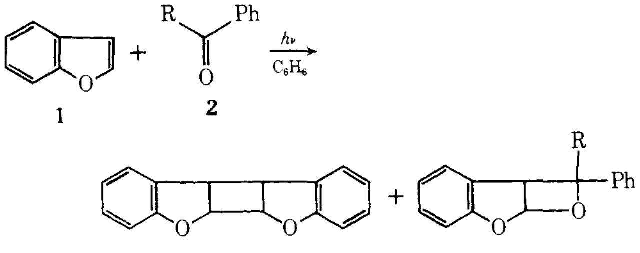
Reversible Energy Transfer and Oxetane Formation in the Photoreactions of Carbonyl Compounds with Benzofurans

S. Farid,* S. E. Hartman, and C. D. DeBoer

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received August 14, 1974*

Abstract: The photoreactions of propiophenone and acetophenone with benzofuran lead both to dimerization of the olefin and to oxetane formation. The dependency of the product ratio on the concentration of the reactants can be rationalized in terms of two different mechanisms. Kinetic studies gave support for the mechanism involving a reversible energy-transfer step as a reaction competing with the oxetane formation. The data implied, however, that the difference in triplet energies of propiophenone and acetophenone is much smaller than the reported values, which were derived from the phosphorescence spectra in glasses. This apparent contradiction was eliminated by establishing that both ketone triplets in benzene at room temperature are practically isoenergetic. This was concluded from a chemical kinetic study based on competing oxetane formation from both ketones with 2-methyl-2-butene.

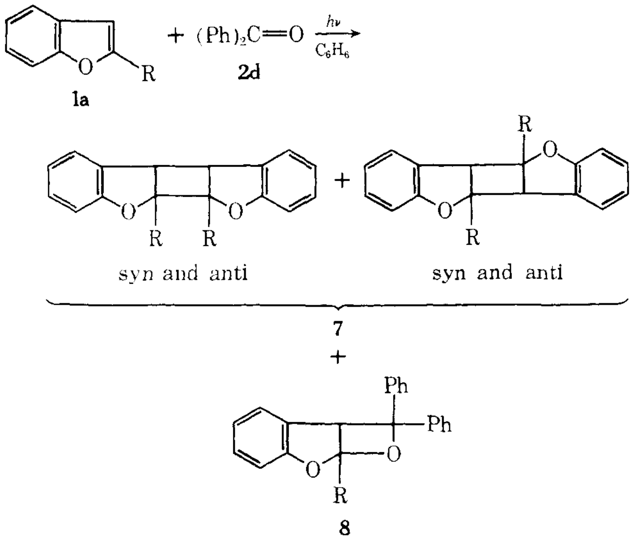
In recent years, photochemical oxetane formation has been subjected to extensive study. These reactions were found to proceed *via* different mechanisms. Examples are known of oxetane formation *via* addition of excited-singlet carbonyl compounds to olefins[1] and of an excited-singlet hydrocarbon to a ground-state carbonyl compound[2] as well as reactions induced by charge-transfer excitation of complexes of both reactants.[3] The most general mechanism of oxetane formation involves, however, addition of $n\pi^*$ excited-triplet carbonyl compounds to ground-state olefins, having higher triplet excitation energies than that of the adding carbonyl compound.[4] In agreement with this mechanism the photoreaction of benzofuran (**1**) with different carbonyl compounds is reported[5] to yield dimers when high-triplet-energy compounds (propiophenone (**2a**) and acetophenone (**2b**)) are used, while oxetanes are formed from the reaction of lower energy carbonyls (benzaldehyde (**2c**) and benzophenone (**2d**)).



1 2

3(syn and anti) 4

a, $R = C_2H_5$
b, $R = CH_3$
c, $R = H$
d, $R = Ph$



1a **2d**

7

8

R = COOMe

Reinvestigation of the reaction of **1** with **2a,b** revealed that, besides the dimers (**3**),[6] oxetanes (**4**)[7] were also formed. As shown below, this is not in any contradiction with the general concept of energy transfer *vs.* cycloaddition.[4]

The ratio of **3**:**4** was found to be dependent on the ratio of the reactants **1**:**2a,b**, similar to the dependency previously reported[8] for the reaction of methyl coumarilate (**1a**) and benzophenone.

The concentration dependency and those observed in similar systems[9] could well be interpreted in terms of Scheme I involving energy transfer from the excited-triplet carbonyl compound (2^{*3}) to the olefin (**1**) followed by the competing reaction of 1^{*3} with **1** or **2** leading to dimerization and oxetane formation, respectively.

The observed dependency of the quantum yield of oxetane and dimer formation in these reactions could, however, also be explained in terms of a reversible energy transfer process as a reaction competing with the oxetane formation according to the mechanism outlined in Scheme II.[10] The formation of the oxetane (**4**) is probably preceded by that of a complex[12] (**2–1**)*, which leads to a biradical, which then cyclizes.

The oxetane:dimer ratio according to Schemes I and II is given by eq 1 and eq 2, respectively.

$$\frac{\Phi_4}{\Phi_3} = \frac{k_6}{k_4}\frac{[2]}{[1]} \qquad \text{(from Scheme I)} \qquad (1)$$

$$\frac{\Phi_4}{\Phi_3} = \frac{k'_6(k_4 + k_5)}{k_2k_4} + \frac{k'_6k_3}{k_2k_4}\frac{1}{[1]} + \frac{k_{-2}k'_6}{k_2k_4}\frac{[2]}{[1]} \qquad \text{(from Scheme II)} \qquad (2)$$

At constant concentration of [**1**], a plot of the product ratio **4**/**3** *vs.* [**2**] should be linear according to both mechanisms, going through the origin in case I and having an intercept in case II. Plots of the data from the reaction of **1** with **2a** or **2b** gave straight lines with intercepts close to zero. This indicates that eq 1 obtains *or* that the intercept in eq 2 is very small. The second term in eq 2 shows that the magnitude of this intercept depends on the decay rate of 1^{*3}. The decay rate can be enhanced if a triplet quencher is added to the system. Whereas eq 1 would remain un-

Scheme I

$$\begin{aligned}
\mathbf{2} &\xrightarrow{h\nu} \longrightarrow \mathbf{2}^{*3}\\
\mathbf{2}^{*3} &\xrightarrow{k_1} \mathbf{2}\\
\mathbf{2}^{*3} + \mathbf{1} &\xrightarrow{k_2} \mathbf{2} + \mathbf{1}^{*3}\\
\mathbf{1}^{*3} &\xrightarrow{k_3} \mathbf{1}\\
\mathbf{1}^{*3} + \mathbf{1} &\xrightarrow{k_4} \mathbf{3}\\
\mathbf{1}^{*3} + \mathbf{1} &\xrightarrow{k_5} \mathbf{1} + \mathbf{1}\\
\mathbf{1}^{*3} + \mathbf{2} &\xrightarrow{k_6} \mathbf{4}\\
\mathbf{1}^{*3} + \mathbf{2} &\xrightarrow{k_7} \mathbf{1} + \mathbf{2}
\end{aligned}$$

Scheme II

$$\begin{aligned}
\mathbf{2} &\xrightarrow{h\nu} \longrightarrow \mathbf{2}^{*3}\\
\mathbf{2}^{*3} &\xrightarrow{k_1} \mathbf{2}\\
\mathbf{2}^{*3} + \mathbf{1} &\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathbf{2} + \mathbf{1}^{*3}\\
\mathbf{1}^{*3} &\xrightarrow{k_3} \mathbf{1}\\
\mathbf{1}^{*3} + \mathbf{1} &\xrightarrow{k_4} \mathbf{3}\\
\mathbf{1}^{*3} + \mathbf{1} &\xrightarrow{k_5} \mathbf{1} + \mathbf{1}\\
\mathbf{2}^{*3} + \mathbf{1} &\xrightarrow{k'_6} \mathbf{4}\\
\mathbf{2}^{*3} + \mathbf{1} &\xrightarrow{k'_7} \mathbf{2} + \mathbf{1}
\end{aligned}$$

changed if reaction 8 is introduced in the schemes, eq 2 would be replaced by eq 3. Accordingly, the intercept of the

$$\mathbf{1}^{*3} + \mathrm{Q} \xrightarrow{k_8} \mathbf{1} + \mathrm{Q}^{*3}$$

$$\frac{\phi_{\mathbf{4}}}{\phi_{\mathbf{3}}} = \frac{k'_6(k_4 + k_5)}{k_2k_4} + \frac{k'_6(k_3 + k_8[\mathrm{Q}])}{k_2k_4}\frac{1}{[\mathbf{1}]} + \frac{k_{-2}k'_6}{k_2k_4}\frac{[\mathbf{2}]}{[\mathbf{1}]} \tag{3}$$

plot of **4**/**3** *vs.* [**2**] at constant [**1**] should increase with increasing (Q) and would offer a means of differentiating between Schemes I and II. Addition of naphthalene (0.02 *M*) as a quencher for the reaction of **1** (0.1 *M*) with **2b** led to a straight linear plot for the above-mentioned relation having, as expected, a slope (2.68 l. mol^{-1}) very similar to that obtained in the absence of a quencher (2.74 l. mol^{-1}) with an intercept of 0.51 (Figure 1). Since the intercept was negligible in the absence of (Q), then eq 3 can be simplified to eq 4. Accordingly, the ratio of k_8/k_{-2} can be determined as

$$\mathbf{4}/\mathbf{3} \simeq \frac{k'_6k_8}{k_2k_4[\mathbf{1}]}[\mathrm{Q}] + \frac{k_{-2}k'_6}{k_2k_4[\mathbf{1}]}[\mathbf{2}] \tag{4}$$

given in eq 5 from the ratio of intercept:slope of the plot of **4**/**3** *vs.* [**2**] at constant [Q]. The value so obtained from the

$$\frac{\text{intercept}}{\text{slope [Q]}} = k_8/k_{-2} \tag{5}$$

above data for the reaction of **2b** with **1** was 9.5. According to eq 4, a plot of **4**/**3** *vs.* [Q] at constant [**1**] and [**2**] should be linear and the ratio k_8/k_{-2} would be given by the slope and intercept interrelation according to eq 6. Figure 2

$$\frac{\text{slope [2]}}{\text{intercept}} = k_8/k_{-2} \tag{6}$$

shows the plot. The value of k_8/k_{-2} from Figure 2 was 10.2, in good agreement with the ratio determined from eq 5.

In an analogous way the ratio of k_8 to the corresponding reaction constant k_{-2} for the propiophenone (**2a**)-benzofuran (**1**) system was determined. The ratio so obtained for this system was 13.5 (Figure 3). These ratios correspond to a ~0.2 kcal/mol higher triplet energy for propiophenone than for acetophenone.[13] The difference in energies so determined is relatively insensitive to the standard deviation in the slope and intercept parameters used in the calculations. The error is estimated to be less than 0.1 kcal/mol.

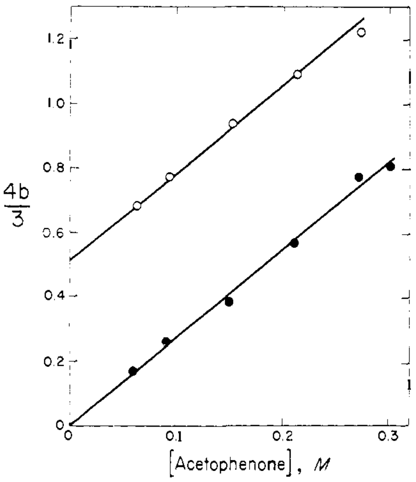


Figure 1. (●) Product ratio of the oxetane **4b** to the benzofuran dimer **3** from the reaction of acetophenone (**2b**) with benzofuran (**1**) (0.1 *M*) in benzene *vs.* the concentration of acetophenone. (○) Same as above for solutions containing a constant amount of naphthalene (0.02 *M*).

The value determined spectroscopically for the difference between these two triplet states in glasses at 77°K, however, is 1.0 kcal/mol.[14] Although there are uncertainties in determining triplet energies from phosphorescence spectra, this method should be fairly accurate (<±0.2 kcal/mol) to determine the difference in triplet energies of very similar compounds such as **2a** and **2b**, measured under the same conditions.

On the other hand, the difference in triplet energies between these two compounds in a rigid matrix at liquid nitrogen temperature might not be the same as that in solution at room temperature.[15] We, therefore, applied the following chemical kinetic approach to obtain a better comparison for the value determined above for the difference in triplet energies in benzene solution. This difference was determined from the equilibrium constant for the reversible energy transfer between **2a***^{3} and **2b***^{3} (k_t/k_{-t}, Scheme III) and from eq 7, which correlates[13] this equilibrium constant

$$\frac{k_t}{k_{-t}} = e^{-\Delta E/RT} \tag{7}$$

with the difference in their triplet energies (ΔE). This equilibrium constant can be determined from the kinetics of competition reactions of **2a***^{3} and **2b***^{3} with the olefin 2-methyl-2-butene (**5**) to give the oxetanes **6a** and **6b**.[18]

On the assumption that rates of the reactions k_t and k_{-t} are much larger than all other rates of decay of the triplet states of the carbonyl compounds, which was found to be the case at the chosen concentrations, it can be shown that the product ratio (**6b**/**6a**)$_{\text{mix}}$ from this reaction mixture at [**2a**] = [**2b**] is given by eq 8. The ratio k_{13}/k_{10} can be determined from the quantum yields[19] of oxetane formation $\phi_{\mathbf{6a}}$ and $\phi_{\mathbf{6b}}$ in separate irradiations of **2a** and **2b** with **5** and the slopes (S_a and S_b) of the Stern-Volmer plots (Figure 4) of

$$\left(\frac{\mathbf{6b}}{\mathbf{6a}}\right)_{\text{mix}} \simeq \frac{k_{13}}{k_{10}}\frac{k_t}{k_{-t}} \tag{8}$$

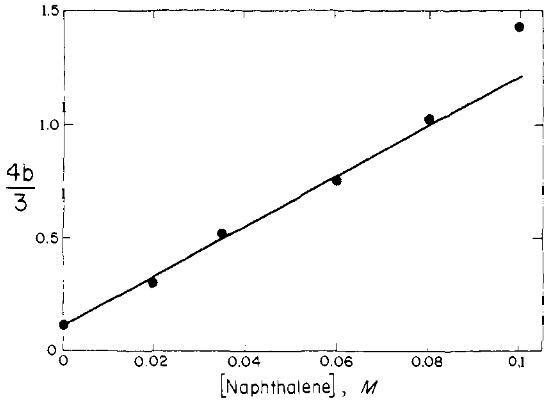
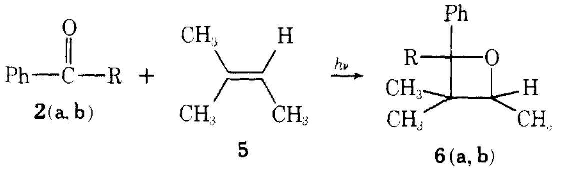


Figure 2. Product ratio of the oxetane **4b** to the benzofuran dimer **3** from the reaction of acetophenone (0.1 *M*) with benzofuran (0.3 *M*) in benzene *vs.* the concentration of added naphthalene.

Scheme III



a, R = C_2H_5
b, R = CH_3

$$2a \xrightarrow{h\nu} \longrightarrow 2a^{*3} \text{ (rate } i_a)^{19}$$
$$2b \xrightarrow{h\nu} \longrightarrow 2b^{*3} \text{ (rate } i_b)$$
$$2a^{*3} + 2b \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} 2a + 2b^{*3}$$
$$2a^{*3} \xrightarrow{k_9} 2a$$
$$2a^{*3} + 5 \xrightarrow{k_{10}} 6a$$
$$2a^{*3} + 5 \xrightarrow{k_{11}} 2a + 5$$
$$2b^{*3} \xrightarrow{k_{12}} 2b$$
$$2b^{*3} + 5 \xrightarrow{k_{13}} 6b$$
$$2b^{*3} + 5 \xrightarrow{k_{14}} 2b + 5$$

the corresponding ϕ_0/ϕ *vs.* the concentration of an added quencher (naphthalene).

$$2a^{*3} + Q \xrightarrow{k_{15}} 2a + Q^{*3}$$
$$2b^{*3} + Q \xrightarrow{k_{16}} 2b + Q^{*3}$$

$$\frac{\phi_{6b}}{\phi_{6a}} = \frac{k_{13}}{k_{10}} \frac{(k_{10} + k_{11})[5] + k_9}{(k_{13} + k_{14})[5] + k_{12}} \tag{9}$$

$$S_a = \frac{k_{15}}{(k_{10} + k_{11})[5] + k_9} \tag{10}$$

$$S_b = \frac{k_{16}}{(k_{13} + k_{14})[5] + k_{12}} \tag{11}$$

Since the triplet energy of naphthalene (60.9 kcal/mol)[14] is considerably lower than that of **2a** and **2b,** k_{15} can be taken as equal to k_{16}. From eq 8–11, eq 12 can be derived. In all

$$\frac{k_t}{k_{-t}} = \left(\frac{6b}{6a}\right)_{mix} \frac{\phi_{6a}}{\phi_{6b}} \frac{S_b}{S_a} \tag{12}$$

these experiments the concentration of methylbutene was kept constant at 0.02 *M*. In the competing reaction [**2a**] = [**2b**] = 0.2 *M* was used; in the separate irradiations the concentration of [**2a**] or [**2b**] was 0.4 *M*. The experimentally determined values were $(\mathbf{6b}/\mathbf{6a})_{mix}$ = 2.45, ϕ_{6a}/ϕ_{6b} = 0.89, S_a = 1900 l. mol^{-1}, and S_b = 900 l. mol^{-1}, which correspond to k_t/k_{-t} = 1.03. According to eq 7 this indicates a negligible difference in triplet energies, *i.e.*, the triplet states of **2a** and **2b** in benzene are practically isoenergetic. This finding is in reasonable agreement with the small difference (0.2 kcal/mol) in energies between these ketones which was implied from the data of the reactions with benzofuran. This points out the consistency of Scheme II.

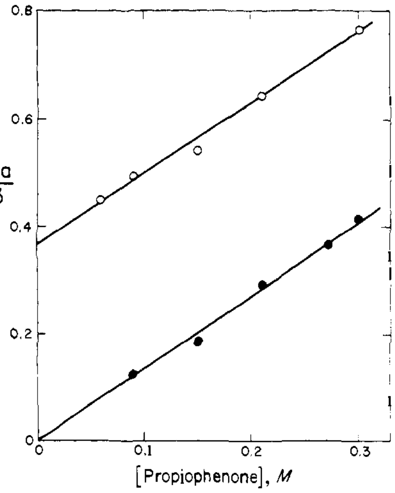


Figure 3. (●) Product ratio of the oxetane **4a** to the benzofuran dimer **3** from the reaction of propiophenone (**2a**) with benzofuran (**1**) (0.1 *M*) in benzene *vs.* the concentration of propiophenone. (○) Same as above for solutions containing a constant amount of naphthalene (0.02 *M*).

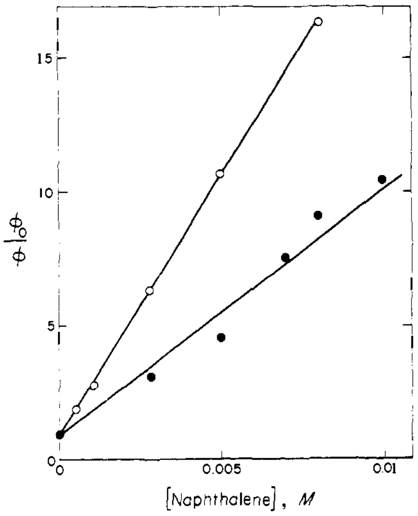


Figure 4. Stern–Volmer plots for the naphthalene quenching of the oxetane formation in the reactions of 2-methyl-2-butene (0.02 *M*) with propiophenone (0.4 *M*) (○), and acetophenone (0.4 *M*) (●).

From the above-determined ratio (9.5) of k_8/k_{-2} for the reaction of acetophenone with benzofuran and the triplet energy (72.6 kcal/mol) of acetophenone, measured in benzene,[21] the energy of the triplet state of benzofuran can be determined using eq 13, which correlates the ratio of k_{diff} to

$$k_{diff}/k_{et} = 1 + e^{-\Delta E/RT} \tag{13}$$

the reaction constant of energy transfer (k_{et}) with the difference in energy between donor and acceptor (ΔE_T).[13]

Although it has been shown[22] recently that even exothermic triplet–triplet energy transfer takes place at a rate two–three times less than diffusion controlled, it has been experimentally demonstrated[23] that the same upper limit for exo-

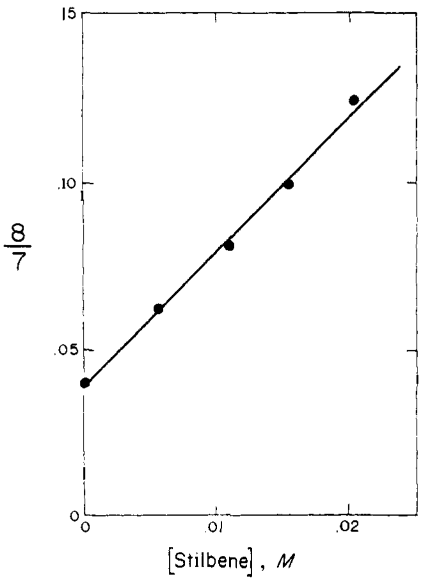


Figure 5. Product ratio of oxetane **8** to dimer **7** from the reaction of 0.166 *M* methyl coumarilate and 0.057 *M* benzophenone in degassed benzene *vs.* the concentration of added stilbene quencher.

thermic energy transfer is reached for widely differing compounds. In eq 13 one might, therefore, replace k_{diff} by k_{lim} (the upper limit for the reaction constant of triplet–triplet energy transfer). Since k_8 can be taken as equal to k_{lim}, then a value of 71.3 kcal/mol for the triplet energy of benzofuran in benzene can be deduced.

The same dependence of product ratio on quencher concentration has been found for methyl coumarilate (methyl benzofuran-2-carboxylate). The photoreaction of methyl coumarilate (**6**) with benzophenone (**2d**), which leads to the dimers (**7**) and the oxetane (**8**), was studied in the presence of a triplet quencher. Irradiation (366 nm) of degassed benzene solutions of **2d** (0.057 *M*), **1a** (0.166 *M*), and varying concentrations of *trans*-stilbene as quencher gave ratios of oxetane to dimers that were dependent on stilbene concentration. These data, which are in agreement with Scheme II, are plotted in Figure 5, from which a slope-to-intercept ratio of 88.5 was obtained. According to eq 6 the ratio of energy transfer from **2d**^{*3} to stilbene to that from **1a**^{*3} to **2d** equals 5. Assuming that the reaction constant for the former process is equal to the upper limit for triplet–triplet energy transfer (k_{lim}), then from eq 13 it can be concluded that the energy transfer from **1a**^{*3} to **2d** is endothermic by 0.8 kcal/mol.

The triplet energy of benzophenone, determined from the phosphorescence spectra in fluid solutions at room temperature, is between 67.6 and 68 kcal/mol.[24] Accordingly, the triplet energy of methyl coumarilate is approximately 67 kcal/mol.

Experimental Section

(A) **Benzofuran Experiments.** Irradiations for small-scale quantitative analyses were conducted with a 200-W PEK super-high-pressure Hg arc, using an Eastman K-18A filter. The reactions were carried out in square quartz cells attached as side arms to glass tubes, which enables degassing the samples by freeze-pump-thaw cycles. After three such cycles using liquid nitrogen and an oil diffusion pump, the tubes were sealed. The irradiation time was chosen so as to obtain product concentrations of 10^{-4} to 5×10^{-4} *M*. The samples were analyzed by gas chromatography using a Hewlett-Packard 7620 instrument equipped with a dual-flame ionization detector. A 5 ft × ⅛ in. stainless steel column packed with 1.5% Dexsil on Chromosorb W was used. Under these conditions (180° isothermal), the two dimers of benzofuran do not separate.

The absorption spectra were measured with a Cary Model 15 spectrophotometer and the nmr spectra on a Varian T-60 instrument. All liquid chemicals were passed through Al_2O_3 columns and were freshly distilled.

(1) **Photoaddition of Acetophenone to Benzofuran.** A solution of 20 g of acetophenone and 5 g of benzofuran in 100 ml of benzene was irradiated for 90 hr inside a Rayonet RPR-100 photoreactor equipped with 3500 Å bulbs through a filter solution No. 9 after Rappoldt.[25] Gas chromatograph analysis indicated the formation of the benzofuran dimers and the oxetane **4b** in the ratio ~1:1. The solvent was removed in a rotary evaporator and the residue was distilled at 50° under 0.1 Torr of pressure to remove the unreacted materials. The residue was chromatographed on a 50-cm column of basic alumina (deactivated with 1.5% water) using cyclohexane as eluent. Analysis of the fractions (50 ml each) by nmr showed the minor benzofuran dimer followed by the major dimer (anti head-to-head) in the first 13 fractions. The acetophenone-benzofuran adduct (**4b**) was eluted in fractions 18 to 22. Recrystallization from methanol-water yielded colorless crystals: mp 86–88°, mass spectrum *m/e* (rel intensity) 238 (11) (M^+), 210 (4), 209 (5), 195 (12), 181 (3), 167 (6), 165 (6), 118 (100) (benzofuran$^+$).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.3; H, 6.1.

(2) **Photoaddition of Propiophenone to Benzofuran.** This reaction was conducted in the same way as described above. The oxetane **4a** had a mp 89–92°; mass spectrum *m/e* (rel intensity) 252 (2) (M^+), 224 (2), 223 (2), 195 (8), 167 (4), 165 (4), 118 (100) (benzofuran$^+$).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.6; H, 6.6.

(B) **Methyl Coumarilate Experiments.** The ketones and the methyl coumarilate used in these experiments were recrystallized and/or distilled until a 1-cm thick layer of the melt was free from visible absorption (water white). Irradiations were done in 13-mm Pyrex test tubes that had been degassed by three freeze-thaw cycles at 10^{-4} Torr. The lamp used was a 450-W Hanovia medium-pressure arc filtered by Corning 7-60 filters. The tubes were held in a rotating turntable to assure equal radiation doses. After irradiation the samples were analyzed by flame ionization gas chromatography using a 1 ft × ¼ in. column packed with silicon oil on firebrick at a temperature of 210°.

The details of the product isolation and identification have already been reported.[8]

References and Notes

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(6) Exact analysis of the AA′BB′ spectrum of the cyclobutane protons of the major dimer of benzofuran led to the following coupling constants: $J_{AB} = 7.05$, $J_{A'B} = -0.85$, $J_{AA'} = 1.73$, and $J_{BB'} = 2.33$ Hz, which confirms the assigned[5] anti head-to-head structure of this dimer.
(7) The stereochemistry of the oxetane **4a** was deduced from the nmr spectrum ($CDCl_3$): τ 3.58 (d, $J = 4.5$ Hz, 1, –OCHO–), 5.65 (d, $J = 4.5$ Hz, broadening due to coupling with aromatic protons, 1, >CH–), 8.42 (q, $J = 7.3$ Hz, 2, CH_2), 9.48 (t, $J = 7.3$ Hz, 3, CH_3). The strong upfield shift of the CH_3 group can only be explained if the ethyl group in this compound lies in the shielding envelope of the benzene ring of the benzofuran moiety; *i.e.*, these two groups are in syn positions. The oxetane **4b** shows a very similar nmr spectrum ($CDCl_3$): τ 3.53 (d, $J = 4.5$ Hz, 1, –OCHO–), 5.66 (d, $J = 4.5$ Hz, 1, CH–), 9.65 (s, 3, CH_3). This may indicate that compounds **4a** and **4b** have the same stereochemistry.
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(15) In fact it has been shown[16] that the triplet energies of butyrophenone

and acetophenone at 77°K are 74.5 and 73.6 kcal/mol, respectively, whereas in benzene at room temperature they were found to be 72.0 and 72.6 kcal/mol, respectively, which shows that under the latter conditions the triplet energy of butyrophenone is even *lower* than that of acetophenone. Furthermore, it was observed[17] that in rigid matrices propiophenone and higher homologs of alkyl phenyl ketones exhibit two emissions ("dual phosphorescence") in varying ratios depending mainly on the viscosity of the glassy solvent. The higher energy ("anomalous") emission has been attributed[17] to a torsional distortion of the triplet molecule and to hindrance to conformational change in the rigid glass.

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(19) The intersystem crossing efficiency of both **2a** and **2b** is reported[20] to be unity. We confirmed that both compounds have the same triplet yields as monitored by the relative quantum yields of isomerization of *trans*-stilbene sensitized by these compounds.

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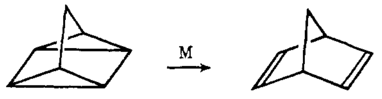
Nickel(0)-Catalyzed Reaction of Quadricyclane with Electron-Deficient Olefins[1]

R. Noyori,* I. Umeda, H. Kawauchi, and H. Takaya

Contribution from the Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan. *Received July 5, 1974*

Abstract: Quadricyclane (**1**) upon treatment with a catalytic amount of nickel(0) complexes isomerizes in a $[_{\sigma}2 + _{\sigma}2]$ fashion to yield norbornadiene (**2**). The reactive intermediate can be trapped intermolecularly, in a formal sense, by activated olefins such as acrylonitrile or acrylic acid esters, giving the adducts, endo- and exo-8-substituted tetracyclo[$4.3.0.0^{2,4}.0^{3,7}$]nonanes **7** and **8**. Methyl α,*cis*-β-dideuterioacrylate enters into the catalytic cycloaddition stereospecifically with retention of configuration. The course of the reaction is formally viewed as a $[_{\sigma}2_s + _{\pi}2_s]$ process and lies in marked contrast with the corresponding uncatalyzed reaction which leads to the $[_{\sigma}2 + _{\sigma}2 + _{\pi}2]$ cycloaddition products, tricyclo[$4.2.1.0^{2,5}$]non-7-enes. Comparative studies on the catalytic reactions of **1** and **2** with acrylates lead to conclusions that (1) **2** reacts with acrylates at a much lower rate than **1**, (2) the presence of **2** results in lowering of the rate of both the isomerization **1** → **2** and the cycloaddition of **1** with olefins giving **7** and **8**, and (3) the product distribution of the cycloaddition (**7**:**8** ratio) does not depend on whether the starting hydrocarbon is **1** or **2** but solely on the reaction conditions. These findings suggest both reactions involve a common intermediate(s) in the product-determining step.

Under the influence of transition metal complexes, strained carbon–carbon σ bonds are activated under mild reaction conditions and undergo characteristic transformations.[2] Quadricyclane (**1**) is a molecule which received early attention in this area. Thermal isomerization of the hydrocarbon to norbornadiene (**2**) proceeds only slowly ($t_{1/2} > 14$ hr at 140°)[3] despite the extraordinarily high strain energy (total 78.7 kcal/mol)[4] which can be released through the isomerization. The remarkable thermal stability of **1** should reflect the fact that the cyclobutane–diolefin transformation, though energetically favorable, is restricted by the orbital symmetry conservation rules.[5] Upon addition of Rh(I) complexes, however, it undergoes the $[_{\sigma}2 + _{\sigma}2]$ valence isomerization very facilely even at low temperature;[6] the presence of 2 mol % of di-μ-chloro-bis(norbornadiene)dirhodium is known to accelerate the reaction by a factor of 10^{19} ($t_{1/2}$ of **1** in 0.7 *M* $CHCl_3$ solution 45 min at −26°).[6a] Pd(II)[6a] and Ag(I)[6c] also catalyze the isomerization.[7] The apparent removal of the symmetry constraints had attracted much theoretical interest, and Pettit, Mango, and Schachtschneider interpreted the phenomenon in terms of the concerted mechanism involving interaction between the strained σ bonds and appropriate d orbitals of the transition metals which may conserve the molecular orbital symmetry throughout the skeletal change.[8] Later Cassar and Halpern isolated the stable acylrhodium complex **3** derived from a stoichiometric reaction of **1** and di-μ-chloro-tetracarbonyldirhodium(I) and suggested the stepwise mechanism involving the Rh(III) intermediate **4** for the catalytic transformation **1** → **2**.[9] Similar nonconcerted processes involving the oxidative addition mechanism have been advanced for the catalyses of other strained hydrocarbon systems.[2a,b,10] Thus the mechanistic implication of the concertedness incipiently postulated[8] is losing its importance or at least would have to be reexamined.[11] In any event, however, transition metal complexes do promote various processes which are not easily attainable because of the orbital-symmetry restrictions. Of numerous metal catalysts so far investigated, only Ni(0) complexes could catalyze the intermolecular cycloadditions involving carbon–carbon σ bonds effectively. Equations 1–3 illustrate examples of the coupling reactions of certain strained hydrocarbons with electron-deficient olefins (Z = CN, $COOCH_3$, etc.). The catalyses with other transition metal complexes, with few exceptions,[15,16] have been limit-



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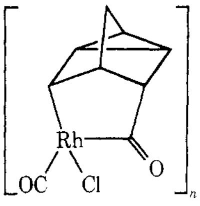

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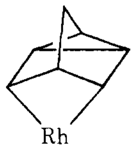

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