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Photochemistry of Polycyclic 5-Acylnorbornenes[1]

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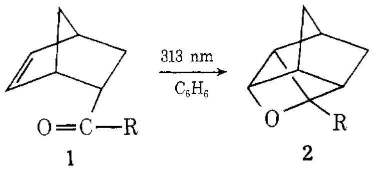
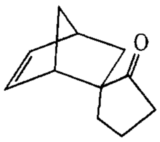
Ketones **3X**, **3N**, **4X**, and **4N** were synthesized and irradiated with ultraviolet light. Compounds **3X** and **3N** gave products, enal **6** and oxetane **5**, respectively, which are believed to have been formed from n,π^* states of the carbonyl groups. Ketones **4X** and **4N** gave products, **8** and **7**, respectively, which were probably formed from π,π^* states of the double bonds.

Earlier studies of the photochemistry of simple *endo*-5-acylnorbornenes[2,3] (**1**) have revealed a photocycloaddition reaction of significant synthetic versatility as well as one which involves intriguing mechanistic subtleties. It has been shown[4] that oxetanes of structure **2** are formed from **1** with quantum efficiencies ranging from 0.10 to 0.22 and that essentially no other products are produced. In particular, type I and type II cleavages were not competitive even in favorable cases, *e.g.*, R = t-C_4H_9, i-C_5H_{11}.[4] Preliminary studies with *exo*-5-acylnorbornenes did not yield well-defined product mixtures, on the other hand. Thus, these results raised several questions concerning the factors which control the efficiency of oxetane formation and the general structural limitations of this reaction. In addition, the behavior of the exo systems was perplexing and a more detailed investigation was clearly of interest in view of the paucity of data on the behavior of constrained γ,δ-unsaturated ketones.[5]

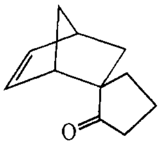


1 2

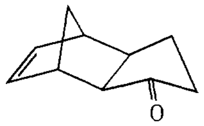
To these ends, an investigation of the synthesis and photochemistry of the following four ketones was initiated: **3X**, **3N**, **4X**, and **4N**.



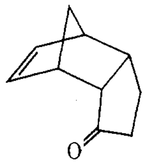
3X



3N

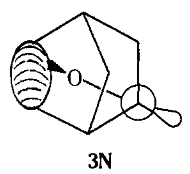


4X

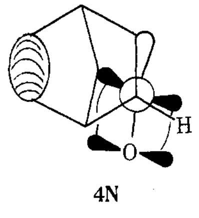


4N

The choice of these systems was governed by the relatively fixed geometrical orientations of the chromophores. From the drawings shown below, it can be seen that only in **3N** is the n orbital of the carbonyl group suitably positioned with respect to the double bond to permit the mode of interaction proposed for exciplex formation in the



3N



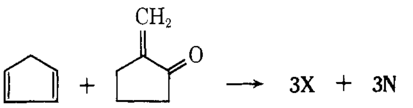
4N

oxetane reaction.[6] On the other hand, the situation in **4N** is such that only the π orbitals of the carbonyl group can interact with the double bond. The behavior of the two exo isomers **3X** and **4X** was of intrinsic interest (see above) in the realm of photochemistry of unsaturated carbonyl systems and it was instructive to use them as model systems for the corresponding endo systems.

We report here the major chemical consequences of irradiations of these four ketones, and assign some tentative mechanistic schemes to rationalize the observed products.

Results

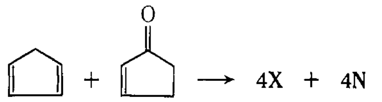
Syntheses. The spiro ketones **3X** and **3N** were conveniently prepared as a 10:1 mixture by the reaction of cyclopentadiene with the Mannich base of cyclopentanone.[7] Presumably, this reaction involves the intermediacy of α-methylenecyclopentanone, which undergoes a Diels–Alder reaction with the diene (eq 1). In agreement with recent



(1)

studies of the stereochemistry of Diels–Alder reactions of methylated dienophiles,[8] we assign the endo stereochemistry to the minor isomer **3N**. Our structural assignment was also based on nmr data which pertains to the chemical shifts of the 3-endo protons in these isomers. This proton in the exo isomer **3X** appeared as a four-line multiplet centered at δ 0.80. The larger coupling (J = 10.7 Hz) is attributed to geminal splitting and the smaller one (J = 2.8 Hz) is the result of long-range coupling with the anti C-7 proton.[9] The origin of the upfield shift of this proton has been attributed[9] to the anisotropy of the carbon–carbon bond at C-2.[10]

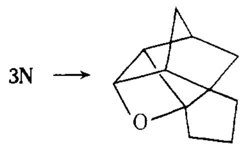
Similarly, the ketones **4X** and **4N** were obtained *via* a Diels–Alder reaction between 2-cyclopentenone and cyclopentadiene (eq 2). It was advantageous to use aluminum



(2)

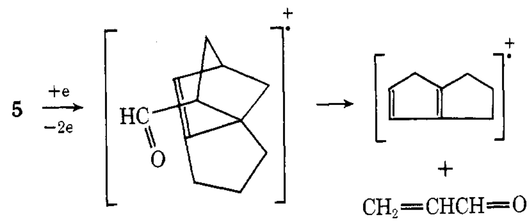
chloride as a catalyst in this sequence, since the yield was doubled under milder reaction conditions.[11] The predominant isomer (80%) was identified as the endo ketone (**4N**) by spectral comparisons with data from an authentic sample.[12]

Irradiations. All four ketones were irradiated in deoxygenated benzene with Pyrex-filtered light. Two volatile products in the ratio 98:2 were produced from **3N**. The major component showed no hydroxyl or carbonyl absorptions in the infrared region and no nmr absorptions below δ 4.48. The latter absorption appeared as a one-proton doublet of doublets and is typical[2] of oxetanes of structure **2**. In view of the earlier precedent, structure **5** is assigned to this photoproduct. Further evidence in support of this



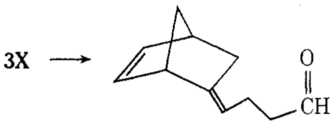
5

assignment was deduced from the mass spectral cracking pattern of **5**. The base peak at m/e 106 corresponds to the molecular ion less the elements of acrolein. The breakdown may be rationalized in terms of oxetane cleavage followed by a reverse Diels–Alder reaction[13] (eq 3).



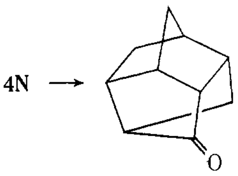
(3)

Compound **3X** led to a five-component product mixture, two components of which were shown to be **3N** (6.5%) and **5** (17%). The other two minor products totaled 5% and were not examined. The major product (72%) displayed absorptions attributable to aldehydic and olefinic groups in both the nmr and ir spectra. This data, the microanalytical results, and the mass spectrum all support the enal structure **6** for this product.



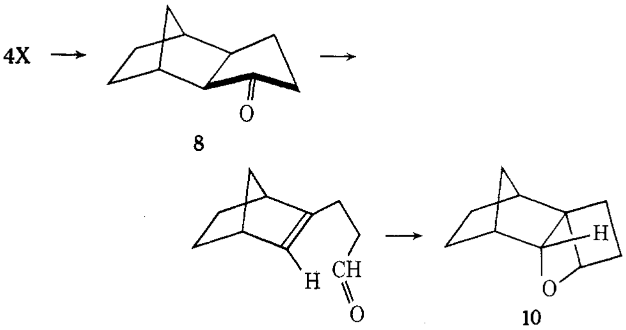
6

Irradiation of **4N** gave a product which was neither an oxetane nor an enal as evidenced by the absence of unsaturation and the presence of a carbonyl group at 5.67 μ. Attempts to define the structure of this compound by various chemical and spectral means failed to point to an unambiguous answer. The crystalline 2,4-dinitrophenylhydrazone derivative was therefore subjected to X-ray crystallographic analysis.[14] This procedure led only to structure **7**, a finding which is consistent with all other data.



7

The last ketone to be studied, **4X**, was found to produce as many as nine products upon irradiation in benzene. Since isolation and identification of these products did not appear feasible, other conditions were examined. Irradiation in methanol proceeded more cleanly to produce one major product which was further degraded on longer irradiation. The initial photoproduct was isolated and identified as the saturated ketone **8** and the degradation products as **9** and **10**. This overall sequence (**8** → **9** → **10**) had been observed in an earlier study[15] and was confirmed in this work.



8

9

10

Discussion

The notable features of these results may be best appreciated by comparisons of behavior within the two main structural and stereochemical groups, *i.e.*, **3X** *vs.* **3N**, **3X**

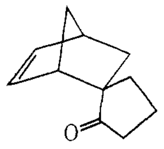
Table I
Quantum Yield and Quenching Data for 4N → 7

Determination	4N, *M*	Norbornene, *M*	ϕ^a
Consumption of 4N	0.139	0	0.26 ± 0.03
	0.139	1.445	0.20 ± 0.02
Formation of 7	0.139	0	0.095 ± 0.005
	0.139	1.445	0.026 ± 0.003
Formation of exo,-trans,endo dimer of norbornene^b	0.139	1.445	0.009 ± 0.002

^{a} Conversions varied from 9 to 14%. ^{b} Other dimers were formed to a minor extent.

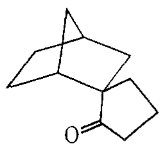
vs. **4X**, etc. In this way the influence of the effect of structure and stereochemistry on the photoreactions may be assessed.

Thus, in the exo, endo pair **3X**, **3N**, it is clear that the proximity and accessibility of the double bond is the decisive factor which diverts the endo ketone away from type I cleavage. Since the efficiency of oxetane formation (0.21) equaled that of ketone loss, it is concluded that rapid exciplex formation[6,16] followed by oxetane formation and radiationless decay account for the fate of most of the excited state(s) of **3N**.[6,16] It is pertinent to note that the absorption spectrum of **3N** exhibits an enhanced intensity characteristic of systems in which the n orbital interacts with the π system.[17] Interestingly, the n → π^* absorption of the exo isomer **3X** also shows enhanced intensity and a red shift. These chromophores have a relative geometry which is ideally suited for σ coupling as defined by Cookson and coworkers.[18] Although the overall course of the reaction **3X** → **6** is not abnormal, the consequences of σ interactions may not be apparent until one takes into account all of the parameters which define excited-state behavior.



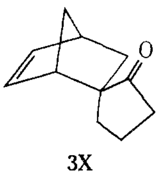
3N

λ_{max} (C_6H_{12}) 307 nm
(ϵ 54.4)



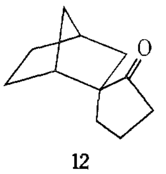
11

λ_{max} (C_6H_{12}) 302 nm
(ϵ 27.4)



3X

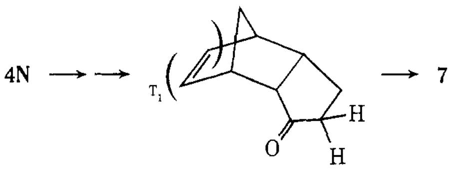
λ_{max} (C_6H_{12})
301, 215 nm (sh)
(ϵ 55, 3200)



12

λ_{max} (C_6H_{12})
300 nm
(ϵ 26.9)

Neither of the fused ketones **4X** and **4N** undergoes reactions typical of cyclopentanones, *e.g.*, type I cleavage or photoreduction, in contrast to the behavior of the saturated analogs.[15] The observed reactions both involved reduction of the double bond, a process which is characteristic of π,π^* states of strained olefins.[19] In these systems a likely sequence of events would entail energy transfer steps from the T_1 state of the excited carbonyl groups to the ground-state olefins.[20] There is precedent in both cases for the requisite subsequent processes. Thus, the triplet olefin in **4N** could undergo intramolecular abstraction followed by cyclization (eq 4) in a fashion analogous to that observed by Scharf[21] (eq 5).



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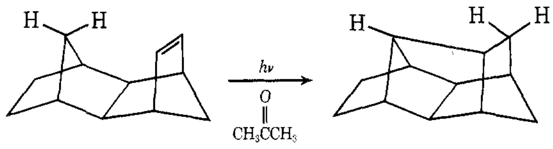
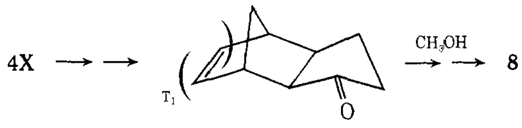


(5)

The overall reaction **4N** → **7** could be quenched by added norbornene with the concurrent production of dimers. From the data in Table I it can be seen that most of the product (**7**) arises from the quenchable state (ϕ_0/ϕ = 3.6). The most straightforward interpretation of this data involves competitive excitation transfer from triplet carbonyl to norbornene or **4N**.[22] The data also demand that a nonquenchable state is involved in those other processes which consume **4N** but which do not lead to **7**.

In the exo system **4X**, energy transfer is followed by a series of radical abstraction reactions[19] which ultimately produce the saturated ketone 8 (eq 6). This sequence parallels the photoreduction of norbornenes, which can be sensitized by acetone or aromatic donors.[23]

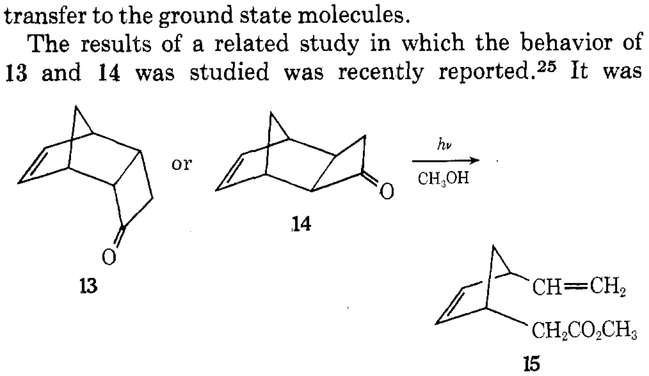


(6)

The contrast in behavior between **3N** and **4N** is instructive in the context of the overall behavior of *endo*-5-acylnorbornene photochemistry. On the one hand, **3N** rapidly forms an oxetane in competition with what must be a facile type I cleavage. On the other hand, the behavior of ketone **4N** resembles that of an isolated carbonyl system. Thus, in constrast to simple *endo*-5-acylnorbornenes, quenchable triplet states of **4N** are formed. We conclude that the singlet state is relatively long lived as a consequence of weak or negligible exciplex formation. These results lend support to the ideas[6] discussed above concerning the geometrical requirements for exciplex formation.

The contrasting behavior between **3X** and **4X** is probably the result of differences in ease of α cleavage toward tertiary and secondary centers.[24] These differences in turn are the deciding factors which control the extent of energy transfer to the ground state molecules.

The results of a related study in which the behavior of **13** and **14** was studied was recently reported.[25] It was



found that irradiation of both isomers produced ester **15**, but that chemical yields were significantly lower in the case of **14**. Conceivably, these reactions may involve ener-

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EXPERIMENTAL SECTION

Infrared spectra were determined on a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance spectra (in CCl_4 or $CDCl_3$) were obtained from Varian A-60 or T60 spectrometers and chemical shifts are relative to internal tetramethylsilane. Ultraviolet spectra were determined on a Cary 14 spectrophotometer. Preparative and analytical gas chromatography was carried out on Aerograph A-90-P instruments using the following columns: A, 16% QF-1: 4% Carbowax 20M (6 ft x 0.25 in); B, 4% QF-1: 1% Carbowax 20M (12 ft x 0.18 in); C, 4% QF-1: 1% Carbowax 20M (15 ft x 0.18 in); D, 45% QF-1: 3% Carbowax 20M (15 ft x 0.18 in); E, 3% QF-1: 2% Carbowax 20M (12 ft x 0.18 in); F, 4% QF-1: 1% Carbowax 20M (18 ft x 0.18 in). Mass spectra were recorded on an Hitachi Perkin-Elmer RMU-7 spectrometer.

endo, exo-5-Norbornen-2-spiro-1'-cyclopentan-2-one (3N and 3X). The Mannich base was prepared from cyclopentanone, formaldehyde, and dimethylamine hydrochloride.[26] A solution of 36.6 g (0.26 mol) of the Mannich base and 1.0 g of hydroquinone in 25.8 g (0.39 mol) of freshly prepared 1,3-cyclopentadiene was heated in a sealed tube at 125° for 4 hr. The crude product was dissolved in ether which was washed with dilute hydrochloric acid, aqueous sodium carbonate, dried, and evaporated. The residue (36.6 g) was distilled to give 19.8 g (47%) of a 9:91 mixture of isomers, bp 49° (4.5 mm) (lit., bp 74-74.5°/12 mm). The isomers were separated by partition chromatography on silica gel (Baker 60-200 mesh) using benzene as an eluent.

The endo-ketone (minor component) 3N showed the following properties: nmr (CCl_4) δ 5.9 (octet, 2H), complex absorption from δ 2.9 to 1.3 (12 H); ir (film) 5.78 (C=O) and 13.98 (HC=CH) μ; mass spectrum m/e 162 (0.19, molecular ion), 97 (0.40), 66 (1.0); $\lambda_{max}^{C_6H_{12}}$ 307 nm (ε 54.4), $\lambda_{max}^{C_6H_6}$ 305 nm (ε 76); semicarbazone mp 188.5-189° (dec).

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.73; H, 7.81; N, 19.16
Found: C, 66.00; H, 8.02; N, 19.09.

The exo-isomer 3X showed the following properties: nmr δ 6.15 (m, 2H), complex absorption between δ 3.0 to 1.0 (11 H), and a one proton quartet centered at δ 0.80 (J = 2.8, 10.7 Hz); ir (CCl_4) 5.80 (C=O) and 13.89 (s, HC=CH) μ; mass spectrum m/e 162 (0.02, molecular ion), 96 (0.21), and 66 (1.0); $\lambda_{max}^{C_6H_{12}}$ 301 nm (ε 55.3), $\lambda_{max}^{C_6H_6}$ 298 nm (ε 93); semicarbazone mp 211-212° (dec).

Anal. Found: C, 65.86; H, 7.84; N, 19.10.

The saturated ketones 11 and 12 were prepared by hydrogenation[7] of the pure ketones 3N and 3X in methanol using 10% palladium on carbon as the catalyst. Ketone 11 showed the following properties: ir (CCl_4) 5.79 (C=O) μ; mass spectrum m/e 164 (molecular ion), 97 (base peak); $\lambda_{max}^{C_6H_{12}}$ 302 nm (ε 27.4). Ketone 12 showed the following properties: ir (CCl_4) 5.79 (C=O) μ; mass spectrum m/e 164 (molecular ion), 97 (base peak); $\lambda_{max}^{C_6H_{12}}$ 300 nm (ε 26.9).

exo, endo-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (4X, 4N). A solution of 8.2 g (0.1 mol) of 2-cyclopentenone[27] in 100 ml of dry methylene chloride was

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added slowly to a stirred, ice-cooled suspension of 13.35 g (0.1 mol) of anhydrous aluminum chloride in 100 ml of dry methylene chloride. After the exothermic reaction subsided, the ice bath was removed and 33.0 g (0.5 mol) of freshly distilled cyclopentadiene in 100 ml of dry methylene chloride was added over a period of 30 min. The reaction mixture was cooled and treated with 300 ml of 1N hydrochloric acid. The organic phase was separated and washed with water, dried (Na_2SO_4) and evaporated to give 35.5 g of a dark oil. The benzene soluble material was chromatographed on silica gel. Elution with benzene gave 6.03 g (41%) of a 20:80 mixture of 4X and 4N, respectively.

The endo- isomer was purified further by sublimation, mp 93-94° (lit., mp 100-103°) and showed ir and nmr spectra identical with those of an authentic sample;[12] $\lambda_{max}^{C_6H_{12}}$ 306 nm (ε 18.9), $\lambda_{max}^{C_6H_6}$ 304 nm (ε 21.4); the 2,4-dinitrophenylhydrazone derivative had mp 180.5-181° after crystallization from ethanol.

Anal. Calcd for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.06
Found: C, 58.55; H, 4.90; N, 16.99.

The exo- ketone (4X) had the following properties: bp 51-52° (0.5 mm); nmr δ 6.2 (t, 2H), 3.2-1.2 (complex absorptions, 10 H)); ir (CCl_4) 5.79 (C=O) and 13.60 (HC=CH) μ; mass spectrum m/e 148 (molecular ion); $\lambda_{max}^{C_6H_{12}}$ 307 nm (ε 39.3), $\lambda_{max}^{C_6H_6}$ 304 nm (42.8); the 2,4-dinitrophenylhydrazone derivative had mp 201-201.5° after crystallization from ethanol-ethyl acetate.

Found: C, 58.52; H, 5.06; N, 17.03.

Photolyses. Irradiations were carried out in nitrogen-purged solvents with a 450 watt Hanovia mercury lamp (Type L). Pyrex filters were used for irradiations of 3X, 3N, and 4N, and a Corex filter was used with 4X. The benzene used was purified by washing with concentrated sulfuric acid, water, aqueous sodium carbonate and water. After drying over $CaCl_2$ it was distilled from P_2O_5. Spectroquality methanol was used in the case of 4X. Internal standards were purified in a similar manner to benzene.

Tetracyclo[5.2.1.$0^{2,6}$.$0^{4,9}$]decan-3-one (7). A solution of 1.481 g (0.010 mol) of ketone 4N in 225 ml of benzene was irradiated for 93 hr. Gc analysis (B) revealed four componenets in the photolysate.

The major constituent (86.5%) was isolated by column chromatography on silica gel (benzene eluent) and had mp 174-175°, yield 0.713 g (48%); nmr[28] δ 1.22 (d,d, J = 12,6 Hz, 1H), 1.42 (d,d J = 12,5.5 Hz, 1H), 1.52 (d, J = 1.8 Hz, 2H), 1.83-1.99 (m, 4H), 2.25 (q, J = 6 Hz, 1H), 2.36 (q, J = 5 Hz, 1H), 2.43-2.59 (m, 2H); ir (CCl_4) 5.67 (C=O); mass spectrum m/e 148 (molecular ion); 2,4-dinitrophenylhydrazone derivative, mp 190-192°.

Anal. Calcd for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.06
Found: C, 58.43; H, 5.20; N, 17.41.

Irradiations of 4X. Benzene. After 14 hr of irradiation of a solution of 4X in benzene (0.060 g in 120 ml) there was observed nine volatile products on gc analysis (D, 82-160°). No single product was prominent enough to render isolation feasible.

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Methanol. A solution of 0.120 g (0.0068 mol) of ketone 4X in 120 ml of methanol was irradiated for 29 hr. Concurrently, the irradiation of a similar solution of ketone 8 was initiated. The gc retention time (D, 84-160°) of the initial product from 4X coincided with that for 8. Gradually, ketone 8 produced 9 and 10 in both cases. Preparative gc and ir comparisons confirmed the identity of the products from 4X.

12-Oxapentacyclo[8.2.1.$0^{1,5}$.$0^{5,9}$.$0^{7,11}$]dodecane (5). Irradiation of a solution of 0.500 g (0.00338 mol) of 3N in 110 ml of benzene for 29 hr gave a photosylate which showed two products on the gc (B, 120°). The major product was isolated by preparative gc (A, 121°) as a colorless oil, yield 0.22 g (44%); nmr δ 4.48 (d,d, J = 3.9, 2.1 Hz, 1H), 3.25 (t, J = 3.9 Hz, 1H), 1.2-2.5 (m, 12H);[29] ir 9.14, 9.56, 9.80, 10.32, 11.16, 11.36 (all m) μ; mass spectrum m/e 162 (0.54, molecular ion), 106 (1.0), 91 (0.83).

Anal. Calcd for $C_{11}H_{14}O$: nuclidic mass 162.1044
Found: nuclidic mass 162.1045.

Irradiation of 3X. Irradiation of a solution of 0.648 g (0.0040 mol) of ketone 3X in 110 ml of benzene for 9.5 hr gave a five component product mixture as shown by gc (B). The identity of the products and their relative proportions are given as follows: 5 (.17), 3N (0.065), two unidentified peaks (0.045) and 6 (0.72). Aldehyde 6 had the following characteristics: nmr δ 9.66 (m, H-C=O), 1H); 6.04 (m, HC=, 2H), 5.2 (m, HC=, 1H), 1.2-3.5 (m, 10 H); ir 3.72 (HCO), 5.82 (C=O), 14.05 (HC=CH) μ; $\lambda_{max}^{C_6H_{12}}$ 295 nm (ε 37); mass spectrum m/e 162 (molecular ion); 2,4-dinitrophenylhydrazine, mp 107.5-109°.

Anal. Calcd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.37
Found: C, 59.40; H, 5.39; N, 16.46.

Quantum Yield Determinations. All determinations were run in duplicate in 13 x 100 mm Pyrex test tubes which had been degassed by four freeze-thaw cycles and sealed under vacuum (5 x 10^{-3} Torr). A potassium chromate-sodium carbonate filter solution was placed in a reaction flask which surrounded the immersion lamp. Solutions to be irradiated were optically dense over 1 cm at 313 nm; concentrations of ketones ranged from 0.0915 to 0.139 M. The actinometer system used was the photocyclization reaction of 1 ($R=CH_3$) to 2 for which a quantum yield of 0.14 has been measured[4] using benzophenone-benzhydrol actinometry.

These analyses were carried out using gc and known concentrations of an appropriate internal standard, usually, a saturated straight chain hydrocarbon. Norbornene dimers were a gift from P. v. R. Schleyer, Princeton University.

In addition to the data in Table I, the following results were obtained:

$$\Phi_{-3N}\ 0.25 \pm 0.03, \quad \Phi_5\ 0.21 \pm 0.02;$$
$$\Phi_{-3X}\ 0.31 \pm 0.03, \quad \Phi_6\ 0.29 \pm 0.03.$$

gy transfer steps which compete to differing extents with the type I cleavages.

Summary. The widely disparate behavior of these four ketones exemplifies the subtleties implicit in the photochemistry of complex molecules. We have rationalized the results in terms of reasonable assumptions about the relative magnitudes of the rates of competing processes. In any case, these results have led to a better understanding of the geometrical requirements for exciplex and oxetane formation and to a useful synthesis of a new tetracyclic ring system (7).[30]

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Registry No.—*endo*-**3**, 51263-64-0; *endo*-**3** semicarbazone, 51263-65-1; *exo*-**3**, 51269-20-6; *exo*-**3** semicarbazone, 51269-21-7; *endo*-**4**, 22981-84-6; *endo*-**4** 2,4-dinitrophenylhydrazone, 51263-66-2; *exo*-**4**, 51269-22-8; *exo*-**4** 2,4-dinitrophenylhydrazone, 51263-67-3; **5**, 51263-68-4; **6**, 51263-69-5; **6** 2,4-dinitrophenylhydrazone, 51263-70-8; **7**, 51263-71-9; **7** 2,4-dinitrophenylhydrazone, 51263-72-0; **11**, 51263-73-1; **12**, 51269-23-9.

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References and Notes

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