propionic acid (30 ml) that had been flushed with dry nitrogen was added 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophen-4-one (2.87 g, 0.0104 mol) and active copper dust[6] (5.30 g, 0.0835 mol). With vigorous mechanical stirring and a slow nitrogen flow through the system, the reactive mixture was held at reflux for 45 hr and cooled to room temperature and the deep green mixture was added to chloroform (150 ml).

Water was added (150 ml) and the acid was neutralized by addition of sodium bicarbonate. The layers were separated and the aqueous layer was extracted with chloroform (5 × 50 ml). The combined organic layers were dried ($MgSO_4$) and evaporated. The crude ketone which remained was dissolved in a minimum amount of chloroform and chromatographed on a column (2 × 34 cm) of neutral alumina. Elution with chloroform provided 1.57 (g (73%) of peach-colored plates. Recrystallization from 1:1 benzene–hexane provided an analytical sample: mp 133–135°; uv max (95% C_2H_5OH) 286 mμ (ϵ 17,400); ir (KBr) 1640 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.15 (t, 2 H, $-CH_2-$), 7.10–7.23 (m, 2 H, C_1 and C_7 hydrogen), 8.31 (d, 1 H, $J_{1,3} = J_{5,7} = 3$ Hz, C_3 and C_5 hydrogen).

Anal. Calcd for $C_{10}H_6OS_2$: C, 58.23; H, 2.93; S, 31.09. Found: C, 57.98; H, 2.86; S, 30.84.

E. Deuteration of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophen-4-one (11). To dry (distilled from lithium aluminum hydride) tetrahydrofuran (25 ml) was added 4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophen-4-one (0.30 g, 0.00145 mol). With vigorous stirring, the solution was flushed with dry nitrogen for 20 min and cooled to −20°. A solution of freshly sublimed potassium *tert*-butoxide (0.179 g, 0.00159 mol) in dry tetrahydrofuran (10 ml) was then rapidly added in one portion. The black reaction mixture was stirred for an additional 2 min and deuterium oxide (1 ml, 0.055 mol) dissolved in dry tetrahydrofuran (5 ml) was rapidly added with a syringe. The reaction mixture was allowed to warm to 2° during a 10-min period, and was then added to ice-cold 1 *M* HCl (20 ml). The red-orange slurry was extracted with chloroform (5 × 20 ml), and the combined organic layers were washed with water (50 ml), dried ($MgSO_4$), and evaporated. Sublimation of the crude residue afforded 0.090 g (30% recovery) of the ketone, mp 131–134°. Nmr analysis indicated 91% monodeuteration at the methylene position.

F. Deuteration of 4,9-Dihydronaphtho[2,3-*c*]thiophen-4-one (22). To a solution of 4,9-dihydronaphtho[2,3-*c*]thiophen-4-one (0.4 g, 0.002 mol) in dry THF (20 ml) cooled to −19° under dry nitrogen was rapidly added with vigorous stirring a solution of potassium *tert*-butoxide (0.24 g, 0.0022 mol) in dry THF (10 ml). The violet reaction mixture was stirred for an additional 2 min and deuterium oxide (1 ml. 0.055 mol) in THF (5 ml) was added rapidly. The reaction mixture was allowed to warm to 0° during a 4-min period and was then quenched with ice-cold HCl. Extraction of the red-orange mixture with ether followed by sublimation of the solid residue obtained upon evaporation afforded 0.066 g (16% recovery) of the ketone, mp 104–106°. Nmr analysis indicated 70% monodeuteration at the methylene position.

G. Attempted Deuteration of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene (20). Similar treatment of the above compound (0.194 g, 0.00101 mol) in THF (7 ml) at 25° with a solution of potassium *tert*-butoxide (0.124 g, 0.0011 mol) in THF (10 ml) for 4 min followed by addition of deuterium oxide (1 ml, 0.055 mol) and workup as before gave only starting material (0.119 g, 61% recovery). Nmr analysis indicated no deuterium incorporation.

Registry No.—**2**, 31936-80-8; **4**, 31936-82-0; **6**, 31936-81-9; **7**, 31981-26-7; **9**, 31936-79-5; **11**, 51472-74-3; **13**, 33527-26-3; **14**, 3172-52-9; **15**, 33527-28-5; **16**, 51472-75-4; **17**, 51472-76-5; **19**, 51540-10-4; **22**, 31926-65-5; **22-*d***, 51472-77-6.

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Photochemical Reactions of 2-Acylthiophenes, -furans, and -pyrroles with Alkenes

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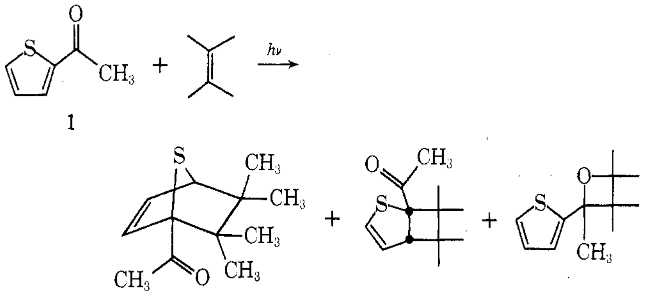
Irradiation of 2-acetylthiophene with tetramethylethylene or isobutene resulted in [4 + 2] addition of the thiophene to the alkene as the major process, as well as a [2 + 2] ring adduct and an oxetane as the minor products, a revision of our earlier structural assignments. 2-Benzoylthiophene and tetramethylethylene on irradiation lead to efficient oxetane formation. 2-Acetylfuran with both olefins mentioned above gave only products of [2 + 2] addition to the ring, in addition to minor amounts of oxetanes. 2-Benzoylfuran and 1-methyl-2-benzoylpyrrole gave only oxetanes or their decomposition products. Triplet excited states of the ketones appear to be intermediates in the formation of at least some of the observed products.

The photochemical behavior of aryl and aryl alkyl ketones has received much scrutiny in the past decde and a half.[1] A fairly clear picture is now available of the factors governing the various transformations of excited states of these carbonyl compounds, including reduction to pinacols,[2] [2 + 2] cycloaddition to olefins leading to oxetanes,[3] and Norrish type II elimination.[4] One structure–reactivity correlation which has emerged is that, in the case of those ketones whose lowest n, π^* triplet state is of an energy similar to or lower than that of the lowest π, π^* triplet, the former species, having considerable odd-electron character on the carbonyl oxygen atom, readily undergoes the transformations mentioned above. Those ketones whose lowest triplet is of predominantly $\pi \rightarrow \pi^*$ character, *e.g.*, naphthyl ketones or 4-biphenylyl ketones, are far less reactive photochemically.

We recently reported in preliminary form some of our results on photochemical cycloadditions of acyl derivatives of thiophene, furan, and pyrrole.[5] The structures of some previously unidentified minor products have now been elucidated; in addition, two of the structural assignments in our earlier report have been found to be incorrect. We present here a more detailed report on the products of irradiation of the 2-acetyl and 2-benzoyl derivatives of thiophene, furan, and *N*-methylpyrrole (**1–6**) in the presence of simple olefins such as tetramethylethylene and isobutene.

2-Acetylthiophene (1). Irradiation through Corex of **1** in the presence of excess 2,3-dimethyl-2-butene until 30% of **1** was consumed gave as the major product the [4 + 2] adduct 1-acetyl-5,5,6,6-tetramethyl-7-thiabicyclo[2.2.1]-2-heptene (**7**, 38%), in addition to lesser amounts (10%) of **8**, 1-acetyl-6,6,7,7-tetramethyl-2-thiabicyclo[3.2.0]-3-heptene, and oxetane **9** (11%). The major product, **7**, had earlier been erroneously assigned the [2 + 2] structure **8** on the following basis. (1) The nmr signal for the methine hydrogen at C-4 was a slightly broadened singlet, an observation seemingly more consistent with structure **8**, with its 70° dihedral angle between the C$_4$-H and C$_5$-H bonds, than **7**, for which Dreiding models indicate an angle of ~15° between the corresponding C-H bonds.[6] (2) The coupling constant between the two vinyl hydrogens (~3 Hz) appeared, at first sight, to be more consistent with **8**, since norbornenes have $J_{2,3}$ = 5.1–6.9 Hz.[6b] However, additional evidence is now available which we feel outweighs that above, and is compelling in favor of structure **7** for the major adduct. (1) The two vinyl carbons of the 7-thianorbornene structure **7** are bonded only to other carbons, and thus should exhibit nearly the same ^{13}C chemical shift. In structure **8**, however, one of the two olefinic carbons is bonded to sulfur and its ^{13}C nmr signal should appear at several parts per million lower field than that of the other. In the observed ^{13}C nmr spectrum of the major isomer, the olefinic carbons appear at 140.15 and 140.69 ppm downfield from TMS, a $\Delta\delta$ of only 0.45 ppm, whereas the olefinic carbons of the minor isomer appear at 128.08 and 123.23 ppm, a $\Delta\delta$ of 4.85 ppm. The olefinic carbons of the model 2,3-dihydrothiophene **10** appear at 129.5 and 123.8 ppm, a difference of 5.7 ppm, clearly favoring structure **8** for the minor isomer and the thianorbornene structure **7** for the major isomer. (2) The photon chemical shifts also support this assignment; the chemical shift difference for the vinyl hydrogens of the major isomer is only 0.08 ppm, whereas the minor isomer shows vinyl hydrogen signals at τ 3.91 and 4.59, a $\Delta\delta$ of 0.68 ppm. The model compound **10** exhibits vinyl hydrogen signals at τ 3.81 and 4.13 ($\Delta\delta$ 0.32 ppm) and the vinyl hydrogens signals of 2,3-dihydrothiophene itself occur at τ 3.94 and 4.52 ($\Delta\delta$ 0.58),[7] the much larger chemical shift differences again favoring structure **8** for the minor isomer. (3) The mass spectrum of the major isomer shows, *inter alia,* a major peak at *m/e* 167 (loss of acetyl) of approximately three times the intensity of the corresponding peak in the spectrum of the minor isomer. On the other hand, the peak at *m/e* 169 is somewhat more intense in the spectrum of the minor isomer. This behavior can best be accounted for as follows: ketone **7** would give on loss of the acetyl group an allyl cation further stabilized by having the positive charge α to sulfur; loss of acetyl from a compound of structure **8** would give a nonallylic cation and thus would not be expected to be as facile as the same process in **7**; consequently, the loss of ketene is resorted to be isomer **8**. (4) Addition of the shift reagent Eu(fod)$_3$ to solutions of the major isomer caused shifting of the two vinyl hydrogen signals to considerably different extents; the lower field vinyl hydrogen multiplet was shifted downfield by 0.55 ppm on addition of 0.3 molar equiv of Eu(fod)$_3$, whereas the higher field multiplet was shifted only 0.14 ppm. Such a difference in the effect of the shift reagent is more in accord with the thianorbornene structure **7**, in which one vinyl hydrogen is much closer to the carbonyl oxygen than the other than is so in structure **8**. It can be concluded from the assembled evidence, then, that the minor isomer must have structure **8**, and the major adduct structure **7**. The identity of oxetane **9** was readily apparent from its spectral data (see Experimental Section). The quantum yield for formation of **7** in solutions 5 *M* in olefin at 3000 Å was found to be 0.026 ± 0.05. The low conversions (~30%) of **1** to products are due to the formation of light-absorbing tarry material.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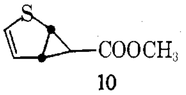
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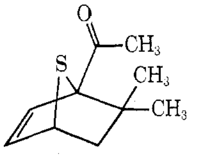
Irradiation of **1** in the presence of excess isobutene gave two major products, **11** and **12** (18 and 23%, respectively), as well as 6% of oxetane **13**. Ketones **11** and **12** are assigned the [4 + 2] structures on the basis of the pronounced similarity of their nmr spectra to that of **7**, with the exception that, in the spectrum of the minor isomer **11**, the C-4 hydrogen signal at τ 6.02 appeared as three sets of overlapping doublets (J = 5.2, J' = 5.0, J'' = 0.8 Hz) from coupling to the adjacent hydrogens on C-5. The nature of this coupling was verified by double resonance.[8] A fourth component was present in amounts too small for positive identification (3% yield), but was probably a [2 + 2] adduct analogous to **8**.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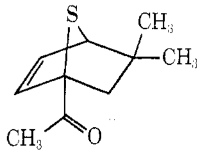
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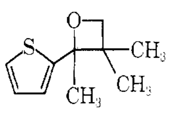
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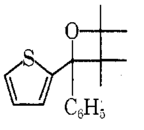
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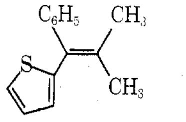
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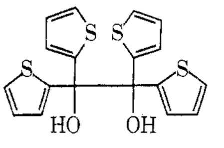
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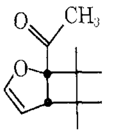
2-Benzoylthiophene. Irradiation of 2-benzoylthiophene (**2**) with excess 2,3-dimethyl-2-butene led to rapid consumption of **2** and formation of the oxetane **14**, mp 108–109°, in 76% yield (Φ = 0.21 in 5 *M* olefin). No ring-addition products were found. Quite different results were obtained on photolysis of **2** in the presence of excess isobutene; there resulted dark tarry mixtures from which could be isolated only unchanged **2** and the olefin **15**. The latter compound is evidently a product of thermal decomposition by [2 + 2] cycloreversion of an oxetane similar to **14**. Indeed, pyrolysis of **14** gave **15** in good yield. Infrared spectral examination of the crude reaction mixtures from **2** and isobutene showed a band of 1680 cm^{-1} of *ca.* one-half the intensity of that for unreacted **2** (at 1656 cm^{-1}) and which might reasonably be attributed to a product of addition of **2** to isobutene across the thiophene ring. The mass spectrum of this crude reaction mixture does exhibit a peak of significant intensity at *m/e* 244; although this may be simply due to an oxetane analogous to **14**, the virtual lack of a parent ion when **14** itself is injected into the mass spectrometer argues for the presence of another product of mass 244 in the crude mixture from irradiation of **2** and isobutene. Unfortunately, our attempts to separate the mixture without decomposition were fruitless.

Irradiation of 2-thenoylthiophene (**16**) in the presence of excess 2,3-dimethyl-2-butene gave the pinacol **17** (24%), in addition to a small amount of unchanged **16** and considerable tarry material. The structure of **24** was apparent from its spectral properties (see Experimental Section). Surprisingly, irradiation of **16** in 2-propanol gave no **24** and led only to slow destruction of **16**.

2-Acetylfuran. Irradiation of 2-acetylfuran (**3**) and excess 2,3-dimethyl-2-butene until 30% of **3** was destroyed gave 1-acetyl-6,6,7,7-tetramethyl-2-oxabicyclo[3.2.0]hept-3-ene (**18**, 33%), oxetane **19** (8%), a third product believed to possess structure **20** (7%) and a trace of a fourth product present in amounts too small for characterization. Assignment of the [2 + 2] structure **18** to the major adduct rested mainly on the close similarity of its nmr spectrum to those of known 2,3-dihydrofurans.[9] In particular, the proton next to oxygen on C-4 is shielded by that oxygen and appears at τ 5.07 as an apparent triplet, J = 3.1 Hz, whereas the proton on C-5 exhibits a pair of doublets at τ 3.65, J = 3.1, J' = 1.6 Hz. The parent 2,3-dihydrofuran displays multiplets at τ 3.78 and 5.18. In the spectrum of the 7-oxanorbornene from [4 + 2] addition of photoexcited methyl 1-cyclohexene-1-carboxylate to furan[10] the two vinyl hydrogens appear as the AB part of an ABX multiplet at τ 3.84 with J_{AB} = 5 and $J_{AX} \cong$ 0 Hz. The data for **18** are similar to those for the [2 + 2] adduct from cyclohexenone and furan, and in distinct contrast to those parameters for the [4 + 2] adduct.[9b]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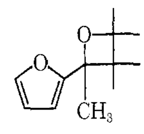
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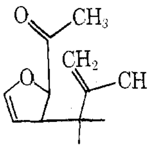
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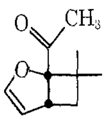
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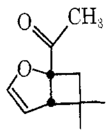
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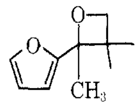
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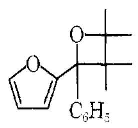
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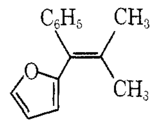
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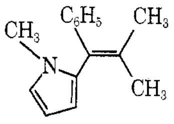
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Irradiation of **3** in the presence of excess isobutene gave a mixture of the [2 + 2] adduct **21** and its orientational isomer **22** (18 and 11%, respectively) as well as oxetane **23** (10%) and a fourth component of unknown structure (6%). The structures of **21**–**23** were assigned on the basis of their nmr and mass spectral data (see Experimental Section).

2-Benzoylfuran. Upon irradiation in the presence of excess 2,3-dimethyl-2-butene, 2-benzoylfuran (**4**) gave modest yields of oxetane **24** (27%), mp 43–44°, and its thermal decomposition product, olefin **25**, in contrast to the clean reaction observed with 2-benzoylthiophene (**2**). In the presence of isobutene as substrate irradiation of **4** gave dark mixtures from which only a small amount of olefin **24**, in addition to unchanged **4**, could be isolated.

1-Methyl-2-acetylpyrrole and 1-Methyl-2-benzoylpyrrole. Irradiation of 1-methyl-2-acetylpyrrole (**5**) with excess tetramethylethylene led to very slow formation, even with Corex filtered light, of ~10% of incompletely characterized materials which appear to arise from radicals produced by hydrogen abstraction from starting olefin by **5**. The benzoylpyrrole **6** on irradiation under the usual conditions gave much tar and 17% of olefin **26**.

Discussion

The [2 + 2] and [4 + 2] photochemical cycloaddition of the ketones **1**–**6** to olefins across the heterocyclic ring as the major process in distinct contrast to the facile addition of phenyl alkyl ketones to olefins and qualitatively suggests that the reactive excited states of **1**–**6** may be predominantly π, π^* rather than n, π^* in nature. This hypothesis is supported by the observation of long-lived phosphorescence from ketones **1**–**4**. In ether–isopentane–ethanol glass at 77°K these ketones show emission with a moderate degree of fine structure, of lifetimes 0.105, 0.152, 0.178, and 0.220 sec, respectively.[11] Such relatively long lifetimes are characteristic of π, π^* triplets; furthermore, the fine structure in each of the spectra is irregular and the spacings do not correspond to the carbonyl stretching frequency as is the case with the emission spectra of those ketones known to possess n, π^* triplets.[12] Recently Arnold and Birtwell have closely examined the emission and absorption spectra of 2- and 3-benzoylthiophene and several para-substituted derivatives thereof.[13] They concluded that the 2-benzoylthiophenes possess a π, π^* lowest triplet, the energy of the triplet of **2** itself being 63.3 kcal above its ground state. What appear to be the 0,0 bands in our spectra are of energies 64.5, 62.6, 64.9, and 64.0 kcal above the ground states for **1**–**4**, respectively, our value for **2** thus being in reasonably good agreement with that of Arnold.

The intermediacy of lowest $\pi \rightarrow \pi^*$ triplet excited states may account for the formation of ring-addition products as the predominant mode of reaction of the methyl ketones **1** and **3**. However, what of the benzoyl derivatives **2**, **4**, and **6**, which lead predominantly, if not exclusively, to products from bonding at the carbonyl group? This behavior has precedent in the behavior of phenyl β-naphthyl ketone and the naphthaldehydes, which undergo oxetane formation with modest efficiency ($\cong$0.05), and whose spectroscopic triplets have been assigned as $\pi \rightarrow \pi^*$.[14] It has recently been established that the naphthaldehydes undergo stereospecific oxetane formation with *cis*- and *trans*-2-butene, and from the fluorescence quenching effect of these and other olefins, naphthaldehyde excited *singlet* states have been implicated as reactive intermediates.[15] It certainly seems reasonable that the presently examined ketones, **2**, **4**, and **6**, react at least partially *via* excited singlet states, perhaps of n $\rightarrow$ π^* configuration. Unfortunately, our attempts to perform quenching and sensitization experiments with **1**–**6** have been frustrated by the combined factors of very low quantum yields and of reaction of sensitizers with the olefinic substrates. In our preliminary communication on this work, we had qualitatively concluded that there was only a small quenching effect with **1**–**4**. It now appears that this result may well have been a consequence of eventual consumption of the dienes used as quenchers (by sensitized dimerization). Because the quantum yields for formation of some of the presently observed products are low (*e.g.*, ~0.03 for the conversion of **1** to **7**), we experienced some difficulty in ascertaining whether quenching was actually occurring. However repeated experiments showed that the conversions of **1** to **6**, **7**, and **8**, and of **4** to **24**, were almost completely quenched by the presence of *cis*-1,3-pentadiene (0.1–0.4 *M*). Further, in the case of addition of **2** to 2,3-dimethyl-2-butene, the quantum yield for formation of oxetane **14** is 0.21, and added *cis*-1,3-pentadiene (0.5 *M*) definitely caused almost complete suppression of the formation of **14**. Experiments with **3** and **4** were less rewarding, but we tentatively conclude that the additions observed here proceed predominantly *via* excited triplet states of the ketones.

A further test of this hypothesis would be a determination of the degree of stereospecificity of the addition of **2** to, for example, *cis*- and *trans*-2-butene. However, experiments along these lines have thus far proven unrewarding. A definitive test awaits the availability of a suitable alkene. Experiments of this type, and with other thiophene and furan derivatives, are in progress.

Experimental Section

Irradiations were conducted in an annular apparatus using light from a Hanovia 450-W medium-pressure mercury arc lamp, filtered through Corex (transmits >260 nm), Pyrex (>290 nm), or uranium glass (>330 nm) and cooled by ice water in an immersion well. All photochemical reaction solutions were flushed with argon for 1 hr prior to irradiation. Nmr spectra were obtained on Varian A-60 and XL-100 instruments. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-6E. Gas chromatography was performed on the following columns: column A, 2 ft × 0.25 in., 10% SE-30 on Chromosorb W; column B, 2 ft × 0.25 in., 15% Carbowax 20M on Chromosorb W; column C, 6 ft × 0.25 in., 10% SE-30; column D, 6 ft × 0.25 in., 15% Carbowax 20M; and column E, 6 ft × 0.375 in., 25% SE-30.

Photochemical Reaction of 2-Acetylthiophene (1) with 2,3-Dimethyl-2-butene. A solution of **1** (3.0 g, 0.03 mol) and 2,3-dimethyl-2-butene (24 g, 0.03 mol) made up to 125 ml with spectrograde hexane was irradiated through Pyrex for 18 hr. The solvent and excess olefin were evaporated from the by now light brown solution and the residual material was distilled in a short-path apparatus (30–40°, 0.1 mm), leaving a small amount of brown, tarry residue. The entire distillate (2.8 g) was redissolved in the recovered olefin and solvent was added to bring the volume up to 125 ml; after flushing with argon, the resulting solution was irradiated for an additional 10 hr. After another such cleansing operation and a third irradiation period the reaction mixture was fractionally distilled to give 2.0 g of recovered **1**, bp 26–40° (0.2 mm), and 1.06 g of a mixture of products as a colorless oil, bp 58–65° (0.08 mm) (58% based on unrecovered **1**). Separation on column A (140°) permitted isolation of the following products. (a) Oxetane **9** (11% yield): ir (film) 1040 cm^{-1}; nmr ($CDCl_3$) τ 2.7–3.3 (AMX at 100 MHz, $J = 5.0$, $J' = 3.5$, J'' 1.3 Hz), and 8.36, 8.61, 8.70, 8.89, and 9.18 (all 3 H, each s); mass spectrum m/e 152 (100, parent − acetone, parent not observed), 137 (12), and 83 (26). *Anal.* Calcd for $C_{12}H_{18}OS$: C, 68.56; H, 8.56. Found: C, 68.32; H, 8.50. (b) Ketone **7** (37%): ir (film) 1704 cm^{-1}; nmr ($CDCl_3$) τ 3.70 (2 H, AB part of ABX, $J = 3.0$ Hz), 6.41 (1 H, s), 7.81 (3 H, s), and 8.50, 8.73, 8.88, and 8.97 (3 H each, s); mass spectrum m/e 210 (parent, 9), 169 (6), 167 (19), 111 (18), 109 (28), 84 (100), and 69 (70). *Anal.* Calcd for $C_{12}H_{18}OS$: C, 68.56; H, 8.56. Found: C, 68.83; H, 8.45. (c) Ketone **8** (10%): ir (film) 1701 cm^{-1}; nmr ($CDCl_3$) τ 3.89 (1 H, 2 d, $J = 6.0$, $J' = 1.2$ Hz), 4.59 (1 H, 2 d, $J = 6.0$, $J' = 3.6$ Hz), 6.20 (1 H, 2 d, J 3.6, $J' = 1.2$ Hz), 7.93 (3 H, s), and 8.72, 8.94, 8.97, and 9.05 (all 3 H each, s); mass spectrum m/e (rel intensity) 210 (parent, 6) 169 (9), 16 (8), 127 (10), 111 (14), 109 (2.5), 84 (100), and 69 (58).

Irradiation of 1 in Isobutene. A solution of **1** (3.0 g) and isobutene (C.P. grade, 40 ml) in spectrograde hexane (90 ml) was irradiated for 18 hr using a Pyrex immersion well. Ice water was circulated through the well and around the irradiation vessel. After evaporation of the solvent and excess olefin, the residue was distilled to give 2.6 g of material, bp 38–90° (0.2 mm). Reirradiation of the distillate for 12 hr in a solution with 35 ml of isobutene and 80 ml of spectrograde hexane gave, after distillation, 1.7 g of recovered **1**, bp 38–40° (0.3 mm), and 0.79 g of a mixture of adducts as a yellow oil, bp 62–64° (0.3 mm). Separation was achieved by gc on column B (130°), giving the following products. (a) Oxetane **13** (6%): ir (film) 1040 cm^{-1}; nmr ($CDCl_3$) τ 3.1–3.5 (AMX, 3 H) 7.3 (2 H, AB, $J = 6$ Hz), 8.65, 8.85, and 8.92 (3 H each, s). (b) Adduct **11** (18%): ir (film) 1701 cm^{-1}; nmr ($CDCl_3$) τ 3.68 (2 H, AB of ABX, $J_{AB} = 2.8$ Hz, $\Delta\nu = 3.6$, upper half further split, $J = 0.8$ Hz), 6.02 (1 H, 3 d, $J = 4.2$, $J' = 5.0$, $J'' = 0.8$ Hz), 7.73 (3 H, s), 8.05 (2 H, AB, $J \cong 5$ Hz), 8.44 and 5.55 (3 H, each, s); mass spectrum m/e (rel intensity) 182 (parent, 39), 149 (14), 139 (30), 127 (92), 125 (55), 111 (100), 97 (26). *Anal.* Calcd for $C_{10}H_{14}OS$: C, 65.96; H, 7.68. Found: C, 65.81; H, 7.52. (c) Adduct **12** (23%): ir (film) 1701 cm^{-1}; nmr ($CDCl_3$) τ 3.68 (2 H, AB of ABX, $J_{AB} = 2.8$ Hz, upper half, $J_{AX} = 0.6$ Hz, lower half, $J_{BX} = 0.9$ Hz) 5.41 (1 H, s, br), 7.75 (3 H, s), 7.89 (2 H, AB, $J = 13.4$ Hz, $\Delta\nu = 17$), 8.40 and 8.57 (3 H each, s); mass spectrum m/e (rel intensity) (parent, 26), 149 (18), 139 (35), 127 (90), and 111 (100). *Anal.* Found: C, 66.29; H, 7.82.

Photochemical Reaction of 2-Benzoylthiophene (2) with 2,3-Dimethyl-2-butene. A solution of **2** (1.8 g, 0.01 mol) and 2,3-dimethyl-2-butene (20 g, 0.25 mol) in spectrograde hexane (80 ml) was irradiated through a uranium glass filter for 1.5 hr. Careful evaporation of solvent and excess olefin at 30–35° left a semisolid residue which was recrystallized from 3:1 hexane–ethyl acetate at 0° to give oxetane **14** (76%) as white prisms: mp 108–109°; ir (KBr) 1010 and 1130 cm^{-1}; nmr ($CDCl_3$) τ 2.6–3.2 (8 H, m), 8.62, 8.77, 8.90, and 9.06 (3 H each, s); mass spectrum no parent, m/e 214 (parent − acetone, 24), 189 (40), and 84 (100). *Anal.* Calcd for $C_{17}H_{20}OS$: C, 75.02; H, 7.36. Found: C, 75.27; H, 7.19.

Heating **14** to 160–170° for 30 min at 2 mm gave a brown oil which was distilled to give olefin **15**: bp 102–105° (0.1 mm); ir (film) 1604 cm^{-1}; nmr ($CDCl_3$) τ 2.6–2.9 (8 H, m), 8.00 and 8.28 (3 H each, s); mass spectrum m/e (rel intensity) 214 (parent, 35), 189 (44), and 84 (100). *Anal.* Calcd for $C_{14}H_{14}S$: C, 78.57; H, 6.53. Found: C, 78.40; H, 6.38.

Photochemical Reaction of 2-Benzoylthiophene with Isobutene. A solution of **2** (2.0 g) and isobutene (40 ml) in pentane (90 ml) was irradiated through Pyrex while being cooled externally with an ice–salt bath. After 5 hr the golden-tan solution was evaporated under reduced pressure to leave a brown oil which showed infrared carbonyl bands for **2** (at 1655 cm^{-1}) and a second substance (at 1680 cm^{-1}) in the approximate ratio 2:1. The nmr spectrum of this crude mixture showed, *inter alia*, singlets at τ 8.87 and 8.98. Distillation of this oil at 0.06 mm gave only olefin **15**.

2-Thenoylthiophene. A solution of bis(2-thienyl) ketone (**16**, 1.00 g) and 2,3-dimethyl-2-butene (30 g) in spectrograde hexane (80 ml) was irradiated through a uranium glass filter for 10 hr. Evaporation of the solvent and excess olefin at ≤40° left a semisolid residue which was triturated with 2:1 hexane–benzene and filtered to give crude **17** (0.29 g). Recrystallization from chloroform–hexane at 0° gave pure **17**, mp 125–126° (0.24 g, 20%), as white prisms: ir (KBr) 3400 (Br), 1280 and 1015 cm^{-1} (s); nmr ($CDCl_3$) τ 2.7 (3 H, m), 3.0 (6 H, m), and 6.43 (2 H, s); mass spectrum (no parent ion) m/e (rel intensity) 355 (1.2), 261 (25), 194 (100), and 111 (80). *Anal.* Calcd for $C_{18}H_{14}O_2S_4$: C, 55.98; H, 3.63. Found: C, 55.79; H, 3.90.

Photochemical Reaction of 2-Acetylfuran (3) with 2,3-Dimethyl-2-butene. A solution of **3** (4.6 g, 0.05 mol) and 2,3-dimethyl-2-butene (42 g, 0.50 mol) in hexane (70 ml) was irradiated in the standard manner for 1 hr, followed by evaporation of the solvent and excess olefin. The residual oil was distilled (bp 33–85°, 2 mm) leaving a brown residue. the distillate was redissolved in the hexane–olefin mixture and reirradiated for an additional 16-hr period. After a third such treatment, the residual liquid was fractionally distilled to give recovered **3**, 2.8 g, and a mixture of products, bp 56–58° (0.1 mm). Separation on column B (140°) led to isolation of three products which are as follows, in order of increasing retention time. (a) Oxetane **19**: ir (film) 1075 cm^{-1}; nmr ($CDCl_3$) τ 2.8, 3.7, 3.8 (3 H, AMX), and 8.48, 8.73, 8.88, 8.95, and 9.02 (3 H each, s); mass spectrum m/e (rel intensity) 194 (parent, 0.6), 136 (42), and 84 (100). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.25; H, 9.26. Found: C, 73.98; H, 9.03. (b) [2 + 2] adduct **18**: ir (film) 1705 (C═O) and 1595 cm^{-1} (enol ether); nmr ($CDCl_3$) τ 3.67 (1 H, 2 d, $J = 3.0$, $J' = 1.6$ Hz), 5.07 (1 H, t, $J = J' = 3.0$ Hz), 6.80 (1 H, 2 d, $J = 3.0$, $J' = 1.6$ Hz), 7.93 (3 H, s), 8.91 (6 H, s), 9.10 (3 H, s), and 9.18 (3 H, s); mass spectrum m/e (rel intensity) 194 (parent, 3), 193 (3.5), 161 (10), 151 (9), 111 (28), and 84 (100). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.25; H, 9.26. Found: C, 74.03; H, 9.17. (c) Compound **20**: ir (film) 1702 cm^{-1}; nmr ($CDCl_3$) τ 3.7 (1 H, t, $J = 2.8$ Hz) 4.8 (1 H, m), 7.2–7.4 (3 H, m), 8.2 (3 H, s), and 8.6 (6 H, s). *Anal.* C, 74.40; H, 9.02.

Photochemical Reaction of 2-Acetylfuran with Isobutene. A solution of **3** (4.6 g, 0.05 mol) and isobutene (~40 ml) in pentane (90 ml) was irradiated through Corex while being cooled externally with an ice–salt bath. After 14 hr the solvent and excess olefin were evaporated and the residue was distilled [bp 35° (5 mm), 80° (0.1 mm)]. The clear distillate (3.8 g) was irradiated for a further 12 hr with fresh olefin and solvent. Fractional distillation of the residue remaining from a second evaporation of solvent and olefin gave 2.9 g of recovered **3**, bp 34–38° (5 mm), and a product mixture, bp 41–53° (0.1 mm) (0.76 g). Separation on column C at 170° gave the following products. (a) Oxetane **23**: nmr ($CDCl_3$) τ 2.6–3.4 (AMX, 3 H), 6.0 (2 H, AB, $J = 8$ Hz), 8.55, 8.76, and 8.97 (3

H each, s); mass spectrum (no parent), *m/e* (rel intensity) 136 (base peak, 3.6), 67 (100). (b) Adduct **21**: ir (film) 1707 cm^{-1}; nmr ($CDCl_3$) τ 3.63 (1 H, 2 d, J = 2.8, J' = 1.6 Hz), 4.88 (1 H, 2 d, J = 2.8, J' = 2.0 Hz), 6.20 (1 H, s, br), 7.2 (AB, J = 12 Hz), 7.78, 8.48, and 8.83 (3 H, each, s); mass spectrum *m/e* (rel intensity) 166 (parent, 31), 110 (100). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.31; H, 8.43. Found: C, 72.02; H, 8.28. (c) Adduct **22**: ir (film) 1700 cm^{-1}; nmr ($CDCl_3$) τ 3.77 (1 H), 4.8 (1 H), 6.85 (1 H, m), 7.4 (2 H, m) and 7.69, 8.57, and 9.06 (3 H each, s); mass spectral parent ion at *m/e* 166.

Photochemical Reaction of 2-Benzoylfuran with 2,3-Dimethyl-2-butene. A solution of 2-benzoylfuran (**4**, 1.0 g, 6.5 mmol) and 2,3-dimethyl-2-butene (30 g) in spectrograde hexane was irradiated through a uranium glass filter for 6 hr. Evaporation of the solvent and excess olefin at reduced pressure left a viscous yellow residue which was distilled in a short-path apparatus at 0.04 mm (bath temperature 60–90°). Two fractions were collected. The first (0.32 g) was purified by gc on column B and was shown by spectral data to be olefin **25**: ir (film) 1590 cm^{-1}; nmr ($CDCl_3$) τ 2.3–2.8 (6 H, m), 3.5–3.8 (2 H, multiplets, furan H), 8.34, and 8.56 (3 H each, s); mass spectrum *m/e* (rel intensity) 198 (parent, 73), 183 (17), and 77 (100). The second, higher boiling fraction on dissolving in pentane and cooling to −20° gave oxetane **24** (0.45 g, 27%) as colorless prisms: mp 43–44°; nmr ($CDCl_3$) 2.6–2.9 (6 H, m) 3.6–3.8 (2 H, m, furan H), 8.33, 8.68, 8.88, and 9.12 (all 3 H each, s); mass spectrum (no parent ion) *m/e* (rel intensity) 198 (22), 183 (15), 174 (40), and 84 (100). *Anal.* Calcd for $C_{17}H_{20}O_2$: C, 79.70; H, 7.81. Found: C, 79.85; H, 7.68.

Irradiation of ketone **4** in the presence of excess isobutene led to dark solutions from which could be obtained by evaporation distillation only low yields of olefin **25**.

Irradiation of 1-Methyl-2-benzoylpyrrole (6) with 2,3-Dimethyl-2-butene. A solution of ketone **6** (1.0 g) and 2,3-dimethyl-2-butene made up to 120 ml in spectrograde hexane was irradiated through Pyrex for 10 hr. Work-up in the usual way gave 0.20 g of an oil, bp 76–80° (0.1 mm), which was impure **26**: ir 1616 cm^{-1}; nmr ($CDCl_3$) τ 2.6–3.0 (5 H, m), 3.6–3.9 (~3 H, m), and 8.34 (6 H, s); mass spectrum *m/e* (rel intensity) 211 (parent, 14), 184 (31), 105 (56), and 84 (100).

Quantum Yields. The quantum yields for reactions of **1** and **2** were measured in a Rayonet Chamber Reactor, using lamps whose output centered at 3000 and 3500 Å, respectively, with a rotating tube holder. For **2**, decafluorobenzophenone–decafluorobenzhydrol was used as the actinometer,[16] and for **1**, the system acetophenone–2-propanol. The measurements were made with solutions which were 0.1 *M* in ketone and 5 *M* in olefin; runs were carried to ≤5% conversion.

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Molecular Design by Cycloaddition Reactions. XV.[1] Transannular Cross Cyclization of Cyclooctatetraene–Maleic Anhydride Adduct by Electrophiles

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Reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives with electrophiles (bromine, *tert*-butyl hypochlorite, iodine chloride, and iodine azide) has been studied, some of which proceed by transannular cross bonding of the proximal π bonds to give novel caged compounds. The structures of these products were determined by spectral means and chemical transformations. Some mechanisms for the formation of the products are discussed.

Facile addition reactions involving transannular π participation between two double bonds are well documented in such systems as norbornadiene,[2] 1,5-cyclooctadiene,[3] and some caged compounds[4,5] containing two isolated double bonds in spatial proximity.

With a hope of providing the synthetic entry of new carbon-skeleton construction and of understanding the capability of the participation between two isolated double bonds in ionic reaction, we have investigated the electrophilic addition reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (a 1:1 adduct of cyclooctatetraene and maleic anhydride).