J. Org. Chem. **1981**, *46*, 2674–2679

Photochemical Reactions of Benzenes with Furans and Cyclic 1,3-Dienes

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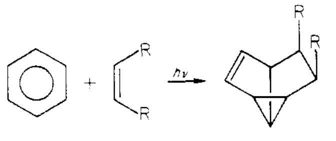
Received August 21, 1980

The photochemical reactions of benzene, toluene, xylene, and anisole with furan, methylated furans, and cyclic 1,3-dienes have been examined. In most cases the major products are those derived from 1,4–1,4 addition, but in all cases substantial amounts of adducts derived from 1,4–1,3 addition (i.e., C_1 and C_3 of benzene bonding to C_2 and C_5 of furan) are formed. The reaction course has been found to depend substantially on the relative amounts of the two reactants, their concentrations, and the wavelength of the light employed. Under certain conditions appreciable amounts of [2 + 2] and of 1,3–1,2 cycloadducts are observed. Structural elucidation was done mainly via NMR, including studies with decoupling and with shift reagents.

Benzene and its simple substituted derivatives undergo ultraviolet light induced cycloaddition reactions to carbon–carbon double bonds in a variety of ways, the exact course of any particular reaction being dependent on the exact structure of the benzene and the substrate, the relative concentrations of the reactants, and the wavelength of the light used.[1] The major process in the photochemical reaction of benzene itself with simple hydrocarbon alkenes and alkyl vinyl ethers is that of addition across C-1 and C-3 of the benzene ring to afford products of type **1**, tricyclo[3.2.1.$0^{2,8}$]octenes.[2] With certain simple alkenes, smaller amounts of [2 + 2] and [4 + 2] cycloadducts (**2** and **3**, respectively) have been observed.[3-13] When one or more electron-withdrawing groups are present in the alkene, the formation of [2 + 2] adducts, or their transformation products, is usually the sole process observed.[14-22]



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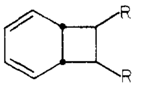

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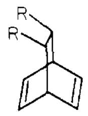

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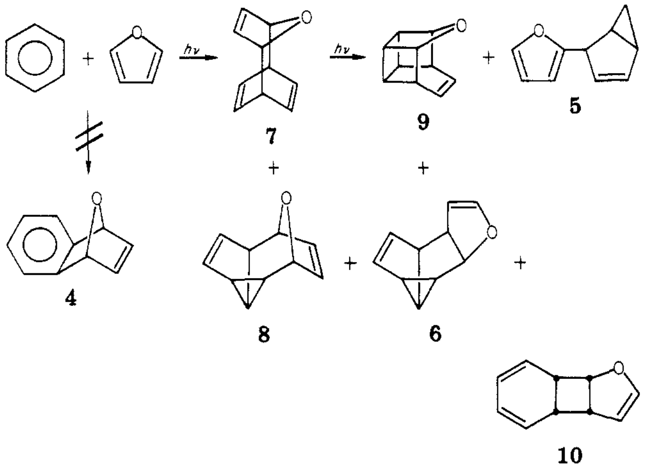
Aldehydes and ketones undergo [2 + 2] cycloaddition reactions at the carbonyl group with many alkenes to afford oxetanes; the process is quite efficient with aromatic carbonyl compounds.[23] Among other substrates successfully employed as alkenes are furan and simple monoalkylfurans.[24] The oxetanes thus produced can often be isomerized by acid to 2-(α-hydroxyalkyl)furans.[25]

Scheme I



We became interested in exploring the reactions of photochemically excited benzene and its simple derivatives with dienes and trienes some years ago by the publication of reports by Kraft and Koltzenburg that irradiation of mixtures of benzene and 1,3-butadiene resulted in a plethora of products.[26] Some of these were [4 + 4] cycloadducts or their further transformation products. Yang and Libman reported the photochemical reaction of benzene with alkylated 1,3-dienes to afford both 1,4–1,4 as well as 1,3–1,2 adducts.[27] Our hope was that benzene and its simple derivatives would add to cyclic 1,3-dienes and related compounds such as furans to give [4 + 4] adducts which would serve as useful intermediates for further synthetic work. In a preliminary paper several years ago we described some of our results on the photochemical reaction of benzene and toluene with furan.[28] The present paper gives the full details of these studies, as well as other subsequent studies on related systems, and, finally, a rationale for the differences in the reaction course in the benzene–furan system obtained by us and by Bryce-Smith and co-workers.[29,30]

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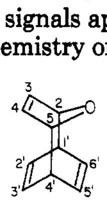
Table I. NMR Data[a] for Compounds 7-9

7			8					9		
position	^{13}C	^1H	position	^1H	LIS[b]	^{13}C		position	^1H	^{13}C
5′,6′	139.37	6.70 (2 d, $J = 8$, $J' = 6$)	9	6.4 (2 d, $J = 7.5$, $J' = 7.4$)	5.18	136.2 135.1 129.9 128.7	C_4, C_5, C_8, C_9	1	6.16 (2 d, $J = 4.8$,	129.1
2′,3′	124.14	6.22 (2 d, $J = 9.5$, $J' = 6.5$)	4	6.15 (2 d, $J = 5.8$, $J' = 2.5$)	10.5			2	4.7–4.5 (m)	81.9
3,4	122.96	6.08 (s)	8	6.04 (2 d, $J = 6.2$, $J' = 1.9$)	5.87	78.3 77.6	C_7, C_{10}	3	3.6 (m)	45.3
2,5	86.43	4.17 (d, $J = 12.5$)	5	5.37 (2 d, br, $J = 5.8$, $J' = 1$)	11.7	42.7 35.0	C_6, C_3	4	3.2 (m)	41.1
1′,4′	45.86	3.04 (m)	10	5.05 (s, br)	18.1			5	1.5	31.5
			7	4.36 (t, $J = 1.8$)	25.4	22.7 21.1	C_2, C_1			
			6	3.00 (2 t, $J = 7.4$, $J' = 2.1$)	10.5					
			3	2.17 (3 d, $J = 7.5$, $J' = 2.5$)	7.00					
			1	1.59 (q, $J = 7.5$)	9.04					
			2	0.70 (3 t, $J = 7.5$, $J' = 1.5$)	7.85					

[a] In parts per million from Me_4Si; coupling constants are given in hertz. [b] Lanthanide-induced shift.

Results

Irradiation through a Vycor filter of 10–20% solutions of benzene in redistilled furan until the formation of colored byproducts prevented further reaction (3–6 h) gave ca. 2% conversion to a distillable mixture of six products, four of which were isolated by GC. The major product in the mixture was the [4 + 4] cycloadduct 7 (ca. 50% of the total; see Scheme I). It proved to be thermally unstable at temperatures necessary for gas chromatographic separation (150–180 °C) and could be obtained in relatively pure form only by complexation with aqueous silver nitrate, followed by decomposition of the complex with ammonia. The other products were, in order of elution from a silicone oil GC column, furan 5 resulting from hydrogen transfer in an intermediate diradical (6% of total), the 1,3–1,2 adduct 6 (3% of the total), the novel 1,3–1,4 adduct 8 (30%), and the cage-type compound 9 (11%), resulting from sensitized intramolecular [2 + 2] cycloaddition of [4 + 4] cycloadduct 7 which did not survive GC temperatures. Compounds 7 and 10 were observed spectroscopically (NMR) in the distilled mixture, and 10 was isolated in the form of Diels–Alder adducts (vide infra). The structures of 5–9 were established from the ^1H and ^{13}C NMR spectra of the parent compounds and of the hexadeuterio derivatives obtained from benzene-d_6 and furan (Table I) and from decoupling experiments on certain NMR signals of 6 and 8. Even at 60 MHz the NMR spectrum of 8 shows ten well-separated multiplets, six of which are first-order even at this relatively low field. At 220 MHz, nine of the ten signals appeared as first-order multiplets. The stereochemistry of 8 was assigned as shown on the basis of the following evidence: (a) addition of increments of the lanthanide shift reagent $Eu(fod)_3$ resulted in a greater shift to lower field of the signals due to H_4 and H_5 than those for H_1 and H_6 (see Table I); (b) inspection of Dreiding models indicates that in structure 8 as shown, the dihedral angles between H_6 and H_7 and between H_2 and H_{10} would be approximately 50° each, whereas in structure 8′ the corresponding angles would be ca. 15°. The observed couplings ($J_{6,7} = 1.9$ Hz, and $J_{2,10} = 1.5$ Hz) are much more in agreement with geometry 8 and 8′. The Karplus equation would predict the couplings of 8′ to be ca. 5–8 Hz.



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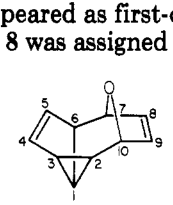

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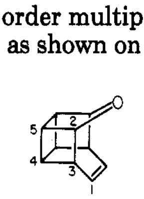

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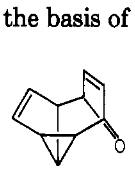
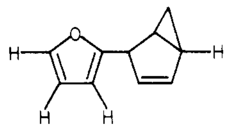


8′

The hexadeuterio derivative of 8, bearing hydrogens only at positions C_7–C_{10}, was of significant aid in making the assignments of signals in conjunction with the lanthanide-induced shift experiments. Hexadeuterated 8 exhibited



8-d_6

in its ^1H NMR spectrum an AB pattern for H_8 and H_9 ($J = 6.2$ Hz), further modified by coupling to H_7 and H_{10}, respectively ($J = 1.8$ Hz). H_7 and H_{10} appear as slightly broadened doublets. Furthermore, the hexadeuterio derivative of 5 provided significant information about its mechanism of formation. The one of the four hydrogens which originated in the furan molecule but is now located on the six-carbon framework that was orginally a benzene molecule was found to be not on the methylene group of the cyclopropane ring but on the cyclopentene ring. The signal for this carbon, C_4, appeared as a 1:2:1 triplet in the off-resonance decoupled ^{13}C spectrum of 5 and as a 1:1:1 triplet in the NORD spectrum of hexadeuterated 5.

The formation of 8 represents a hitherto unobserved type of photochemical cycloaddition reaction for benzene, the addition of benzene at C_1 and C_3 to the 1,4-positions of the diene moiety of furan. Kraft and Koltzenburg reported the presence in their benzene–butadiene reaction mixtures of many minor products which were not obtained pure.[26] It is quite possible that one or more such products have structures of the type corresponding to 8, for example, 11. The reaction mixtures of Yang and Libman[27] may also have contained minor amounts of such products.

Shortly after the publication of my initial report[28] on the present products, there appeared a communication by

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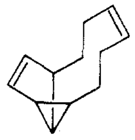

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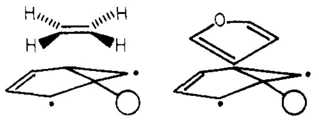
Berridge, Bryce-Smith, and Gilbert[29] describing their results in benzene–furan irradiations. They found the major product to be **10**, and neither **8** nor **9** was mentioned as being present. In subsequent experiments, performed in both England and the United States, the major reasons for the differences in the two sets of results were delineated. It turns out that the ratio of the six products depends greatly on the various experimental variables, including the relative concentrations of the two reactants, the irradiation time, the wavelength of the light employed, and the intensity of the light source. In a subsequent joint communication, the investigators from the two laboratories "substantially reconciled the differences".[30]

In experiments performed at the American University, irradiation of mixtures of benzene and furan in which benzene was present in 2:1 molar excess led to mixtures rich in the [4 + 4] adduct **7** and also the [2 + 2] adduct **10**. The ratio of **5**–**10** was 3:1:41:20:15:10. The 1,3-cyclohexadiene derivative **10** was, like **7**, too thermally labile to survive temperatures necessary for gas chromatographic purification. It was isolated and identified as its Diels–Alder adducts with *N*-phenylmaleimide and maleic anhydride, compounds **12** and **13**, mp 228–229 °C dec and 237 °C dec, respectively. The [2 + 2] and [4 + 4] cyclodimers of benzene have been prepared by circuitous routes and have been found to be thermally unstable above ca. 50 °C.[31]

The NMR data on **7** and **10** agree with those reported by the Reading group;[29] what is puzzling is that their reported melting points for the *N*-phenylmaleimide and maleic anhydride adducts, **12** and **13**, of **10** are 188 and 181 °C, respectively, whereas in our hands the materials we obtained, whose 220-MHz NMR and mass spectra fully support the assigned structures, melt at 228 and 237 °C, respectively. These differences remain to be resolved.

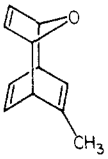
The profound differences in proportions of products caused by changes in the relative concentration of reactants, wavelength of light used, etc. are surprising at first sight but can, for the most part, be rationalized. When furan is present in large excess (i.e., "U.S." conditions), the excited state of benzene leading to the 1,4–1,4 adduct **7** and the 1,4–1,3 adduct **8** is efficiently trapped. When excess benzene is present, processes leading to **5**, and now **10**, predominate. That more **10** is not observed under "U.S." conditions is also due to the fact that the strongly absorbing 1,3-cyclohexadiene moiety of **10** absorbs light in the 240–280-nm region, leading to the destruction of **10** via photodimerization and other processes. Under "British" conditions the excess benzene acts as a filter and screens out most of the light which might otherwise be absorbed by **5**. On the other hand, intramolecular [2 + 2] photochemical cycloadditions of the type **7** → **9** are usually sensitized via triplet excited benzene or acetone;[32] hence it is puzzling that more of **9** is found when less benzene is used. We also observe that under "British" conditions the proportion of **10** in the reaction mixture is greatest under conditions of short reaction times and low conversions. Longer reaction times lead to secondary photoproducts (dimers, etc.). Under the "U.S." conditions the quantum yields of the formation of the three major photoproducts **7**–**9** are 0.13, 0.09, and 0.04, respectively. The actinometer used was the photochemical cycloaddition of benzene to cyclopentene as reported by Srinivasan et al. ($\Phi = 0.17$).[6] It is both puzzling and disturbing that the Reading group finds the total quantum yield for all products (combined) to be only 0.06; the reasons for this discrepancy remain to be clarified.

Chart I



A B

The effect of substitution of simple groups onto the benzene ring in these reactions was next investigated. Irradiation of toluene with excess furan ("U.S." conditions) led to products **12**–**15** in the ratio 25:41:26:8. Compounds **13**–**15** were isolated by GC; the presence of **12** was deduced from signals in the 220-MHz NMR spectrum of the distilled mixture. The assignment of position of the methyl group in the products was made by simply observing which signal in the spectrum of the corresponding product from benzene (**7**–**9**) was missing. The chemical shifts of the signals were in all cases essentially the same as those of **7**–**9**, so the assignments were made with confidence. What is at first surprising about the results is that the studies by Srinivasan et al. on the addition of toluene[5,6] and anisole[32] show the sole products to be those in which the methyl is located at C_1, as opposed to the reactions with furan observed here, where the methyl is at C_3 or C_4.[33] The most likely explanation which comes to mind is that in the exciplexes which are intermediates in the addition of photochemically excited toluene to monoalkenes, the geometry is as shown in Chart I, structure A, where hindrance between the methyl and the remainder of the alkene molecule (e.g., cyclopentene) is minimized. However, if the methyl is at the same location in exciplexes of excited toluene and furan (or other cisoid 1,4-dienes), hindrance between C_3 and C_4 of the diene (or furan) and the methyl will result, as shown in Chart I, structure B. However, if the methyl is located at C-3 or C-4, then in many of the possible exciplexes which one can conceive of, little if any steric congestion results.[33]



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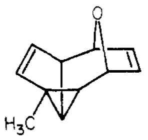

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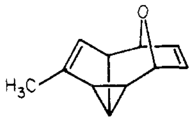

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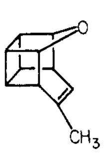

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Irradiation of *p*-xylene in excess furan gave **16**–**19** in the ratio of 23:25:32:22. The structures were apparent from the ^{1}H NMR data in the same way as were the structures of the toluene–furan adducts. Note that none of the products have a methyl at C-1.

Irradiation of anisole in the presence of excess furan led to a mixture of **20**, **21**, and an unidentified minor component in the ratio 55:38:7. The reaction was much less

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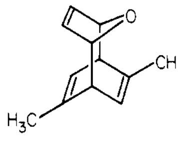
(31) (a) Rottele, H.; Merter, W.; Oth, J. F. M.; Schroder, G. *Chem. Ber.* **1969**, *102*, 3985–3992. (b) Berson, J. A.; Davis, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 3658–3659.

(32) (a) Ors, J. A.; Srinivasan, R. *J. Org. Chem.* **1977**, *42*, 1321. (b) Srinivasan, R.; Ors, J. A. *Tetrahedron* **1975**, *31*.

(33) However, it has more recently been reported that the major product from toluene and cyclooctene has the methyl at C-5: Bryce-Smith, D.; Dodson, W. M.; Gilbert, A.; Orger, B. H.; Tyrell, H. M. *Tetrahedron Lett.* 1977, 1093–1096.



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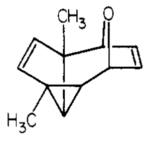

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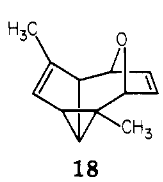

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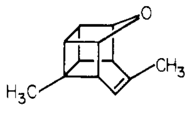

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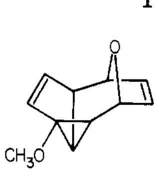

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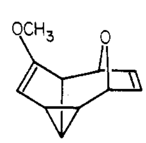

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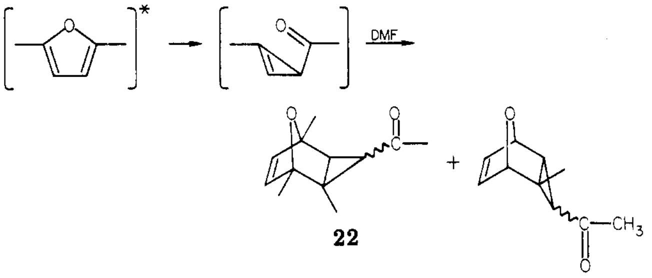
efficient than those of anisole with most simple alkenes, where Ors and Srinivasan report[32] $\Phi = 0.17$ for addition to cyclopentene. We find that quantum yield for the anisole–furan overall process to be ca. 0.01–0.015.

It was considered worthwhile to examine the effects of methyl substitution on the furan substrates upon the reaction pathway, and accordingly, the irradiation of solutions of benzene and excess 2,5-dimethylfuran was performed, affording a complex mixture which was inseparable on the eight GC columns tried. The IR and NMR spectra of this complex mixture were very similar to, although not precisely identical with, those of the mixture of compounds obtained by direct irradiation of solutions containing only 2,5-dimethylfuran. The presence of NMR singlets in the spectrum of the mixture in the region characteristic of acetyl methyl signals and of vinyl hydrogens in a bicyclo[2.2.1]heptene system suggests that at least some of the major components are of types **22** and **23**, the product of Diels–Alder trapping by the dimethylfuran present of the 1-methyl-3-acetylcyclopropene, a valence isomer of 2,5-dimethylfuran which has been detected by Srinivasan et al. in mixtures obtained upon direct irradiation of this and other simple furans.[34,40]



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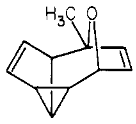
23

Evidently the effect of simple alkyl substitution upon the excited-state energies of furans is much greater than for most other aromatic systems. The excited singlet of benzene is ca. 110–113 kcal above the ground state, whereas those of toluene and xylene are, respectively, 108 and 106 kcal above the ground state.[35] The energies of the respective excited triplet states are 84 and ca. 82 kcal.[35b] No values could be found for the isomeric xylenes. It would appear most likely that the energy of the lowest excited triplet state of furan itself lies above ca. 85 kcal, so that sensitization by benzene triplets does not occur, but rather, exclusively photochemical reactions. On the other hand, the presence of two methyl groups in 2,5-dimethylfuran results in a lowest excited triplet state for that compound of E_T = 73–83 kcal/mol, with the consequence that only energy transfer occurs from benzene triplets to ground state dimethylfuran. Such a great reduction in the triplet energy of the furan system is supported by examination of the absorption spectra of the two compounds. Furan itself shows only end absorption with a possible maximum at ca. 214 nm; it seems likely that an absorption maximum is buried in the end absorption at ca. 220–230 nm. On the other hand, 2,5-dimethylfuran exhibits a broad maximum in cyclohexane at 230–250 nm,[36b,c] indicative of an excited singlet state lying some 10–15 kcal below that of furan itself. It would seem reasonable that the corresponding triplet states would have approximately the same relative relationship.

As a test of the reasonableness of the proposition that simple alkyl substitution could have such a large effect upon the energies of arene excited states, the photochemical behavior of mixtures of benzene and 2-methylfuran was examined. From these reaction mixtures were isolated the two cross adducts **24** and **25**, as well as a complex mixture of carbonyl compounds of the type described above obtained from benzene–dimethylfuran mixtures. It would appear that the triplet energy of 2-methylfuran is intermediate between that of furan and 2,5-dimethylfuran, i.e., ca. 84–85 kcal, and intermolecular photochemical cycloaddition and sensitization are occurring at similar rates.



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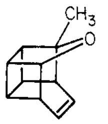

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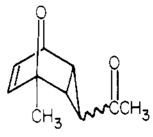
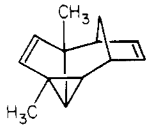


26

Recently a full paper by Bryce-Smith's co-workers has appeared describing in full detail their results.[37] They consider the intermediary of a furan excited state to be unlikely, a view with which the present author concurs.

Attention was now turned to the photoproducts from benzene and its simple derivatives with cyclic 1,3-dienes, which was the original impetus for this study. The initial pair of compounds examined was *p*-xylene and cyclopentadiene, since the various types of adducts predicted would have relatively simple NMR spectra and since they (C_{13} compounds) should be more easily separable by fractional distillation from the inevitable diene dimers (C_{10} hydrocarbons) than would adducts from benzene and cyclopentadiene (C_{11} hydrocarbons). Irradiation of *p*-xylene and a fivefold excess of cyclopentadiene at −10 °C gave a low conversion to a mixture of compounds **27** and **28**, identified by their NMR spectra (see Experimental Section). A [4 + 4] cycloadduct of type **7** and like that reported by Yang et al. from 1,2-dihydrophthalic anhydride[38] is also probably present but was not obtained pure (**29**).



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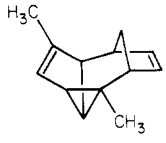

28

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[34] (a) Hiraoka, H.; Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 4812–4813. (b) Hiraoka, H.; Srinivasan, R. *Ibid.* **1968**, *90*, 2720–2722.

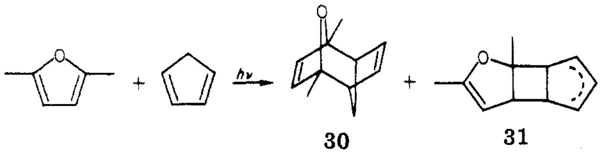
[35] (a) Yang, N. C.; Murov, S. L. "Handbook of Excited States"; Plenum Press: New York, 1971. (b) Wright, M. R.; Frosch, R. P.; Robinson, G. W. *J. Chem. Phys.* **1963**, *38*, 1187–1195.

[36] Kamlet, M.; Ungnade, H. E. "Organic Electronic Spectral Data"; Wiley-Interscience: New York, 1953; Vol. I.

[37] Berridge, J. C.; Gilbert, A.; Taylor, G. N. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2174.

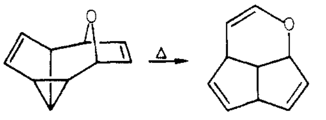
Irradiation of *p*-xylene with excess 1,3-cyclohexadiene gave only diene dimers and compounds derived from the electrocyclic ring opening of the diene to 1,3,5-hexatriene.

Since 2,5-dimethylfuran had been observed not to act as a substrate, but rather as an aromatic compound with an accessible excited state, the chemical behavior of that excited state in the presence of other substrates than ground-state dimethylfuran was briefly examined. Irradiation of 2,5-dimethylfuran in the presence of a tenfold excess of cyclopentadiene led to the isolation of two 1:1 adducts, assigned structures **30** and **31** on the basis of their NMR spectra. The significant features of these were the single methyl resonances at δ 1.8 and 1.5 in the spectrum of **31**. It is not obvious which reactant is acting as the excited partner and which as the ground-state partner, even though the cyclopentadiene must certainly possess a lower energy excited triplet state.



30 **31**

Finally, the pyrolysis of tricyclic ether **8** was briefly examined, since it has been reported that numerous 1,3–1,2 adducts of benzene and monoalkenes undergo simultaneous vinylcyclopropane rearrangement and 1,4 alkyl shift to afford derivatives of bicyclo[3.3.0]octadiene.[39,40] Accordingly, pyrolysis of **8** in sealed tubes at 200–300 °C was examined, and there was found in the resulting mixtures, in addition to unchanged **8** and gummy polymers, low yields of a product assigned structure **32**, in which migration of the vinyl moiety in a 1,4 sense has occurred.



32

Experimental Section

Infrared spectra were obtained on either a Perkin-Elmer Model 237 or a Model 397 grating instrument. NMR spectra were obtained at 60 MHz on Varian A-60 or EM-360 instruments, at 100 MHz on a Varian XL-100, and at 220 MHz on a Varian HR-220 instrument; the coupling constants are given in hertz. ^{13}C spectra were obtained on a Nicolet NT-200 in the FT mode. The following GC columns were employed: column A, 6 ft × $^3/_8$ in. 20% SE-30 on 30–60 AW/DMCS Chrom W; column B, 10 ft × $^1/_4$ in. 10% CW-20M on 60–80 AW/DMCS Chromosorb W; column C, 12 ft × $^1/_4$ in. 5% OV-17 on 60–80 AW/DMCS Chrom W; column D, 20 ft × $^1/_4$ in 5% CW-20M on 60–80 AW/DMCS Chrom W. Quantum yields were determined by using as the reference the photochemical reaction of benzene and cyclopentene.[5,6]

Irradiation of Benzene through Vycor in the Presence of Excess Furan ("U.S." Conditions). A solution of benzene (20 mL) and furan (100 mL) was flushed with argon for 1 h and irradiated through a Vycor filter (cutoff 220 nm) with an Engelhard-Hanovia 450-W, medium-pressure, mercury arc for 4–6 h. By this time the solution had become yellow, owing to the presence of UV–visible-absorbing byproducts (probably including fulvene[34]). The resulting reaction mixture was concentrated on a rotary evaporator to give ~1 g of orange residue. Two such residues were combined to give, after distillation, 1.5 g of faintly yellow liquid, bp 47–49 °C (0.08 mm). Examination of this distilled mixture revealed the major product to be [4 + 4] cycloadduct **7**, with lesser amounts of **5**, **6**, and **8–10**. Stirring a hexane solution of the mixture with aqueous silver nitrate under a nitrogen atmosphere overnight led to the precipitation of a dull gray-silver complex of triene **7**, 11-oxatricyclo[4.2.2.1^{2,5}]undeca-3,7,9-triene, (1.2 g). Preparative GC on column B at 170 °C allowed isolation of **5**, **6**, **8**, and **9**. The first eluted was furan **5**, 4-(2-furyl)bicyclo[3.1.0]-2-hexene: rt (retention time) = 4.1 min (11% of total material eluted); NMR δ 7.37 (1 H, d, *J* = 1.4, H-5 of furan), 6.60 (1 H, 2 d, *J* = 3.0, *J′* = 1.4, H_4 of furan), 6.09 (1 H, d, *J* = 30, H_3 of furan), 5.80 (1 H, 2 d, br, *J* = 3.8, *J′* = 1.2, H_2 or H_3), 5.62 (1 H, br m, H_2 or H_3), 2.50 (1 H, br m, H_4), 2.45 (1 H, br d, H_1), 2.23 (1 H, m, H_5), 2.10 (2 H, AB further split, *J* = 7, H_{6a} + H_{6b}). This was followed by the 1,3–1,2 adduct **6**: rt (retention time) = 4.9 min (6% of total); NMR δ 6.42 (1 H, t, *J* = 1.4), 5.54 (2 H, m), 4.82 (1 H, m), 4.74 (1 H, d, *J* = 7), 3.33 (1 H, dm, *J* = 7), 3.18 (1 H, dm, *J* = 7), 2.49 (1 H, dd, *J* = 7.8, *J′* = 7), 1.88 (1 H, d, *J* = 7.8); mass spectrum, *m/e* (relative intensity) 146 (P, 32), 117 (95), 115 (50), 81 (100), 68 (48). Next eluted was 1,3–1,4 adduct **8** (rt = 6.8 min, 60% of total), whose NMR data are in Table I; mass spectrum, *m/e* (relative intensity) 146 (P, 8), 145 (10), 117 (47), 115 (38), 81 (100). Last eluted was the cage-type molecule **9** (21% of total), whose NMR parameters also are in Table I; mass spectrum, *m/e* (relative intensity) 146 (P, 11), 145 (14), 117 (60), 115 (53), 91 (35), 78 (57), 68 (100).

Irradiation of 2:1 Solutions of Benzene and Furan ("British" Conditions). A solution of 80 g of benzene and 34 g of furan was flushed with nitrogen for 0.5 h and irradiated in a Rayonet chamber reactor equipped with four 8-W lamps emitting 2537-Å light for a 24-h period. Two such reaction mixtures were evaporated under reduced pressure and evaporatively distilled in a short-path apparatus to afford 1.4 g of liquid [bp 30–40 °C (0.05 mm)] whose NMR spectrum showed signals for **5–10** in the ratio 3:1:41:20:10:15. The distillate was dissolved in 5 mL of benzene together with 1.5 g of *N*-phenylmaleimide, and the mixture was allowed to stand under nitrogen for 20 h. Addition of 3 mL of hexane and cooling gave 0.86 g of adduct. Recrystallization of this material from benzene–hexane gave white needles: mp 228–229.5 °C dec; IR (KBr) 1675 cm^{-1}; NMR ($CDCl_3$) δ 7.50 (3 H, m), 7.20 (3 H, m), 6.23 (1 H, t, *J* = 1.6), 6.08 (2 H, m), 4.96 (1 H, m), 4.92 (2 H, br s), 3.72 (1 H, br s), 3.60 (1 H, br s), 3.44 (1 H, br s), 3.04 (1 H br s), 2.92 (2 H, s), 2.87 (1 H br d, *J* = 5); mass spectrum, *m/e* 321 (P).

Irradiation of Toluene and Furan under "U.S." Conditions. A mixture of 20 g of toluene and 80 g of furan was irradiated in exactly the same way as described above for the benzene–furan mixture under "U.S." conditions for 4-h periods. Combination of three such irradiation mixtures and evaporation of excess furan and toluene gave 1.9 g of product, bp 59–63 °C (0.01 mm). Analysis of this mixture on GC column A gave three components of relative retention times (180 °C) 6.7, 8.1, and 9.1 min, respectively. These were identified as, first, **13** (41% of total product, including **12**): NMR ($CDCl_3$) δ 6.48 (1 H, m, br, H_9), 6.26 (1 H, br m, H_4), 6.0 (1 H, br m, H_8), 5.5–5.6 (1 H, br m, H_5), 5.04 (1 H, m, H_7), 4.39 (1 H, t, *J* = 2.2, H_{10}), 2.97 (1 H, 2 t, *J* = 7.3, *J′* = 2.2, H_6), 1.29 (3 H, s, CH_3), 1.23 (1 H, br t, *J* = 7.3, H_2), 0.66 (1 H, 2 t, *J* = 8.5, *J′* = 2, H_1); mass spectrum, *m/e* (relative intensity) 160 (P, 11), 145 (32), 91 (100). Compound **14** was second (26% of total): NMR ($CDCl_3$) δ 6.53 (1 H, 2 d, *J* = 6.1, *J′* = 1.1, H_9), 6.38 (1 H, 2 d, *J* = 6.1, *J′* = 1.6, H_8), 5.68 (1 H, m, H_{10}), 5.05 (1 H, m, H_7), 2.68 (1 H, 2 m, *J* = 7.5, H), 2.17 (1 H, 3 m, *J* = 7.5, H_3), 1.75 (1 H, m, H_2, 1.70 (3 H, br s, CH_3), 0.77 (1 H, 3 m, *J* = 7.5, H_1); mass spectrum, *m/e* (relative intensity) 160 (P, 20), 91 (100). Finally, compound **15** was obtained (8% of total): NMR ($CDCl_3$) δ 5.9 (1 H, br m), 4.9–4.7 (2 H, m), 3.6–3.1 (4 H, m), 2.7 (2 H, m), 1.89 (3 H, d, *J* = 1.7); mass spectrum, *m/e* (relative intensity) 160 (P, 8), 91 (100). Examination of the distilled reaction mixture by NMR before gas chromatographic separation of **13–15** revealed signals at δ 6.3, 6.0, 4.2, 3.0, and 1.8, indicative of the presence of ca. 25% of **12**.

Irradiation of *p*-Xylene and Furan. Irradiation of two batches of a 5:1 furan-*p*-xylene mixture for 5 h each and distillation of the combined reaction mixtures gave 0.72 g of pale yellow oil, bp 65–68 °C (0.08 mm). Purification by GC on column A allowed isolation of three products. Compound **17**: 27% of

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[38] Yang, N. C.; Neywick, C. V.; Srinivasachar, K. *Tetrahedron Lett.* **1975**, 4313–4316.

[39] (a) Srinivasan, R. *J. Am. Chem. Soc.* **1970**, *92*, 7542–7546. (b) Srinivasan, R. *Ibid.* **1972**, *94*, 8117–8122. (c) Srinivasan, R. *Tetrahedron Lett.* **1973**, 4029–4032.

[40] **Note Added in Proof.** Recent experiments with this system at high benzene concentrations, which avoids direct excitation of DMF, show that products analogous to **7–9** are formed.

total; rt = 7.8 min at 180 °C; NMR (60 MHz, $CDCl_3$) δ 6.42 and 6.13 (AB part of ABX, *J* = 5.2, *J′* = 1.6, H$_8$ and H$_9$), 5.70 (1 H, d, *J* = 5.4, H$_4$), 5.13 (1 H, br d, *J* = 5.4, H$_5$), 4.90 (1 H, br s, H$_6$), 4.56 (1 H, br s, H$_2$), 1.25 and 1.10 (3 H each, s, CH_3), 0.68 (2 H, AB, *J* = 8.1, H$_1$); mass spectrum, *m/e* (relative intensity) 174 (11, P), 159, 38), 106 (100). (b) Compound **19**: 30% of total; rt = 9.0 min at 180 °C; NMR (60 MHz) δ 5.7 (1 H, br s), 4.9–4.6 (2 H, br m), 3.6–2.7 (5 H, br m), 1.8 (3 H, d, *J* ≃ 1, =CCH_3), 1.4 (3 H, s, CH_3). Compound 18: 43% of total; rt = 10.8 min; NMR (60 MHz) δ 6.56 (1 H, br d, *J* = 5.8, H$_8$), 6.19 (1 H, 2 d, *J* = 5.8, *J′* = 1.7, H$_9$), 5.46 (1 H, m, H$_5$), 4.78 (1 H, br s, H$_7$), 4.32 (1 H, br t, *J* = 2, H$_{10}$), 2.55 (1 H, d, *J* = 8, H$_6$), 1.75 (1 H, br m, H$_3$), 1.4 (3 H, br s, =CCH_3), 1.1 (1 H, br t, H$_1$), 0.83 (3 H, s, CH_3). All three isomers exhibited mass spectral parent ions at *m/e* 174 with base peaks at *m/e* 106.

Photochemical Reaction of *p*-Xylene and Cyclopentadiene. Irradiation of 80 g of reagent grade *p*-xylene and 20 g of freshly distilled cyclopentadiene at −10 °C for 6 h gave a yellow solution. Two such runs were combined and fractionally distilled after considerable diene thermal photodimers [bp 32–35 °C (3 mm)], and there was obtained 0.82 g of a faintly yellow mixture of products, bp 53–58 °C (0.07 mm). Separation of two components was achieved on column B at 160 °C. The first product isolated was **26**: 58% of total; NMR ($CDCl_3$, 220 MHz) δ 6.1 (2 H, 2 sets of 4 lines, *J* = 6.7, *J′* = 6.0), 5.7 (1 H, 2 br m, *J* = 7), 5.12 (1 H, m), 3.0–2.0 (3 H, br m), 1.73 (1 H, t, *J* = 1.4), 1.18 (1 H, d, *J* = 3.0), 1.25 and 1.30 (3 H each, s), 0.8 (1 H, m); mass spectrum, *m/e* (relative intensity) 172 (P, 40), 157 (67), 142 (58), 129 (52), 106 (100). The second adduct to be eluted was **27**: 31% of total; NMR ($CDCl_3$, 220 MHz) δ 6.1–5.4 (3 H, m), 4.6–4.3 (3 H, m), 2.7–2.4 (3 H, m), 2.0 (2 H, m), 1.54 (3 H, br s), 1.48 (3 H, s); mass spectrum, *m/e* (relative intensity) 172 (P, 11), 157 (15), 106 (86), 91 (100). A third adduct, not obtained pure, exhibited in its NMR spectrum signals for four vinyl hydrogens and two methyls on sp^2 carbon and is thought to possess structure **28**.

Photolysis of Benzene and 2,5-Dimethylfuran. A mixture of 2,5-dimethylfuran (40 g) and benzene (80 g) was flushed with argon and irradiated through Vycor for 60 h. After evaporation of unchanged starting materials there was obtained 1.8 g of yellow oil, bp 45–100 °C (0.1 mm). Fractional distillation of this material through a Vigreux column gave a low-boiling fraction [bp 44–48 °C (0.1 mm); 0.9 g] whose NMR spectrum showed signals in the δ 6.5 and 5.8–5.6 regions, major singlets at δ 2.8 and 2.7, and less intense (methyl) singlets at δ 2.1, 1.9, 1.65, 1.58, and 1.35. A strong infrared absorption at 1710 cm^{-1} was exhibited. A higher boiling fraction [bp 78–80 °C (0.1 mm)] exhibited NMR signals (60 MHz) at δ 6.4–5.9 (2 H, m), 3.2 (1 H), 2.4–2.2 (several s, 6 H), and 1.9–0.9 (singlets, 9 H); mass spectrum, *m/e* 192 and 149.

Irradiation of Benzene and 2-Methylfuran. A solution of equimolar amounts of benzene and 2-methylfuran was irradiated through Vycor in the manner described. Distillation gave 1.2 g of pale yellow oil, bp 65–69 °C (0.1 mm). Preparative GC on column A gave three peaks which could be collected as pure compounds plus a fourth which was an inseparable mixture. The first eluted (180 °C, 7 min) compound was cross product **24**: 52% of total; NMR ($CDCl_3$) δ 6.45 (1 H, m), 6.38 (1 H, m), 5.80 (1 H, m), 5.70 (1 H, m), 4.2 (1 H, br s), 3.0–1.8 (3 H, m), 1.55 (3 H, s); mass spectrum, *m/e* (relative intensity) 160 (20), 145 (16), 82 (100), 78 (61). The next compund obtained was cage compound **25**: 22% of total; NMR ($CDCl_3$) δ 6.2 (2 H, m), 4.6 (1 H, m), 3.5 (1 H, m), 3.3 (1 H, m), 3.1 (1 H, m), 2.5 (2 H, m), 1.7 (1 H, s), 1.42 (3 H, s); mass spectrum, *m/e* (relative intensity) 160 (P, 10), 145 (12), 82 (100), 78 (42). Anal. C, H. A peak of longer retention time (18 min) showed carbonyl absorption at 1710 cm^{-1} in the infrared, as well as acetyl singlets at δ 2.2–2.0, and is assigned the gross structure **26** (mixture of isomers).

Irradiation of 2,5-Dimethylfuran and Cyclopentadiene. A solution of 2,5-dimethylfuran (40 g) and freshly cracked cyclopentadiene (20 g) in spectrograde pentane (90 mL) was irradiated through Vycor at −10 to 0 °C for 2 h. Distillation afforded 1.6 g of yellow oil, bp 55–56 °C (0.1 mm). Separation by GC on column B gave two peaks of retention times 4.1 and 6.3 min at 140 °C. The first peak (a) showed the following: NMR δ 6.32 (2 H, m), 5.82 (2 H, m), 2.9 (2 H, m), 2.0–1.9 (2 H, m), 1.6 (6 H, s); mass spectrum, *m/e* (relative intensity) 162 (P, 8), 147 (11), 96 (100). Anal. $C_{11}H_{14}O$: C, H. The minor peak (b) gave the following parameters: NMR (60 MHz) δ 6.4 (2 H, m), 6.0 (1 H, m), 2.5–2.3 (2 H, m), 1.7 (3 H, br s), (3 H, s), 1.8–1.5 (2 H, br m); mass spectrum, *m/e* (relative intensity) 162 (P, 13), 147 (29), 96 (100).

Pyrolysis of Adduct 8. Adduct **8** (0.30 g) in a Pyrex tube of ca. 50 mL was evacuated to 0.05 mm and sealed. The tube was heated in a 220 °C silicone oil bath for 3 h, cooled, and opened, and the contents were taken up in dichloromethane. Analysis of the extract (ca. 0.18 g) on column C at 160 °C gave, besides recovered **8** (30%), bicyclic ether **32**: NMR ($CDCl_3$) δ 6.62 (2 d, *J* ≈ 5, *J′* 1.5), 6.45 (1 H, 2 m), 5.90 (1 H, 2 m, *J* ≈ 5), 5.90 (1 H, m), 5.71 (1 H, 3 d, *J* ≈ 4), 5.16 (1 H, m), 5.10, 3.68 (1 H, br d, *J* ≈ 5), 3.15 (1 H, m), 2.2 (1 H, m); mass spectrum, *m/e* (relative intensity) 136 (9), 110 (100), 78 (61). This material amounted to 36% of the total extract.

Acknowledgment. The author expresses his gratitude to Dr. Herman Ziffer of the NIH for providing access to the 220-MHz NMR instrument, to Mr. William Landis of the NIH for the mass spectra on the new compounds reported herein, and to Dr. Anne Turner for the ^{13}C NMR spectra.

Registry No. 5, 77224-10-3; **6**, 55165-00-9; **7**, 55230-19-8; **8**, 75879-04-8; **9**, 55165-04-3; **10**, 55230-20-1; **12**, 77224-11-4; **13**, 55165-01-0; **14**, 55165-02-1; **15**, 55165-05-4; **16**, 77224-12-5; **17**, 55164-99-3; **18**, 77224-13-6; **19**, 77224-14-7; **20**, 77224-15-8; **21**, 77224-16-9; **24**, 77224-17-0; **25**, 77224-18-1; **26** (isomer 1), 77224-19-2; **26** (isomer 2), 77285-88-2; **27**, 77224-20-5; **28**, 77224-21-6; **32**, 77224-22-7; benzene, 71-43-2; furan, 109-99-9; toluene, 108-88-3; *p*-xylene, 106-42-3; cyclopentadiene, 542-92-7; 2-methylfuran, 534-22-5; anisole, 100-66-3; 2,5-dimethylfuran, 625-86-5.