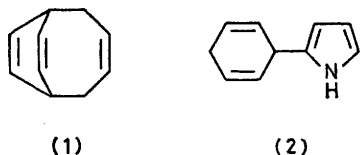


## The Photochemical Cycloaddition of Furan and Benzene

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Irradiation (254 nm) of furan–benzene mixtures results in the formation of the 2,5;1',4'- and 2,3;1',2'-photocycloadducts (3) and (4) respectively as the major chemical processes: 2,3;1',3'- and 2,5;1',3'-cycloadducts are minor reaction products. Adduct (3) yields the isomer (4) by a reversible thermal or irreversible photochemical Cope rearrangement and both isomers undergo retroaddition on sensitised irradiation. Furan quenches the fluorescence of benzene but no exciplex emission is observed. A 1:1 photoadduct of thiophen and benzene is formed in trace amounts but only in the presence of proton donors.

CERTAIN naphthalenes<sup>1-3</sup> and anthracene and its derivatives<sup>3,4</sup> undergo [4 + 4] photodimerisation but in contrast benzenoid compounds, although displaying a very diverse range of photochemical reactions,<sup>5</sup> neither photodimerise nor have been reported to yield cycloaddition products with other aromatic compounds. The 1,4;1',4'-photocycloaddition of dienes to benzene giving *cis*- and *trans*-isomers of (1) has been investigated with a variety of systems<sup>6</sup> but pyrrole and benzene gave the acyclic addition product (2)<sup>7</sup> and attempts to



photoadd thiophen to arenes have been unsuccessful.<sup>8</sup> It was, therefore, of interest to investigate the photo-reaction of benzene with furan which may be considered to be the least 'aromatic' of the heterocyclopentadienes<sup>9</sup> and which during the early part of the present study was reported to yield [4 + 4] photocycloadducts with  $\alpha$ - and  $\beta$ -naphthonitriles<sup>8,10</sup> and 9-cyanoanthracene, but not with 9-cyanophenanthrene:<sup>11</sup> from kinetic and spectroscopic data, an exciplex was proposed to be the precursor of these adducts.

The preliminary account of our present results on the furan–benzene system,<sup>12</sup> coincided with a report of the same reaction by Cantrell.<sup>13</sup> The two sets of results appeared to conflict markedly particularly with respect to the types of adducts formed but these aspects were subsequently<sup>14</sup> reconciled by the observations that the initially major products were both photochemically and thermally labile<sup>12</sup> and these features could account for the separation and isolation by preparative g.l.c. of the more minor stable products<sup>13</sup> from irradiation of the system with medium-pressure mercury lamps.

The present paper describes and discusses the details of our studies on the furan–benzene system which were briefly outlined in ref. 12 and which provide the first example of the photocycloaddition of two monocyclic aromatic compounds.

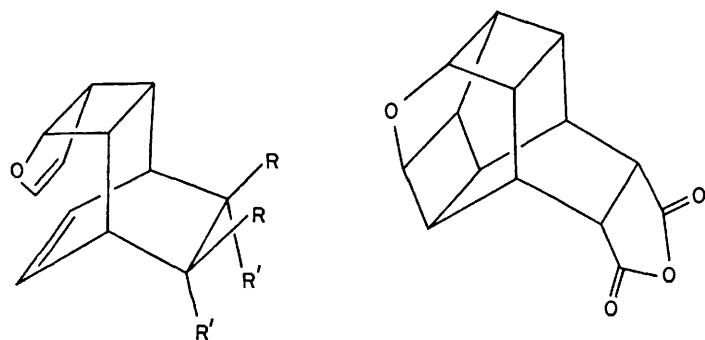
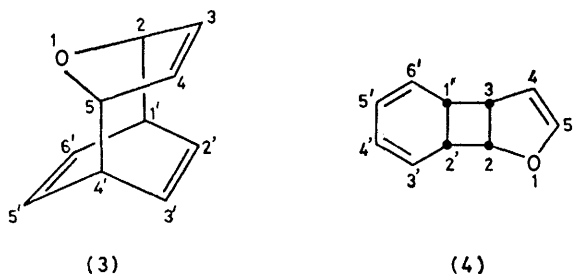
### RESULTS AND DISCUSSION

Details of the irradiation conditions are described in the Experimental section. For preparative experiments, equivolume mixtures of the reactants were irradiated under air as nitrogen degassing had no detectable effect on product ratios or yields within the time limits set for the reactions. Prolonged irradiations under an oxygen-containing atmosphere did, however, lead to increased amounts of polymeric materials which may have resulted from photo-oxidation of furan<sup>15</sup> and the products derived therefrom.

Irradiation of benzene–furan mixtures gave five products and unlike benzene–ethylene systems,<sup>16</sup> fulvene formation was not significantly quenched. Analytical g.l.c. was suitable for the detection of the reaction components but their ratios changed markedly with temperature within the apparatus; however, with cyanopropylmethylphenylmethyl silicone/Universal B packed columns and temperatures <115 °C, a reproducible ratio of 1:1 adducts ( $M^+ = 146$  m.u. m.s.–g.l.c.) of approximately 1:1:6:20:4 (elution sequence) was determined for the distilled (70–80 °C/0.1 mmHg) mixture: the conditions were unsuitable for successful preparative separations. It was subsequently shown that the major adduct was converted thermally and photochemically into the isomer which eluted immediately before it, and both adducts reverted to starting materials under the conditions of their formation. Thus the relative proportions of the adducts were very dependent upon the irradiation time, light intensity, relative concentrations of the reactants, and temperature of the irradiated solution but at the shortest feasible reaction time at 15 °C, the ratio was assessed to be approximately 1:1:10:40:2. Prolonged irradiation and/or the use of high temperatures in the work-up/isolation procedures allowed the separation of the minor reaction components. Column chromatography and t.l.c. gave inadequate separation of the adducts but extraction of their pentane solution with methanolic silver nitrate produced a white precipitate and only removed the major 1:1 adduct from the chromatogram. The silver nitrate complex was photochemically and

thermally labile but treatment with aqueous ammonia afforded the major 1 : 1 furan-benzene adduct in >95% purity: the 2,5; 1',4'-structure (3) was assigned to this product on the basis of its chemical and spectroscopic properties. Thus ready reversion to starting materials occurred in the mass spectrometer which is an indication of an *ortho*- or *para*-cycloaddition product<sup>17</sup> but the adduct was unreactive towards common dienophiles. Complete confirmation of the structure followed from the <sup>1</sup>H n.m.r. spectrum (Experimental section) and decoupling experiments.

The second most abundant 1 : 1 adduct reacted readily with common dienophiles and could be extracted from the irradiation mixture as Diels-Alder crystalline derivatives, but was conveniently obtained in >95% purity by simply heating a solution of (3) at 60–70 °C for 5 h: decomposition under these conditions was not observed. The adduct readily fragmented to furan and



(5) R = H, R' - R' = CO-O-CO

(8)

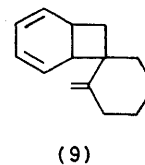
(6) R = R' = CN

(7) R = H, R' - R' = CO-N(Ph)-CO

benzene in the mass spectrometer and the assigned 2,3; 1',2'-structure (4) followed from analysis of the <sup>1</sup>H n.m.r. spectrum (Experimental section) and decoupling experiments. The products of (4) with maleic anhydride, tetracyanoethylene, and *N*-phenylmaleimide were obtained quantitatively from ethereal solution and were assigned the 1 : 1 : 1 Diels-Alder adducts structures (5), (6), and (7) respectively on the basis of their elemental analyses and spectroscopic properties: an *endo*-configuration about the cyclobutane ring in (5) and (7) and hence in the 1 : 1 adduct (4) was deduced as follows. We have previously used the n.m.r. spectra of 1 : 1 : 1 Diels-Alder adducts of *N*-phenylmaleimide and *ortho*-

photocycloadducts of benzene with vinyl compounds or *cis*-1,2-unsymmetrically disubstituted ethylenes to assign the stereochemistry of the original addition process.<sup>18</sup> Thus with an *exo*-substituent on the cyclobutane ring of the 1 : 1 : 1 adduct, the ethenyl protons are essentially equivalent and would be expected to resonate as a double doublet in the <sup>1</sup>H n.m.r. spectrum: in fact in such compounds  $J_{vic} \approx J_{allylic}$  and the resonance appears as a triplet. For the case of an *endo*-substituent or for two dissimilar *endo*-substituents, the ethenyl protons are no longer equivalent and resonate generally as two overlapping multiplets. This latter feature was evident in the spectrum of (7) and the non-equivalence of the ethenyl protons was further indicated by decoupling of the allylic protons. The conclusion was not quite as firm as in other cases because of the overlapping resonance of these ethenyl protons with the  $\alpha$ -ethenyl proton of the 2,3-dihydrofuran moiety. Similar problems were encountered with the spectra of (5) and (6) but conclusive proof of the *endo*-stereochemistry about the cyclobutane ring was provided by the medium-pressure mercury arc irradiation of an acetone solution of (5) ( $\lambda_{max}$ , 225 nm,  $\epsilon \approx 1870 \text{ m}^{-1} \text{ l cm}^{-1}$  indicating substantial interaction between the ethylenic groups<sup>19</sup>) which produced an isomer of (5) having no ethenyl protons and for which the 'cage' structure (8) was deduced. The assignment of *endo*-stereochemistry of (4) is consistent with its formation by a thermal Cope rearrangement of (3) which must *a priori* yield this stereoisomer.

In principle, compounds (3) and (4) may be interconvertible thermally by the Cope rearrangement and hence an equilibrium may exist between the two isomers. The position of the equilibrium was found to be very temperature-dependent. Thus, whereas a slow conversion of (4) into (3) was noted at 20 °C (but not at -10 °C) in the dark, at 70 °C (3) was completely isomerised to (4) and from a kinetic analysis of this latter reaction by <sup>1</sup>H n.m.r. spectroscopy a value for the rate constant of  $1.03 (\pm 0.02) \times 10^{-2} \text{ min}^{-1}$  was determined. The rate of thermal isomerisation of (4) into (3) was far too slow to account for the formation of more than a trace of (3) by this route in the photochemical reaction of furan and benzene and (3) gave no detectable amount of (4) after standing for seven days at 20 °C. It is interesting to note here that although the analogous adduct



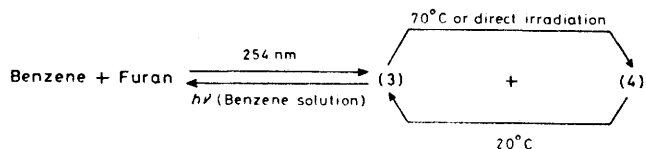
(9)

to (3) from 1,2-dimethylenecyclohexane and benzene was also thermally labile, decomposition to tetralin and butadiene as well as to starting materials occurred rather than a Cope rearrangement to (9):<sup>20</sup> the former products were accounted for by a series of intramolecular and retro-Diels-Alder processes but if a similar reaction

sequence operated in the present case, this would simply yield benzene and furan as in the direct decomposition.

Direct irradiation of solutions of (3) in cyclohexane at 254 nm at 20 °C resulted in the quantitative conversion into (4), but irradiation of benzene or acetone solutions of either (3) or (4) resulted in their decomposition to starting materials. These observations are simply rationalised in terms of the involvement of singlet excited states in the (3) into (4) conversion and triplet excited states of (3) and (4) leading to the retro-addition process. The survival of major amounts of (3) from preparative irradiations is considered to be a combination of the screening effect of benzene for direct excitation of (3), a more rapid photoaddition process than the sensitised decomposition, and use of concentrations of benzene in which the triplet yield of the arene is not maximised.<sup>21</sup> Since (3) and (4) were photolabile under the conditions of their formation, reproducible quantum yield data were not easily obtained but the highest value recorded for the formation of (3) from 1M-benzene and 1M-furan in cyclohexane was  $0.045 \pm 0.005$  which conflicts markedly with that of 0.27 reported for one of the minor products of this reaction.<sup>13</sup>

In view of the above thermal and photoconversions of (3) and (4), it was deduced that (3) was a primary photochemical product of this system and since (4) was detected from irradiation experiments under conditions which (3) was essentially thermally stable and its concentration was too low for direct photoexcitation, we consider that (4) was also a primary photoadduct of furan and benzene. We have recently noted that 2,3-dihydrofuran undergoes *ortho*-photocycloaddition to benzene to yield both *exo*- and *endo*-stereoisomers<sup>22</sup> but from the present system no evidence was obtained for the formation of an *ortho*-adduct with the former stereochemistry. The relationship of (3) and (4) to each other and to the starting materials is summarised in the Scheme.

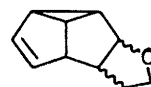


SCHEME

Removal of (3) and (4) from the reaction mixture or prolonged irradiation of the benzene–furan system with a medium-pressure mercury arc lamp gave the minor products which could be separated by preparative g.l.c. The three 1 : 1 adducts (approx. ratio 1 : 1 : 3) which were separated had spectroscopic data essentially the same as those described earlier from which structures (10), (11), and (12), respectively, were deduced.<sup>13</sup>

From the lack of effect on relative initial yields of the adducts by change in addend concentrations and proportions which would be expected to vary the singlet-triplet ratio,<sup>17</sup> it appears that all the 1 : 1 adducts of furan and benzene are derived from the same excited

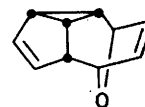
state. We have no conclusive evidence that the reactive state is the singlet state but from the absence of any effect of oxygen on the reaction, and by analogy with the ethylene<sup>23</sup> and diene<sup>24</sup> photoadditions to benzene, we consider that the involvement of  $T_1$  benzene



(10)



(11)



(12)

in the present additions is most unlikely: similarly direct excitation of furan ( $\epsilon$  at 254 = *ca.* 5 mol<sup>-1</sup> l cm<sup>-1</sup>) under the present experimental conditions was highly improbable. It is, however, interesting to realise that from orbital symmetry analyses of concerted photoaddition reactions of benzene,<sup>25</sup> the formation of the major 1 : 1 adducts (3) and (4) are 'forbidden' from  $S_1$  ( $B_{2u}$ ) benzene whereas the minor primary reaction products (10) and (12) are 'allowed' but the converse was deduced for  $T_1$  or  $S_2$  (inaccessible in the present experiments) ( $B_{1u}$ ) benzene and all these modes of addition are allowed from  $S_1$  or  $T_1$  addend. The rigour of such analyses decreases as the polar character of the reaction increases and it has, for example, been noted with the *ortho*-cycloadditions of ethylenes of low ionisation potential to benzene that the efficiency of the reaction increases in polar solvents.<sup>22,26</sup> The observation of the 'forbidden' cycloadditions may also be rationalised by the intermediacy of an excited state complex formed between  $S_1$  benzene and  $S_0$  furan: mixing of states in such a species removes the orbital symmetry restrictions.<sup>17,27</sup> In view of such considerations we investigated the possibility of ground and excited state complexation between benzene and furan.

The reaction efficiency and product ratios appeared to be independent of solvent polarity but for preparative purposes both acetonitrile and cyclohexane were poor reaction media as polymer formation became a serious problem: this was not experienced to the same extent with methanol as solvent. This result argues against the involvement of a polarised species in the reaction pathway leading to the 1 : 1 adducts.<sup>26</sup> We examined the possibility of ground-state interactions between the addends by u.v. spectroscopy, both of dilute solutions and neat mixtures by the thin-film technique,<sup>28</sup> and by n.m.r. spectroscopy.<sup>29</sup> The absorption spectrum of furan–benzene mixtures was additive of those of the components but in 1.5 mol % solutions of furan in  $C_6D_6$ , both sets of proton resonances were shifted upfield by 13 Hz compared to a solution in  $CCl_4$ . This shift may suggest that the preferred orientation of the addends in

a weak ground-state complex is *endo* in which the furan ring is situated parallel to the benzene ring and directly above it and hence the stereochemistry of (4) reflects this. We<sup>22</sup> and others<sup>30</sup> have, however, recently noted that despite earlier results,<sup>29</sup> there is little correlation between preferred orientation of the addends in the ground-state as deduced from <sup>1</sup>H n.m.r. spectroscopy and the stereochemistry of *ortho*-cycloaddition: any correlation which is observed may well be fortuitous.

The photoadditions of furan to cyanopolynuclear arenes is proposed to proceed by way of an exciplex,<sup>10,11</sup> and even though quenching of benzene fluorescence by ethylenes is weak,<sup>31</sup> this type of species has also been suggested as the precursor of their photoadducts.<sup>17,27</sup> Furan quenched benzene fluorescence in cyclohexane and acetonitrile solution, and in nitrogen-degassed solutions the efficiency approached a diffusion-controlled rate in both solvents; in neither case, however, either in  $5 \times 10^{-4}$ M or 0.5M benzene solutions,<sup>32</sup> was a longer wavelength emission observed which could be attributed to that of an exciplex. Nevertheless the involvement of an excited-state complex in the present reaction cannot be discounted on this evidence alone, and such a species does provide a convenient intermediate to circumvent the orbital symmetry restrictions.

In contrast to the above results with furan, irradiation of the thiophen-benzene system gave only trace amounts of two products, the mass spectra of which were inconclusive and could not be interpreted in terms of simple 1 : 1 adducts. It is known that tertiary amines<sup>33</sup> and *N*-methylpyrrole<sup>34</sup> only yield acyclic photoadducts with benzene with reasonable efficiency in the presence of proton donors, hence the thiophen-benzene system was examined in methanol and methanol-trifluoroacetic acid solutions. In both cases brown intractible multi-component oils were formed. Mass scanning of the eluted components from g.l.c. showed that only one, which constituted *ca.* 5% of the total product mixture, had  $M^+$  of 162 m.u. constituent with a 1 : 1 adduct of thiophen and benzene. The major product which was *ca.* 50% of the mixture had  $M^+$  160 m.u. which was also the base ion, but the extremely obnoxious nature of the mixture dissuaded us from further investigation of the system.

Thus we have shown that in its photoreaction with benzene, furan behaves as a *cis*-1,3-diene and yields 2,5;1'4'- and 2,3;1'2'-cycloadducts as the major products. The former gave the latter both thermally and photochemically but sensitised irradiation of either resulted in retro-addition. Formation of such adducts provides the first example of cycloaddition between two monocyclic aromatic systems.

#### EXPERIMENTAL

In order to obtain the two major products, the irradiation source for preparative experiments was an Hanovia 15-W low-pressure mercury arc lamp. Use of an Hanovia 500-W medium-pressure mercury arc lamp was made to obtain the minor 1 : 1 adducts in isolable amounts: this also

caused the reversion of (3) and (4) into starting materials in acetone or benzene solution. Quantum yields were determined for 1M-solutions in each addend in cyclohexane solution and the effect of solvent on the addition reaction was studied for 2.3M-solutions in each addend in methanol, acetonitrile, and cyclohexane: low-pressure lamps were employed in both series of experiments. <sup>1</sup>H n.m.r. spectra were recorded for CDCl<sub>3</sub> or CCl<sub>4</sub> solutions at 60 MHz.

*Irradiation of Furan and Benzene.*—In a typical preparative experiment, an equivolume solution (400 ml) of benzene and furan was irradiated in fused silica tubes for up to 60 h at 20 °C. The progress of the reaction was monitored by g.l.c. At the end of the irradiation period the walls of the quartz tubes were coated with polymer and the solution was golden yellow. Distillation of the solution at reduced pressure (maximum temperature 40 °C) gave *ca.* 3 g of a brown oily residue and a yellow distillate. The distillate had a  $\lambda_{\text{max}}$  at 360 nm and the yellow colour was discharged by the addition of maleic anhydride, piperidine, or benzylamine: the properties are entirely consistent with the yellow colour being due to fulvene.<sup>35</sup> The residue was vacuum-distilled to give *ca.* 1 g of a pale yellow oil which comprised the five 1 : 1 adducts ( $M^+$  146 m.u. m.s.-g.l.c.) (10), (11), (4), (3), and (12) (elution sequence on 10% cyanopropylmethylphenylmethyl silicone/Universal B packed columns).

*Separation of Compounds: (3) and (4).*—The undistilled adduct mixture (1 g) in pentane solution (10 ml) was shaken with a saturated methanolic solution of silver nitrate. A white solid (0.5 g) precipitated immediately, was filtered off, and washed with acetone and pentane. The solid discoloured in light and had no apparent melting point but charred at >130 °C. Digestion of the white silver complex with 2M-aqueous ammonia followed by extraction with carbon tetrachloride afforded a solution of (3) with 95% purity, the impurity being (4) and (12). Adduct (3) had  $\delta$  values at 6.35–6.6 (2 H, H-5' and H-6', octet,  $J$  5.0, 3.5, and 0.3 Hz), 6.0–6.25 (4 H, octet, 2 H, H-2 and H-3', and doublet 2 H, H-3 and H-4,  $J_{\text{octet}}$  as above,  $J_{\text{doublet}} = 0.6$  Hz), 3.95–4.15 (2 H, H-2 and H-5, dd,  $J$  6.6 and 0.6 Hz) and 2.7–3.1 p.p.m. (2 H, H-1' and H-4', m), irradiation at 2.95 p.p.m. caused collapse of the octets and the resonance centred at 4.05 p.p.m. to broad singlets;  $\nu_{\text{max}}$  (liquid smear) 3 040s, 2 950s, 1 590s, 1 355s, 1 240s, 1 220s, 1 210s, 1 040s, 970s, 925br s, 845s, 715s, and 645s,  $\text{cm}^{-1}$ ; no  $\lambda_{\text{max}}$  (cyclohexane) above 220 nm but  $\epsilon$  at 254 nm of 250 l mol<sup>-1</sup> cm<sup>-1</sup> [Found for compound (sticky solid) from AgNO<sub>3</sub> complex: C, 81.95; H, 7.1. C<sub>10</sub>H<sub>10</sub>O requires C, 82.19; H, 6.85%].

Heating solutions of compound (3) to 60–70 °C or direct irradiation (254 nm) caused a quantitative conversion into (4). A sample of (4) prepared in this way had  $\delta$  values centred at 6.30 (1 H, H-5 dd,  $J$  2.8 and 1.2 Hz), 5.55 (5 H, H-3', H-4', H-5', H-6', and H-3), 4.95 (1 H, H-4, t, two couplings of 2.8 Hz), and 3.3–3.9 (3 H, H-1', H-2', and H-2, m); the assignments were confirmed by decoupling experiments;  $\nu_{\text{max}}$  (liquid smear) 3 030s, 2 960m, 2 910s, 1 600s,d, 1 135s, 1 045s, 785s, 760s, and 725s  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (cyclohexane) 284 nm ( $\epsilon$  1 200 l mol<sup>-1</sup> cm<sup>-1</sup>) [Found: for (4) from heating (3) at 60 °C for 3 h: C, 81.90; H, 7.3. C<sub>10</sub>H<sub>10</sub>O requires C, 82.19; H, 6.85%]. Solutions of compound (4) allowed to stand at 20 °C for 16 h showed an approximately 20% reversion to (3).

*Reaction of Compound (4) with Maleic Anhydride, Tetracyanoethylene, or *N*-Phenylmaleimide.*—The 1 : 1 : 1 Diels-Alder adducts of (4) with dienophiles could be obtained

either from solutions of (4) prepared from (3) as above or directly from the distilled adduct mixture.

(a) *Adduct (5)*. To an ethereal solution (1.5 ml) of the distilled adduct mixture (0.8 g) was added maleic anhydride (0.2 g) in diethyl ether (1.5 ml). After 24 h at room temperature, the 1:1:1 adduct (5) (0.2 g) was filtered off, m.p. 180–183 °C (decomp),  $M^+ = 244$  m.u. (Found: C, 68.7; H, 4.85.  $C_{14}H_{12}O_4$  requires C, 68.9; H, 4.9%);  $\nu_{\max}$  (Nujol) 1 860m, 1 782s, 1 605w, 1 238m, 1 225m, 1 220m, 1 070s, 963s, 931s, and 738s  $cm^{-1}$ ;  $\lambda_{\max}$  (ethanol) 225 nm ( $\epsilon \approx 1 870 \text{ mol}^{-1} \text{ l cm}^{-1}$ );  $\delta$ ( $CDCl_3$ ) 5.65–6.1 (3 H, overlapping m's), 4.5–4.8 (2 H, m), 3.0–3.7 (3 H, m's), and 2.5–3.0 p.p.m. (4 H, m's). Irradiation of a saturated solution of (5) in acetone with a medium-pressure mercury arc lamp produced the isomer (8) ( $M^+ = 244$  m.u.) of (5);  $\nu_{\max}$  (Nujol), 1 860m, 1 780m, 1 230m, and 1 170s  $cm^{-1}$ . The  $^1H$  n.m.r. spectrum had no ethenyl proton resonances.

(b) *Adduct (6)*. Tetracyanoethylene (0.4 g) was shaken with diethyl ether (2 ml) and the solution was decanted into an ethereal solution (5 ml) of the distilled 1:1 adduct mixture (1.5 g). A deep brown colour was produced but discharged within 1 min. Further 2-ml portions of the tetracyanoethylene ethereal solution were added until a persistent colouration was obtained for 24 h at 5 °C. The precipitated grey solid was recrystallised twice from acetone to yield fine white crystals (0.5 g), m.p. 218–222 °C (decomp.),  $M^+ 274$  m.u. (Found: C, 68.9; H, 3.8; N, 19.07.  $C_{16}H_{10}N_4O$  requires C, 70.07; H, 3.65; and N, 20.44%);  $\nu_{\max}$  (Nujol) 1 605m, 1 255s, 1 210s, 1 130s, 1 050s, and 730s  $cm^{-1}$ ;  $\delta$  (pentadeuteriopyridine) 6.3–6.6 (3 H, m), 5.9–6.05 (1 H, m), 4.5–5.0 (4 H, m), and 3.0–3.8 (2 H, m).

(c) *Adduct (7)*. A solution of *N*-phenylmaleimide (0.12 g) in diethyl ether (2 ml) was added to a solution of the distilled adduct mixture (0.8 g) in diethyl ether (1 ml). After 36 h at 20 °C, filtration afforded the 1:1:1 adduct (7) (0.1 g)  $M^+ = 319$  m.u., m.p. 188–190 °C (decomp.) (Found: C, 75.9; H, 5.15; N, 4.3.  $C_{20}H_{17}NO_3$  requires C, 76.5; H, 5.3; N, 4.4%);  $\nu_{\max}$  (Nujol) 1 772w, 1 704s, 1 600m, 1 500m, 1 200s, 1 065m, and 748m  $cm^{-1}$ ;  $\delta$ ( $CDCl_3$ ) 7.3–7.55 (2 H, m), 7.10–7.30 (3 H, m), 5.90–6.30 (3 H, two overlapping s), 4.70–5.15 (2 H, overlapping m's  $J$  2.6 and 1.8 Hz), 3.10–3.80 (3 H m), and 2.60–3.10 p.p.m. (3 H, m).

*Minor 1:1 Adducts*.—Irradiation of equivalent mixtures (400 ml) of furan and benzene with medium-pressure mercury arc lamps provided 1:1 adduct mixtures relatively rich in (10), (11), and (12). Preparative g.l.c. of the mixture using injection-block temperatures of 250 °C [which caused decomposition of adducts (3) and (4) to starting materials] gave the minor adducts in >90% purity. Their spectroscopic data have been previously described.<sup>13</sup>

*Irradiation of Thiophen and Benzene*.—A solution of thiophen (10 ml) in benzene (100 ml) in a quartz tube was irradiated with low-pressure mercury arcs for 48 h. Removal of the starting materials *in vacuo* gave a brown viscous residue (ca. 0.5 g) which had traces of two volatile components, the mass spectra of which (m.s.–g.l.c. Carbowax 20M) gave no structural information. Similar irradiation of thiophen (10 ml) and benzene (10 or 100 ml) in methanol (100 ml) with or without trifluoroacetic acid (1 ml) gave a brown viscous oil (ca. 1 g). Analysis by m.s.–g.l.c. of the oil revealed a component (ca. 5%) with  $M^+ = 162$  m.u. and other abundant ions at  $m/e$  values of 97, 88, and 75 m.u. The major component (ca. 50%) of the mixture had  $M^+ = 160$  m.u. (1:1 adduct minus  $H_2$ ) which was also the base ion and the only other significant ion was at 110 m.u.

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