0 $J_{1,2\text{-Me}}$ 0·1 $J_{3,4}$ 6·0 $J_{4,5}$ *ca.* 0·4	1-H 2-CH$_3$ 3-H 4-H	4·74(dd) 1·38(s) 2·94(dd) 4·41(ddm)

[a] In [^{2}H]chloroform (figures in parentheses are data in [^{2}H$_6$]acetone). [b] In [^{2}H$_6$]acetone. [c] In [^{2}H$_6$]dimethyl sulphoxide.

EXPERIMENTAL

Materials.—Benzophenone was used as received from Eastman Kodak. 2-Methylfuran (1b), furfuryl alcohol (1c), and 2,5-dimethylthiophen (1e) (Aldrich) were distilled before use. 3-Methylfuran (1a)[13] and 2,3-dimethylfuran (1d)[14] were prepared by literature procedures. Thiophen (7a), its methyl derivatives (7b—d), benzo[*b*]thiophen (15),

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[13] D. M. Burness, *Org. Synth.*, 1959, **39**, 46.

[14] A. L. Mndzhoian and M. T. Grigorian, 'Synthesis of Heterocyclic Compounds,' ed. A. L. Mndzhoian, Consultants Bureau Inc., New York, 1959, vol. 2, p. 26.

and citraconic anhydride (8a) (Aldrich) were distilled before use. 2,3-Dimethylmaleic anhydride (8b) was used as received (from Aldrich).

Photoreactions Leading to Oxetans.—Irradiation of benzophenone in the presence of each of the heterocycles was carried out as previously described,[3] except in the case of (1d).

Photoreaction of Benzophenone with 2,3-*Dimethylfuran* (1d).—A solution of benzophenone (1 g, 0·0055 mol) in the dimethylfuran (1d) (15 ml) was placed in a spiral tube (Pyrex, 5 mm diam.) surrounding a quartz immersion well which contained a Hanovia 450 W lamp at its centre. The solution was then irradiated at −10° (Colora Kälte thermostat), while nitrogen gas was bubbled through by means of a capillary tube, until no carbonyl band was detected in the i.r. spectrum (4 h). The solvent was distilled off, and the residue solidified. The ^1H n.m.r. spectrum of the crude product exhibited signals characteristic of the adduct, 1,5-*dimethyl*-6,6-*diphenyl*-2,7-*dioxabicyclo*[3.2.0]*hept*-3-*ene* (the total yield was virtually quantitative on the basis of benzophenone consumed). The solid was crystallised from benzene–petroleum (b.p. 60—65°); m.p. 159—160° (Found: C, 81·7; H, 6·3. $C_{19}H_{18}O_2$ requires C, 82·05; H, 6·45%).[15]

Photoreactions with Thiophen and Methylthiophens.—The irradiations were all carried out as in the following example. A solution of citraconic anhydride (8a) (5 g, 0·045 mol) and benzophenone (2 g, 0·0105 mol) in 2-methylthiophen (7b) (60 ml) was placed in a vessel into which a quartz immersion well containing a Pyrex filter sleeve and a Hanovia 450 W lamp was fitted. The double-walled immersion well containing the light source was cooled to −10° (Colora Kälte thermostat) and nitrogen was bubbled through the solution before and during the irradiation: at the end of 14 h (optimum exposure time on the basis of the yields of product isolated) the irradiation was discontinued and the liquid portion distilled under vacuum without heating. The residue, in a small quantity of 2-methylthiophen was stored at 0° for several days until a mass of yellowish crystals appeared; these were filtered off and washed with carbon tetrachloride to remove benzophenone and other impurities. The solid, crystallised from carbon tetrachloride–ethanol (3 : 1), had m.p. 225°; yield 0·5 g [14% on the basis of (8a) consumed].

Photoreaction with Benzo[b]*thiophen.*—These irradiations were carried out as in the following example. A solution of 2,3-dimethylmaleic anhydride (8b) (5 g, 0·039 mol) and benzophenone (2 g, 0·0109 mol) in benzo[*b*]thiophen (15) (60 ml) (warmed in a water-bath to keep it liquid at room temperature) was placed in a vessel into which a quartz immersion well containing a Pyrex filter sleeve and a Hanovia 450 W lamp was fitted. The double-walled immersion well containing the light source was kept at about 40° by circulating water from the tap through it, and nitrogen was bubbled through the solution before and during irradiation. The irradiation was stopped at the end of 12 h and the solvent was distilled off under vacuum. The residue was dissolved in a little ether and kept for 24 h at 0°. At the end of this time a white precipitate appeared, which was crystallised from carbon tetrachloride–diethyl ether; m.p. 160°, yield 85%.

Spectral Measurements.—The ^1H n.m.r. spectra were recorded on a Varian HA-100 spectrometer for *ca.* 6, 8, and 5% (w/v) degassed solutions of the samples of oxetans, derivatives of thiophen and methylthiophens, and of benzo[*b*]thiophen, respectively, in various solvents (see Tables 1—3) with Me_4Si as internal reference. The NOE experiments were performed as previously described.[16] Estimated errors for NOE values are ±2% or less.

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[15] Franz Paschler Mikroanalytisches Laboratorium, Bonn, Germany.

[16] K. Takeda, K. Tori, I. Horibe, M. Ohtsuru, and H. Minato, *J. Chem. Soc.* (*C*), 1970, 2697.