phenyllithium, 1076-44-4; $\alpha$-naphthylmethyl-(−)-menthoxychlorosilane, 37787-19-2; (+)-$\alpha$-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, 37787-20-5; (−)-$\alpha$-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, 37787-21-6; (+)-$\alpha$-naphthylmethylpentafluorophenylsilane, 36411-23-1; (+)-$\alpha$-naphthylphenylmethylpentafluorophenylsilane, 37781-10-5; (+)-phenylmethylpentafluorophenylsilane, 36358-49-3.

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# Photochemistry of 2-Acetylbenzonorbornenes

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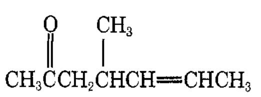
*Received July 12, 1972*

The synthesis and photochemistry of *exo*- and *endo*-2-acetylbenzonorbornenes (8 and 9) is described. The exo isomer yields benzonorbornene upon irradiation at 310 nm, conditions under which the endo isomer is inert.

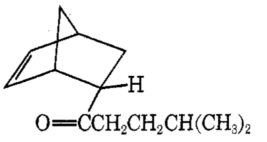
The presence of proximate n electrons is known to significantly modify the reactivity of photoexcited carbonyl groups. Examples include reactions of amino ketones,[1,2] alkoxy ketones,[3] and thiaketones.[4] In one of these studies,[2] the magnitude of the effect was shown to be a function of the distance between the interacting centers.

Similarly, the presence of $\pi$ electrons can modify the excited-state behavior of ketones. Thus, neither ketone **4** or **5** undergoes appreciable type II photoelimination.[4,5] Rapid exciplex formation between the carbonyl singlet state and the double bond has been postulated to rationalize the diminished reactivities. In a related study, Cowan and Baum[6] have shown that intramolecular energy transfer was the principal mode of deactivation of the carbonyl triplets in systems **6a–c.**

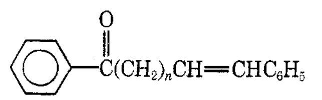


$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH{=}CHCH_3$

**4**

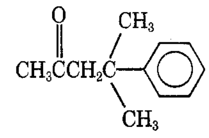


**5**



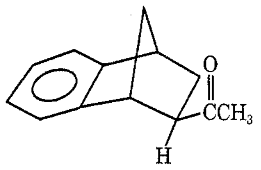
**6a**, $n = 2$
**b**, $n = 3$
**c**, $n = 4$

Lastly, several groups[7,8] have recently reported on the diminished reactivity of certain $\alpha$- and $\beta$-phenyl ketones toward photoreduction and/or type II eliminations. Thus, ketone **7** undergoes photoelimination with unusually low efficiency, $\Phi = 0.02$.[8]

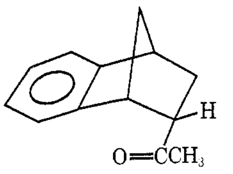


**7**

The foregoing results may be summarized with the statement that the presence of electrons in n or $\pi$ orbitals significantly shortens the excited state lifetimes of nearby carbonyl groups. Although varied mechanisms may prevail, a common feature would appear to require significant overlap of the orbitals on the two interacting groups. In view of the fact that this orientational factor has not been tested, we wished to investigate the behavior of rigid analogs of **7** in which the relative positions of the two functions were more restricted. To this end, we synthesized *exo*- and *endo*-2-acetylbenzonorbornenes (**8** and **9**, respectively), and initiated photochemical studies which were designed to evaluate their relative excited state lifetimes.

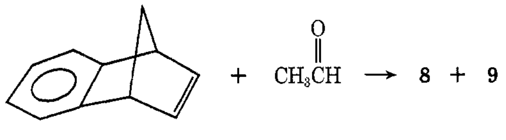


**8**



**9**

**Syntheses.**—A mixture of **8** and **9** was produced by the addition of acetaldehyde to benzonorbornadiene (**10**) as catalyzed by azobisisobutyronitrile.[9] By analogy with norbornene,[9] it was assumed that the major product (*ca.* 90%) was the exo isomer and this supposition was supported by spectral evidence presented below. For example, the chemical shifts of the methyl protons in the two isomers were found in the expected relative positions ($\delta$ 2.15 and 1.87 for **8** and **9**, respectively) if it is assumed that the



**10**

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[1] A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **93**, 6998 (1971).

[2] P. J. Wagner and T. Jellinek, *ibid.*, **93**, 7328 (1971).

[3] F. D. Lewis and N. J. Turro, *ibid.*, **92**, 311 (1970).

[4] A. Padwa and A. Battisti, *ibid.*, **94**, 521 (1972).

[5] S. R. Kurowski and H. Morrison, *ibid.*, **94**, 507 (1972); R. R. Sauers, A. D. Rousseau, and B. Byrne, Abstracts, XXIIIrd IUPAC Meeting, Boston, Mass., July 1971, p 96.

[6] D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 1153 (1971); see also P. A. Leermakers, J.-P. Montillier, and D. R. Rauh, *Mol. Photochem.*, **1**, 57 (1969).

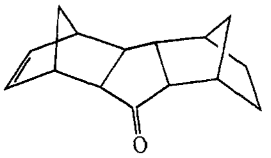
[7] P. J. Wagner and P. A. Kelso, *Tetrahedron Lett.*, 4151 (1969); R. A. Caldwell and P. M. Fink, *ibid.*, 2987 (1969).

[8] D. G. Whitten and W. E. Punch, *Mol. Photochem.*, **2**, 77 (1970); P. J. Wagner, P. A. Kelso, A. E. Kemppainen, A. Haug, and D. R. Graber, *ibid.*, **2**, 81 (1970); F. R. Stermitz, D. E. Nicodem, V. P. Muralidharan, and C. M. O'Donnell, *ibid.*, **2**, 87 (1970).

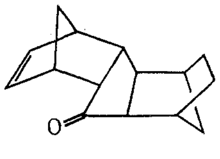
[9] H. Stockmann, *J. Org. Chem.*, **29**, 245 (1964).

methyl group of **9** resides at least part of the time in the shielding cone of the phenyl ring.[10]

The finding that the compound assigned the exo structure showed an enhanced ultraviolet absorption for the n,$\pi^*$ transition ($\epsilon_{293}^{\max}$ 77) relative to the endo system ($\epsilon_{293}^{\max}$ 28) may be taken as further proof of the stereochemistry of **8** and **9**. As a literature analogy, the following example is illustrative.[11]



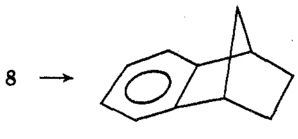
$\epsilon_{307}^{\max}$ 79



$\epsilon_{303}^{\max}$ 27.5

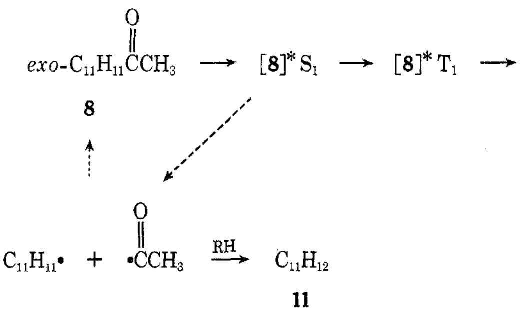
## Results and Discussion

Irradiation of the exo isomer **8** in benzene with Pyrex-filtered light ($\lambda > 290$ nm) or in cyclohexane with short-wavelength light (254 nm) produced one major volatile product and several very minor ones. The major product was isolated by preparative gas chromatography and shown by spectral comparisons to be benzonorbornene (**11**). Quantum yields were determined in degassed benzene at 313 nm: $\Phi_{11} = 0.015$, $\Phi_{-K} = 0.018$. Similar irradiations of **9** for extended periods yielded no significant amounts of volatile products and led to a very slow loss of starting material. Intersystem crossing yields[12] for **8** and **9** were 0.83 and 0.20, respectively.



**11**

Quenching studies were carried out using *cis*-cyclooctene[13] (0.1 *M*) and either 0.1 *M* or 0.01 *M* ketone. In both cases, the rate of production of **11** from **8** decreased by *ca.* 43%. We interpret these results to mean that most of the reaction proceeds *via* triplet states.[14] The following scheme is proposed to rationalize our results. The low quantum yield for the formation of **11** and the near equivalency of the efficiency of formation of **11** *vs.* the loss of **8** requires an efficient deactivation step. The most likely possibility is recombination of the radical pair.[15] The nature of the hydrogen donor (RH) in this reaction is unknown. It seems unlikely that the solvents or impurities in them play this role, since few by-products, *e.g.*, bicyclohexyl, could be found in the cyclohexane photolyses. One intriguing possibility is that the radical pair disproportionates to give **11** and ketene. The latter would have been too volatile to detect by our analytical procedures. Although this mode of disproportionation is not normally observed in type I cleavage products,[16] it may be that the normal reaction is inhibited as a consequence of the unusually high degree of strain associated with norbornene double bond formation.[17]



$$exo\text{-}C_{11}H_{11}\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow [8]^*S_1 \longrightarrow [8]^*T_1 \longrightarrow$$

$$C_{11}H_{11}\cdot + \cdot\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{RH} C_{11}H_{12}$$

In contrast to the behavior of **8**, the endo ketone **9** proved to be quite stable toward irradiation at 310 nm. This observation and the lower intersystem crossing yield obtained for **9** are indications that the carbonyl triplet state is less efficiently formed and/or has a shorter lifetime than that in **8**. We cannot say whether or not the exo system itself behaves entirely normally, but there was no obvious manifestation of any behavior which could be related to the anomalous absorption of **8**, with the possible exception of the somewhat high intersystem crossing yield compared to **7** (0.15).

In any event, we wish to emphasize that the *differences* in behavior between **8** and **9** clearly require an explanation which takes into account their relative geometries. Thus, the anomalous absorption of **8** is associated with the exo configuration,[11] while the diminished reactivity of **9** is associated with the endo structure. We assume that direct interaction of the n orbital of oxygen with the $\pi$ system is a requisite feature of whatever mechanism is responsible for the rapid deactivation of the excited carbonyl groups of these[8] $\beta$-phenyl ketones.

## Experimental Section

Nuclear magnetic resonance (nmr) data was obtained from a Varian Model T-60 spectrometer in carbon tetrachloride solution using tetramethylsilane as an internal standard. Infrared (ir) spectra were determined on thin films using a Perkin-Elmer Model 137 spectrometer. Ultraviolet (uv) spectra was recorded on a Cary 14 spectrometer. Gas chromatograms (gc) were obtained on either a Varian Aerograph Model A-90-P or a Barber-Colman Model 5000 chromatograph. The following three columns were used: A, 15% FFAP (5 ft × 0.25 in.); B, 20% FFAP (8 ft × 0.25 in.); C, 15% $\beta,\beta'$-oxydipropionitrile (20 ft × 0.25 in.). Chromosorb G was the solid phase in all cases.

Benzene was purified by washing with portions of sulfuric acid until no coloration developed. The benzene was then washed with water, 10% sodium carbonate solution, and water. After drying over anhydrous calcium chloride the benzene was distilled and stored over calcium chloride.

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(10) A similar, but smaller, difference has been found for the analogous protons in the 5-norbornenyl methyl ketones: $\delta_{CH_3}^{exo}$ 2.12; $\delta_{CH_3}^{endo}$ 2.00. See Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, **92**, 6548 (1970), for other examples.

(11) R. C. Cookson, J. Henstock, and J. Hudec, *ibid.*, **88**, 1059 (1966); 5-norbornenyl methyl ketones also show this trend.

(12) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(13) It has been shown that acetone triplets react with *cis*-cyclooctene with a rate constant of $1.3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$; see K. Shima, Y. Sakai, and H. Sakuri, *Bull. Chem. Soc. Jap.*, **44**, 215 (1971).

(14) This analysis is based on the assumption of a normal rate of intersystem crossing, *ca.* $2\text{-}5 \times 10^8\ \text{sec}^{-1}$, and similar rates of reaction of singlets and triplets with the olefin.[13] For references see N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).

(15) For a recent demonstration of this process in aliphatic systems, see J. A. Den Hollander, R. Kaptein, and P. A. T. M. Brand, *Chem. Phys. Lett.*, **10**, 430 (1971).

(16) For recent references see ref 15 and N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, **90**, 504 (1968); M. Tomkiewicz, A. Groen, and M. Cocivera, *Chem. Phys. Lett.*, **10**, 39 (1971).

(17) R. D. Miller and V. Y. Abraitys, *J. Amer. Chem. Soc.*, **94**, 663 (1972). It is significant that we could not detect any buildup of **10** during the photolysis. This finding rules out formation–destruction of **10** as an explanation for its absence.

Benzonorbornadiene (**10**) was prepared by the method of Wittig and Knauss.[18]

*exo,endo*-**2-Acetylbenzonorbornene (8, 9).**—A mixture of 3.0 g (0.021 mol) of benzonorbornadiene, 6.0 g (0.136 mol) of freshly distilled acetaldehyde, and 150 mg (0.0011 mol) of azobisisobutyronitrile was heated at 80° in a pressure tube for 43 hr. The resulting mixture was distilled at 96–98° (0.6 mm) to yield 1.51 g (39%) of a mixture of **8** and **9**. Gc analysis (A, 200°) revealed two components in a 10:1 ratio. The separate isomers were collected by preparative gc (B, 200°).

The structure assigned to the major component was that of *exo*-2-acetylbenzonorbornene (**8**): nmr $\delta$ 7.02 (m, 4 H), 3.42 (m, 2 H), 2.15 (s, $CH_3$), 1.82 (m, 5 H); ir 5.84 (C=O) and 13.36 $\mu$ (*o*-ArH); uv max (cyclohexane) 293 nm ($\epsilon$ 77), 272 (1104), 266 (1037), and 259 (684); mass spectrum (70 eV) molecular ion at *m/e* 186.

*Anal.* Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.05; H, 7.88.

The structure assigned to the minor component was that of *endo*-2-acetylbenzonorbornene (**9**): nmr $\delta$ 7.03 (m, 4 H), 3.58 (m, 1 H), 3.32 (m, 1 H), 3.07 (m, 1 H), 1.87 (s, $CH_3$), 1.82 (m, 4 H); ir 5.84 (C=O) and 13.27 $\mu$ (*o*-ArH); uv max (cyclohexane) 293 nm ($\epsilon$ 28), 272 (958), 264 (844), 258 (538); mass spectrum molecular ion at *m/e* 186.

*Anal.* Found: C, 84.25; H, 7.50.

**Photolysis Apparatus.**—Preparative-scale irradiations were carried out in a Rayonet photoreactor[19] using either the 3000-Å or the 2537-Å sources. From the literature supplied by the manufacturer it may be calculated that, of the irradiation emitted between 2537 and 3129 Å, *ca.* 72% appears between 2537 and 2652 Å and 28% appears between 2804 and 3129 Å. Quantum yields were determined on an optical bench using an Osram 200W super-pressure mercury arc and a 5-cm quartz cell containing 0.00139 *M* aqueous potassium chromate solution buffered with 1% potassium carbonate. This filter solution used in conjunction with 13 × 100 mm Pyrex test tubes served to isolate the 310-nm line.

**Irradiations of 8.** **A.**—A benzene solution of **8** (0.181 g in 10 ml) was flushed with nitrogen and irradiated for 19 hr with the 3000-Å source. Preparative gc (B, 217°) yielded 0.119 g of recovered starting material whose ir spectrum was unchanged. Also isolated was 5.3 mg of benzonorbornene (**11**), which was identified by its ir spectrum by direct comparison.[20]

**B.**—In a second experiment, 0.0984 g of **8** in 5 ml of cyclohexane was purged with nitrogen and irradiated in a quartz nmr tube with the 2537-Å source. The reaction was monitored periodically by gc (A, 200°). A gradual accumulation of **11** and two other very minor photoproducts with similar retention times was observed. Since the gc conditions used were capable of effecting separation of **11** and **10**, it can also be noted that essentially no **10** was formed at any time. In addition, no bicyclohexyl could be detected. Although small amounts of **9** did appear, it was not established that its formation was the direct result of the irradiation as opposed to a chemically catalyzed route.

**C.**—The quantum yield for the formation of **11** was determined by use of octadecane (0.0053 *M*) as an internal standard. A benzene solution of **8** (0.101 *M*) and the standard in duplicate 13 × 100 mm Pyrex test tubes was degassed by four freeze–thaw cycles and sealed under vacuum (*ca.* 5 × $10^{-4}$ Torr). The light intensity was monitored by benzophenone-sensitized isomerization of *cis*-piperylene.[21] The quantum yield for appearance of **11** was 0.018 after 180 min of irradiation and 0.015 after 335 min. The quantum yield of disappearance of **8** was 0.018 after 335 min, at which time 5% of the starting material had disappeared.

**D.**—The following cyclohexane solutions were prepared and irradiated at 2537 Å in standard 10-mm quartz cells by means of a rotating cell holder which was suspended in the Rayonet reactor: A, 0.10 *M* **8**, 0.043 *M* octadecane; B, 0.010 *M* **8**, 0.0043 *M* octadecane; C, 0.10 *M* **8**, 0.10 *M* *cis*-cyclooctene, 0.016 *M* octadecane; D, 0.010 *M* **8**, 0.016 *M* octadecane, and 0.10 *M* *cis*-cyclooctene. Solutions A and B were irradiated together for 200 min. Solutions C and D were subsequently irradiated for 210 min. After irradiation, the solutions were analyzed by gc (A, 180°) with the following results expressed in terms of molarity of **11**: A, 0.0047; B, 0.0030; C, 0.0027; D, 0.0017.

**Irradiation of 9.** **A.**—A solution of **9** (0.0768 *M*) in benzene was degassed and irradiated as in C above. After 210 min the concentration of **9** was measured against octadecane (0.0405 *M*) and found to be 0.0798 ± 0.004 *M*. Essentially no **11** was detected.

**B.**—The same solution was irradiated for 67 hr at 3000 Å in the Rayonet reactor with similar results. Likewise, irradiation of this solution with the 2537-Å source produced no significant changes.

**Intersystem Crossing Yields.**—A benzene solution of **9** was prepared which contained 0.5 *M* freshly distilled *cis*-piperylene and 0.0898 *M* ketone. After 60-min irradiation on the optical bench the per cent conversion to *trans*-piperylene was 8.7 from which $\phi_T$ was calculated to be 0.83.

Similarly, a solution of **8** (0.0885 *M*) was irradiated for 305 min with a 10.6% conversion to *trans*-piperylene. The calculated $\phi_T$ was 0.20.

**Registry No.**—**8**, 23537-82-8; **9**, 37614-83-8; **10**, 236-73-7; acetaldehyde, 75-07-0.

**Acknowledgments.**—We wish to acknowledge the financial support of the National Science Foundation (GP 26371) and the NDEA Title IV Fellowship Program.

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[18] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[19] Available from the Southern New England Ultraviolet Co., Middletown, Conn.

[20] The authentic sample was prepared by catalytic reduction of benzonorbornadiene; see P. Bruck, *Tetrahedron Lett.*, **No. 10**, 449 (1962).

[21] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).