Photochemical, Photophysical, and Theoretical Studies of 3,5-Cycloheptadienones[1] †

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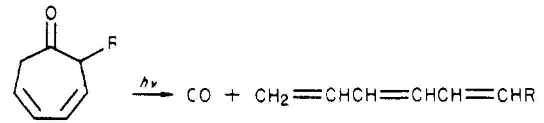
Reinvestigation of the photochemistry of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (**16**) reveals that decarbonylation to 2,7-dimethyl-2,4,6-octatriene (**18**) is a major photoprocess (ϕ = 0.11 at 313 nm in cyclohexane), in contrast to an earlier report. Formation of the oxa-di-π-methane rearrangement product **17**, as reported earlier, is also observed (ϕ = 0.29). Irradiation of **16** at 254 nm leads to formation of cyclobutene **24** and to the [1,3]-sigmatropic shift product **27**, as well as to **17** and **18**. Formation of **17** occurs from a triplet excited state, as determined by sensitization and quenching experiments, of energy ≤50 kcal/mol and of a lifetime of ~3.0 ns. The observed wavelength-dependent photochemistry of **16** can be rationalized from results of INDO/S calculations, which indicate that wavelength-dependent photochemistry should be observed for 3,5-cycloheptadienones of C_2 but not of C_s symmetry, as confirmed experimentally. Fluorescence is observed for a number of 3,5-cycloheptadienones in dilute cyclohexane solution at room temperature. Singlet excited-state lifetimes are obtained by single-photon counting using iterative convolution in the data treatment. Alternative mechanisms for decarbonylation are considered, and it is concluded that a singlet concerted mechanism appears preferable at this time. On this basis, rate constants for the various singlet-derived photoprocesses are calculated from measured lifetimes and quantum yields. The four methyl groups in **16**, as compared with unsubstituted 3,5-cycloheptadienone (**1**), have little effect on the rate constants for fluorescence or decarbonylation but lead to a >100-fold increase in the rate constant (k_{ST}) for intersystem crossing. A concerted sigmasymmetric mechanism is suggested for decarbonylation of C_s dienones, while an axisymmetric expulsion of CO is suggested from C_2 dienones. No correlation is observed between the effect of α-methyl substitution on k_{ST} values of 3,5-cycloheptadienones vis a vis saturated ketones.

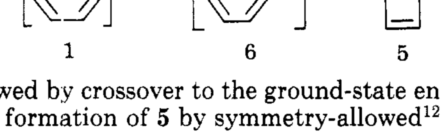
Since the first report of 3,5-cycloheptadienone photochemistry by Chapman and co-workers[2] in 1961, this class of compounds has received much attention from photochemists, spectroscopists, and theoreticians.[3-5] Chapman et al.[2,6] found that direct irradiation through Pyrex of the parent compound (**1**) and its 2-methyl derivative (**2**) gave



1, R = H
2, R = Me

3, R = H
4, R = Me

carbon monoxide and mixtures of geometric isomers of 1,3,5-hexatriene (**3**) and 1,3,5-heptatriene (**4**), respectively. The quantum yield (ϕ) for decarbonylation of **1** was later found by us[7] to be 0.74 at 313 nm. Also, the decarbonylation of **1** could not be quenched by triplet quenchers (piperylene or naphthalene) while triplet sensitization of **1** by a variety of triplet sensitizers gave only the valence isomer **5**,[8,9] with ϕ = 0.64 at 366 nm when β-acetonaphthone was the sensitizer.[10] It was suggested[8,9] that decarbonylation arose directly from S_1 while the reactive triplet excited state of **1** twists toward a *cis,trans*-dienone



1 6 5

(**6**), followed by crossover to the ground-state energy surface and formation of **5** by symmetry-allowed[12] thermal conrotatory ring closure. However, attempts to trap **6** by using cyclopentadiene or furan at room temperature and −70 °C were unsuccessful.[9] Compound **5** was not detected in the direct irradiation of **1**, implying a very low intersystem crossing efficiency (ϕ_{ST}).

Chapman et al.[6] recognized the highly twisted ground-state geometry of **1**. Dreiding models indicated a dihedral diene angle of about 45° and a C_2 axis through the carbonyl group and the midpoint of the diene moiety. The photochemical behavior of the bridged dienone **7** where the diene moiety necessarily is planar was therefore of interest. We found[7] that **7** gave decarbonylation (ϕ = 0.66 at 313 nm) and cyclobutene formation (ϕ = 0.14 at 313 nm) from presumably the singlet excited state, whereas triplet sensitization (sens) led to the [1,2]-sigmatropic shift (oxa-di-π-methane) product **10** (ϕ = 0.89 with Michler's ketone). In terms of this mechanistic description, intersystem crossing again was not detectable. Very similar photochemical reactions were observed with trienone **11**,[13-15] where trace amounts of **14** were seen[13] in the photolysate through Pyrex, indicating inefficient but detectable inter-

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† Dedicated to Professor E. Havinga of the State University of Leiden, The Netherlands, on the occasion of his 70th birthday.

[1] Photochemistry of Ketones in Solution. Part 56. Part 55: D. I. Schuster and V. A. Stoute, *Mol. Photochem.*, **9**, 93 (1978).

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[10] This value is obtained from a measured value of 0.54[9] and the intersystem crossing efficiency of 0.84 for β-acetonaphthone.[11]

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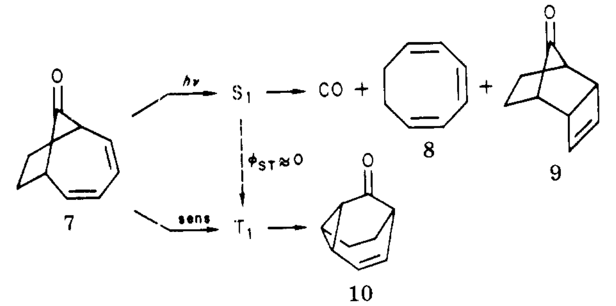
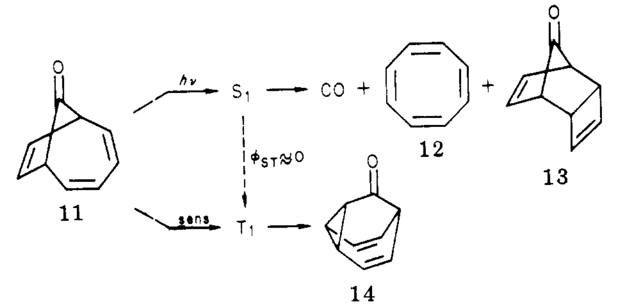
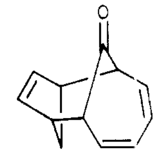




system crossing in this case. Direct photolysis of **11** in ether at 254 nm gave carbon monoxide, **12**, and **13**.[13]

Independent work by Mukai[16] and Houk[3,17a] and their co-workers on the tropone–cyclopentadiene adduct **15** and



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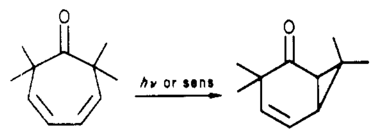


16

similar compounds reveals a complicated concentration- and solvent-polarity-dependent photochemistry which includes decarbonylation and cyclobutene formation apparently from excited singlets and dimerization and 1,2-shift products via triplet excited states. A discussion of the behavior of **15** is presented elsewhere along with new concentration-dependent fluorescence data.[17b]

For all of the 3,5-cycloheptadienones discussed above, decarbonylation was a major reaction. In contrast, Paquette et al.[18] reported that 2,2,7,7-tetramethyl-3,5-cycloheptadienone (**16**) gave the product of a [1,2]-acyl shift (**17**) as the only product on either direct or triplet-sensitized irradiation. The formation of **17** in the direct photolysis could not be quenched by 1,3-pentadiene (2.7 M) or naphthalene (0.3 M). The authors suggested either that **17** was derived from both singlet and triplet excited states of **16** or that efficient intersystem crossing gave the reacting triplet state of **16** which was too short-lived to be quenched. The lack of decarbonylation from **16** was attributed[18] to steric effects, due to two methyl groups brought into close proximity during a concerted expulsion of carbon monoxide.

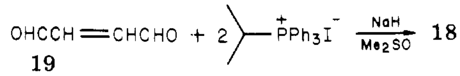
Clearly, more work was needed to clarify the puzzling results obtained on **16** vis a vis other cycloheptadienones. Preliminary reports on these studies have been published elsewhere.[19]

Results

Direct Photolysis of 16 at 300 nm. Irradiation of a 0.01 M ether solution of **16** at 300 nm at room temperature gave two photoproducts, A and B, as determined by GLC analysis.[20] This experiment was repeated about a dozen times, and it became clear that the earlier report by Paquette et al.[18] describing a single photoproduct was erroneous. The two products were isolated from a preparative-scale (1.0 g) photolysis of **16** and separated by column chromatography (silica gel, 30 × 1 cm, 9:1 hexane/ether). The first compound to be eluted was product A, a white solid, mp 35–36 °C. The spectral properties of A were as follows: ν (CCl_4), 3040, 2975, 2920, 2860, 1640, 1445, 1380, 995, 960, 860 cm^{-1}; λ_{max} (C_6H_{12}), 292 nm (ϵ 38600), 280 (55000), 269 (38600); ^1H NMR (CCl_4) δ 5.5–6.3 (m, 4 H), 1.80 and 1.73 (s, 12 H); *m/e* 136 (M^+, 100%), 121 ($M^+ -$ Me), 107, 105, 93, 91, 79. Compound A was identified as the expected decarbonylation product 2,7-dimethyl-2,4,6-octatriene (**18**) from the following observations: (a) the IR spectrum shows no carbonyl band; (b) the parent peak in the mass spectrum corresponds to a loss of CO from **16**; (c) the very intense UV absorption bands of A are consistent with a conjugated triene; indeed, the absorption spectrum of A is very similar to that of 1,3,5-hexatriene (**3**) [λ_{max} (C_6H_{12}), 248 nm (ϵ 36000), 258 (48000), 268 (39000)] but shifted ~22 nm as expected[21] from the presence of four methyl groups in **18**; (d) the spectroscopic data are virtually identical with those obtained for **18** by Coates and Robinson;[22] (e) product A is identical with the product obtained from the Wittig reaction of 2-butenedial (**19**)[23] with 2 equiv of isopropyltriphenylphosphonium iodide (**20**).[24] The geometric configuration of **18** (i.e., *Z* or *E* at C_4–C_5) obtained from irradiation of **16** or from the independent synthesis was not established. The *Z* configuration is drawn for simplicity only.

18

3



$$\underset{\mathbf{19}}{OHCCH{=}CHCHO} + 2\,(CH_3)_2CH\overset{+}{P}Ph_3\overset{-}{I}\ \underset{\mathbf{20}}{} \xrightarrow[Me_2SO]{NaH} \mathbf{18}$$

The second compound to be eluted from the chromatographic column was identified as unreacted starting material (**16**) from its spectral properties. Finally, photoproduct B was isolated as a colorless oil and identified as 3,3,7,7-tetramethylbicyclo[4.1.0]hept-4-en-2-one (3-methyl-4-caren-2-one, **17**) from its spectral data: ν (neat), 3000, 2950, 2910, 1690 (s), 1650, 1460, 1375, 1220, 1170, 1160, 1125, 1010, 890, 740 cm^{-1}; λ_{max} (C_6H_{12}), 292 nm (ϵ 246); ^1H NMR ($CDCl_3$) δ 5.44–5.95 (m, 2 H), 1.70–1.82 (m, 2 H), 1.23, 1.11, 1.08, and 0.98 (s, 3 H each); ^{13}C NMR ($CDCl_3$) δ 209.4 (C=O), 134.8 and 120.4 (C=C), 42.7, 34.6, 29.6,

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(20) The retention times of A, **16**, and B were 4.6, 5.7, and 7.5 min, respectively, on a $^1/_8$ in. × 180 cm 10% Carbowax 20 M on 60–100 Chromosorb P column operated at 140 °C with flow rates as follows: N_2, 30 mL/min; H_2, 30 mL/min; air, 240 mL/min.

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(25) We originally thought that CCl_4 might promote intersystem crossing of **16**, leading to a reduction in the quantum yield for decarbonylation. However, the fluorescence intensity of **16** is twice as great in CCl_4 as in CH_3CN.

29.5, 27.4, 22.4, 15.9, 0.4 ppm; *m/e* 164 (M^+), 149 (M^+ − Me), 136 (100%, M^+ − CO), 121 (M^+ − Me − CO), 93, 91, 79, 77, 67, 65, 55, 53, 51. These spectral data are consistent with the structure of **17** and are in good agreement with the reported[18] IR and ^1H NMR data.

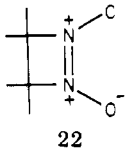
The effect of the solvent on the photochemical behavior of **16** was studied. Little effect on the ratio of **17**/**18** (1.5–3.0) was observed in cyclohexane, benzene, acetonitrile, methanol, 2-propanol, and *tert*-butyl alcohol. In carbon tetrachloride, however, no decarbonylation product could be detected. Subsequently, it was discovered that **18** rapidly disappears on photoexcitation in CCl_4 by an as yet poorly understood reaction (work in these laboratories by Mr. O. Roberto). Quantum yields for disappearance of starting material (ϕ_{-K} = 0.41) and for formation of **17** (ϕ = 0.29) and **18** (ϕ = 0.11) were measured at 313 nm at 25 °C in cyclohexane. Triene **18** was not a secondary photoproduct from **17**, since irradiation of **17** in cyclohexane at 300 nm resulted only in very slow disappearance of starting material.

Sensitization and Quenching Experiments on 16. Sensitized photolysis of **16** with enough triplet sensitizer (acetone or benzophenone) to absorb 99% of the incident light gave a single product which was isolated from a preparative-scale (1.0 g) irradiation in acetone and identified as the 1,2-sigmatropic shift product **17**, in agreement with the earlier report by Paquette and co-workers.[18] The reported[18] failure of naphthalene (E_T = 61 kcal/mol[26a]) to quench formation of **17** was confirmed by us in experiments using up to 2 M naphthalene in tetrahydrofuran (THF); in addition, no quenching of **18** was observed. However, inefficient quenching of the formation of **17**, but not **18**, was observed when up to 8.4 M 1,3-cyclohexadiene (CHD; E_T = 53 kcal/mol[26]) in THF was used, accompanied by formation of the characteristic CHD dimers,[27] indicating that triplet energy transfer from **16** to CHD had indeed taken place. Equation 1 is the familiar Stern–Volmer

$$P_0/P_Q = 1 + k_q\tau_T[Q] \qquad (1)$$

equation, where P_0 and P_Q are the relative amounts of product formed in the absence and presence of quencher (Q), respectively, k_q is the bimolecular quenching rate constant, and τ_T is the triplet lifetime of the substrate (**16**). A plot of P_0/P_Q for product **17** vs. [CHD] gave a straight line with a slope ($k_q\tau_T$) of ~0.1 M^{-1}.

Much more efficient quenching of the formation of **17** was found when the low-energy triplet quencher 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide (**22**, E_T = 35–42 kcal/mol[28]) was used. Plots of P_0/P_Q vs. [**22**] gave $k_q\tau_T$ values of 29.5 M^{-1} in acetonitrile and 38.5 M^{-1} in chloroform. On excitation of **16** at 340 nm in the presence of 0.05 M **22** in acetonitrile, conditions which cause ~60% quenching of formation of **17**, the fluorescence of **16** was not quenched. Thus **17** does not arise directly from S_1 and is logically concluded to be derived from a triplet excited state (T_1). If a diffusion-controlled quenching rate constant ($k_q \approx 10^{10}$ M^{-1} s^{-1}) is assumed,[29,30] the triplet lifetime of **16** can be estimated as ~3.0 ns. The only prior report of a triplet lifetime of a β,γ-unsaturated ketone is that of Engel et al.,[31] who estimated $\tau_T \approx 4.0$ ns for **23**. The triplet energy of **16** can be estimated as ~50 kcal/mol from the inefficient quenching observed with CHD and the much more efficient quenching by **22**. The photolysates from **16** in the presence of **22** at concentrations as low as 6.7 × 10^{-3} M contained absolutely no octatriene **18**, a curious result that is tentatively attributed to destruction of **18** by reaction with **22**, perhaps involving oxidation. Ullman (private communication) informs us that **22** is a potent oxidizing agent under certain conditions. We have recently shown (O. Roberto, unpublished results) that the disappearance of 2,6-dimethyl-2,4,6-octatriene, an analogue of **18**, was markedly accelerated in the presence of **22** on irradiation in spectrograde acetonitrile at 300 nm, although the products of this reaction have not been characterized as yet. No reaction occurred between this triene and **22** in the dark during the same time interval (30 min).



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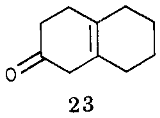

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These experiments suggest that **17** originates exclusively from a triplet excited state of **16**, in which case ϕ_{ST} must be appreciable. The quantum yield ($\phi_P{}^{dir}$) for formation of a product derived from a triplet excited state upon direct irradiation, given in eq 2, equals the efficiency of forming

$$\phi_P{}^{dir} = \phi_{ST}F \qquad (2)$$

$$\phi_P{}^{sens} = \phi_{ST}{}^{sens}\phi_{ET}F \qquad (3)$$

this state (ϕ_{ST}) times the fraction (F) of triplets that go on to form this product. In a triplet-sensitized photolysis, the quantum yield ($\phi_P{}^{sens}$) for formation of the same product is given by eq 3, where $\phi_{ST}{}^{sens}$ is the intersystem crossing efficiency of the sensitizer, and ϕ_{ET} is the efficiency of triplet energy transfer from the sensitizer to the substrate. In cases where $\phi_{ST}{}^{sens}$ is unity (e.g., acetone and benzophenone[29]) and energy transfer can be reasonably expected to be totally efficient from its exothermicity (>3 kcal/mol) and the substrate concentration (0.05 M in this case),[29,30] eq 3 reduces to eq 4. Thus, from eq 2 and 4 one

$$\phi_P{}^{sens} = F \qquad (4)$$

obtains eq 5. For formation of **17** from **16**, $\phi_P{}^{dir}$ = 0.29

$$\phi_{ST} = \phi_P{}^{dir}/\phi_P{}^{sens} \qquad (5)$$

(see above) and $\phi_P{}^{sens}$ = 0.81.[7] Hence, from eq 5, ϕ_{ST} = 0.29/0.81 = 0.36.

Direct Photolysis of 16 at 254 nm. An interesting wavelength dependence in the photochemistry of **16** was observed. Irradiation of **16** at 254 nm in a variety of solvents (cyclohexane, acetonitrile, methanol, 2-propanol, and *tert*-butyl alcohol) gave four major and four minor (unidentified) products. The four major products (A, B, C, and D) were isolated in approximate yields of 24, 30, 14, and 16%, respectively, from a preparative-scale (1.0 g) photolysis in cyclohexane. After partial separation by column chromatography (silica gel, 80 × 3 cm, hexane) and purification by preparative scale GLC,[32] A and B were identified as triene **18** and the 1,2-shift product **17**. Complete separation of C and D was unsuccessful, partly due to the instability of D under the separation and purifica-

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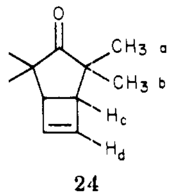
[32] The column was 1/4 in. × 200 cm, 20% PDEAS on 60–80 Chromosorb P operated at 190 °C.

Table I. Calculated and Experimental Energies, Oscillator Strengths and Configurational Compositions in Compounds 1, 16, 7, and 11

	E, nm		oscillator strength (*f*)		
state	calcd	exptl	calcd	exptl[a]	confign (% comp)[b,c]
			Compound 1		
S_1	294	278-290[d]	0.0024	0.0070	n,π^*_{CO} (83); n,ψ_3 (10); ψ_1,π^*_{CO} (5)
S_2	229	204-225[d]	0.32	0.115	ψ_2,ψ_3 (95)
S_3	207		0.058		n,ψ_3 (63); ψ_1,ψ_3 (13); ψ_2,ψ_4 (17)
T_1	478	539[e]			ψ_2,ψ_3 (78); ψ_1,ψ_4 (15)
T_2	403				ψ_2,ψ_4 (52); ψ_1,ψ_3 (32); n,ψ_3 (13)
T_3	326				n,π^*_{CO} (84); n,ψ_3 (7); ψ_1,π^*_{CO} (5)
T_4	208				n,ψ_3 (57); ψ_2,ψ_4 (31); ψ_1,ψ_3 (6)
			Compound 16		
S_1	291	290[f]	0.0015	0.0068	n,π^*_{CO} (80); ψ_1,π^*_{CO} (10); n,ψ_3 (7)
S_2	237	243[f]	0.31	0.10	ψ_2,ψ_3 (95)
S_3	220		0.90		n,ψ_3 (66); ψ_1,ψ_3 (16); ψ_2,ψ_4 (13)
T_1	503	572[g]			ψ_2,ψ_3 (77); ψ_1,ψ_4 (15); n,ψ_4 (6)
T_2	437				ψ_2,ψ_4 (46); ψ_1,ψ_3 (34); n,ψ_3 (17)
T_3	321				n,π^*_{CO} (81); ψ_1,π^*_{CO} (10); n,ψ_3 (4)
T_4	220				n,ψ_3 (58); ψ_2,ψ_4 (35); n,π^*_{CO} (3)
			Compound 7		
S_1	299	310[f]	0.018		χ_2,π^*_{CO} (58); χ_1,π^*_{CO} (23)
S_2	272	264[f]	0.19	0.056	χ_2,ψ_3 (79); χ_2,π^*_{CO} (12)
S_3	213		0.025		χ_1,ψ_3 (94)
T_1	569				χ_2,ψ_3 (57); χ_1,ψ_3 (33)
T_2	353				χ_2,ψ_4 (39); ψ_1,ψ_3 (30)
T_3	326				χ_2,π^*_{CO} (68); χ_1,π^*_{CO} (28)
T_4	232				χ_1,ψ_3 (57); χ_2,ψ_3 (38)
			Compound 11		
S_1	301	320[h]	0.022	0.0072	χ_2,π^*_{CO} (51); χ_2,ψ_3 (30)
S_2	281	280[h]	0.082	0.040	χ_2,ψ_3 (68); χ_2,π^*_{CO} (22)
S_3	237	230 sh[h]	0.23		χ_2,ϕ_2 (98)
S_4	213	215[h]			
T_1	542				χ_2,ψ_3 (62); χ_1,ψ_3 (30)
T_2	419				ϕ_1,ϕ_2 (94)
T_3	339				χ_2,ψ_4 (37); ψ_1,ψ_3 (28)
T_4	326				χ_2,π^*_{CO} (71); χ_1,π^*_{CO} (25)
T_5	239				χ_2,ϕ_2 (92)

[a] Calculated from electronic absorption spectra by using standard methods. See N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra", Marcel Dekker, New York, 1970, p 212. [b] Only those configurations contributing at least 5% to each state are indicated. [c] n = nonbonding orbital on oxygen; π_{CO} and π^*_{CO} are the carbonyl π orbitals; ψ_1-ψ_4 are the diene ψ orbitals; ϕ_1 and ϕ_2 are the bonding and antibonding orbitals of the C_7-C_8 bond in compound 11; χ_1 and χ_2 are the symmetric and antisymmetric orbitals formed by interaction of n and ψ_2 in 7 and 11, where $\chi_1 = n + \lambda\psi_2$ and $\chi_2 = \psi_2 - \lambda n$. [d] In 95% ethanol.[7,8] [e] Estimated in ref 8 and 9. [f] In methanol, ref 18 and this work. [g] Estimated in ref 19a. [h] In cyclohexane.

tion conditions. A pure sample of C, obtained by preparative scale GLC,[32] was a colorless oil with the following spectral properties: ν (neat) 3020, 2950, 2900, 2850, 1725 (s), 1470, 1380, 1360, 1305, 1040, 1000, 890, 840, 780, 755 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 6.16 (br s, 2 H), 3.10 (br s, 2 H), 1.08 and 1.02 (s, 6 H each); *m/e* 164 (M$^+$), 149 (M$^+$ − Me), 136 (100%, M$^+$ − CO), 122, 121 (M$^+$ − Me − CO), 83. These spectral data strongly suggest that C is 2,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-3-one (24) and agree well with those of model compounds 25[8] and 26.[33]



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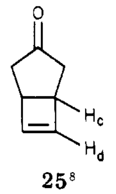
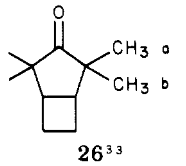


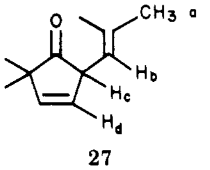
25[8]



26[33]

24: a, δ 1.02 (s); b, δ 1.08 (s); c, δ 3.10 (br s); d, δ 6.16 (br s); ν_{CO} 1725 cm^{-1}. 25: c, δ 3.5; d, δ 6.13 (br s); ν_{CO} 1745 cm^{-1}. 26: a, δ 1.03 (s); b, δ 1.06 (s); ν_{CO} 1731 cm^{-1}.

A pure sample of D could not be obtained, and its identification is consequently less reliable. However, subtraction of the spectral data of pure C (24) from the spectra of a 1:1 mixture of C and D gave the following spectral data for D: ν (neat) 1740 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 5.92 (br s, 2 H), 4.80 (br d, 1 H), 3.70 (br d, 1 H), 1.75 (br s, 6 H), 1.07 (s, 6 H). These data are consistent with the structure 2,2-dimethyl-5-isobutenyl-3-cyclopentenone (27) for D and are in good agreement with data for model compound 28.[18]



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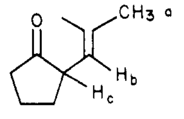

28[18]

27: a, δ 1.75 (br s); b, δ 4.80 (br d); c, δ 3.70 (br d); d, δ 5.92 (br s); ν_{CO} 1740 cm^{-1}. 28: a, δ 1.76, 1.68 (s); b, δ 4.97 (br d); c, δ 3.0 (br m); ν_{CO} 1750 cm^{-1}.

It was important to demonstrate that 24 and 27, which were seen only upon irradiation of 16 at 254 nm, would have survived the reaction and detection conditions at 300 nm had they also been formed at that wavelength. A solution of 16 in cyclohexane containing a small amount of 24 was irradiated at 300 nm and analyzed by GLC after 5, 10, 20, 30, 50, and 70% conversion of 16. Products 17

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(33) P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.*, 94, 4357 (1972).

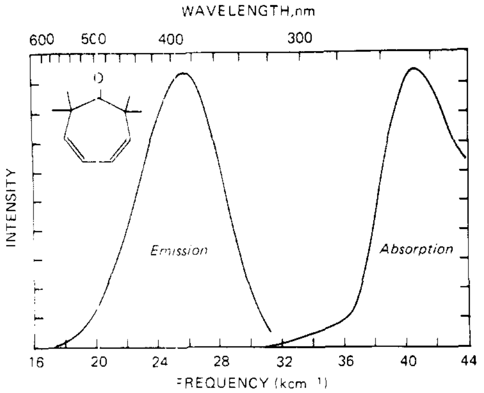

Figure 1. Absorption and corrected fluorescence spectra of **16** in cyclohexane. Note the n → π^*_{CO} and $\pi \rightarrow \pi^*$ absorption bands centered at ~300 and 243 nm, respectively.

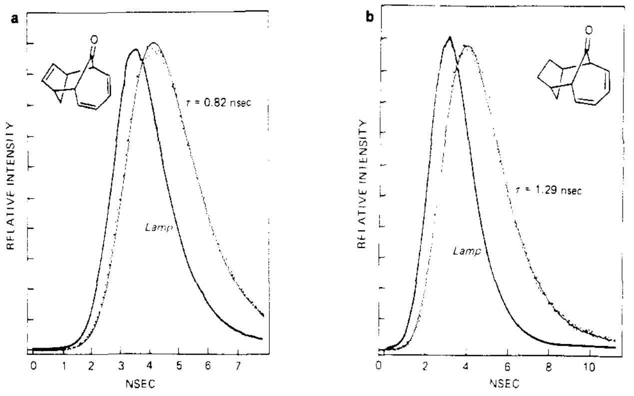

Figure 2. Lamp profile, fluorescence decay (···), and computer calculated convoluted decay curve for compounds **15** (a) and **29** (b).

and **18** were formed without any change in the amount of **24**. Thus, **24** is stable to photolysis at 300 nm and would, if present, have been detected in our GLC analysis. The same control experiment could not be performed on **27** due to its instability and due to the fact that the GLC retention time of **27** is not distinguishable from those of either **16** or **24** on at least six columns. Therefore, the possibility that **27** might have been formed upon irradiation of **16** at 300 nm but reacted further at this wavelength (but not at 254 nm) and thus escaped detection can not be rigorously excluded. However, it seems more likely that both **24** and **27** are formed from **16** only upon excitation at 254 nm into the S_2 state, providing another case of reaction from S_2 competive with internal conversion from S_2 to S_1 or S_0.[34] Formation of **27** also represents the first example of a [1,3]-sigmatropic shift in 3,5-cycloheptadienone photochemistry.

Theoretical Predictions of Wavelength Dependence. With the object of attaining a more detailed description of the excited states in 3,5-cycloheptadienones, molecular orbital calculations have been carried out by using an INDO model, described in detail below. The results are summarized in Table I. The calculated electronic states and their energies were in good agreement with observed spectroscopic data and with the estimation of E_T from quenching experiments on **1** and **16**. The calculations proved useful in interpreting the observed photochemistry of **16**. Thus, in the S_1 state the excitation energy is calculated to be localized largely in the carbonyl group, and expulsion of CO is found to be the dominant if not the exclusive reaction mode. In S_2 where the excitation is calculated to be localized mainly (~95%) in the diene moiety, electrocyclic ring closure to a cyclobutene (**24**) is observed. It has previously been concluded[7] that a planar diene was necessary (such as in **7**, **11**, and **15**) for cyclobutene formation from the singlet manifold of 3,5-cycloheptadienones. Conceivably, the S_2 state of **16** relaxes from a twisted (C_2 symmetry) toward a planar (C_s symmetry) diene conformation, allowing disrotatory ring closure to compete effectively with internal conversion. It should be noted that the lowest n,π* triplet state in **1** and **16** is T_3.

Calculations were also performed on dienones **1** and **7** and on trienone **11**. The calculated properties of **1** (energies and configurational compositions) were in all respects very similar to those calculated for **16**, leading to the prediction[19] that **1** should also show wavelength-dependent photochemistry. Calculations on **7** and **11** gave results markedly different from those obtained for **1** and **16** (see below). For the former compounds, the calculations indicated that $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions would give excited states with similar electronic configurations, and it was predicted that wavelength-dependent photochemistry should not be observed for these ketones. These predictions were explored.

Wavelength-Dependent Photochemistry of 1. Direct irradiation of **1** in cyclohexane at 300 nm at room temperature gave 1,3,5-hexatriene (**3**), in agreement with earlier reports.[6,8] In the identification of **3** the characteristic UV absorption spectrum of a conjugated triene was particularly useful: λ_{max} (C_6H_{12}) 248 nm (ε 36 000), 258 (48 000), 268 (39 000). Triplet-sensitized irradiation of **1** in acetone gave cyclobutene **5**, as reported.[8,9] The spectral properties of **5** were as follows: ν (CCl_4), 3090, 3020, 2930, 2875, 1740 (s), 1660, 1405, 1320, 1240, 1160, 1100, 1030, 890 cm^{-1}; λ_{max} (C_6H_{12}) 289 nm (ε 25), 298 (24), 308 sh (17); ^{1}H NMR ($CDCl_3$) δ 6.13 (s, 2 H), 3.4–3.7 (m, 2 H), 2.2–2.5 (s, 2 H); ^{13}C NMR ($CDCl_3$) 210.1 (C=O), 140.7 (C=C), 40.9, 42.3 ppm; *m/e* 108 (M^+), 80 (100%, M^+ - CO), 79, 77, 66 (M^+ - CO - CH_2), 65, 54, 53, 52, 51, 50, 41, 40, 39. These spectral data are consistent with the structure of **5** and with reported values[8] (IR and ^{1}H NMR). Since **5** was not observed in the direct irradiation of **1** at 300 nm, it was desirable to estimate an upper limit for ϕ_{ST}. By addition of **5** to a cyclohexane solution of **1**, it was found that **5**, if formed in a yield equal to 2% of **3**, would have survived the reaction conditions and would have been detected by GLC. Since $\phi_5^{dir} \leq 0.02 \times 0.74^7$ and $\phi_5^{sens} = 0.64,^{10}$ we obtain from eq 5 that $\phi_{ST} \leq 0.74(0.02/0.64)$ or ≤0.02. This value is to be compared with the value of $\phi_{ST} = 0.36$ obtained for the tetramethyl analogue **16**.

Direct irradiation of **1** in cyclohexane at 254 nm gave not only triene **3** but also a detectable amount of cyclobutene **5**. Hence, wavelength-dependent photochemistry for **1** is indeed observed, as predicted by our theoretical calculations.[19a]

Miscellaneous Results on 7 and 11. From the quantum yields of product formation from **7**, an upper limit to ϕ_{ST} can be estimated in the same way as employed above for **1**. If one assumes that 2% of **10** relative to the major product **8** would have been detected if formed, then $\phi_{10}^{dir} < 0.02 \times 0.66.^7$ Since $\phi_{10}^{sens} = 0.89,^7$ eq 5 reveals that $\phi_{ST} \leq 0.02(0.66/0.89)$ or ≤0.015. A similar estimation of ϕ_{ST} for **11** cannot be performed since quantum yields for product formation were not reported.[13-15] Irradiation of **11** at 300 nm and at 254 nm in cyclohexane gave photolysates with identical vapor chromatograms, indicating the absence of wavelength dependence in this system, in agreement with the prediction based on the theoretical calculations.

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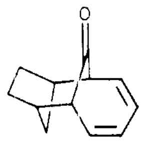
[34] For other examples, see N. J. Turro, J. Ramamurthy, W. Cherry, and W. Farneth, *Chem. Rev.*, 78, 125 (1978).

Fluorescence and Singlet Lifetimes. We have shown that fluorescence is a general property of β,γ-unsaturated ketones in solution.[35,36] Fluorescence emission spectra of several 3,5-cycloheptadienones were obtained at room temperature in cyclohexane solution.[19b] Broad structureless emissions were observed for **1**, **15**, **16**, and **29** with maxima of the corrected fluorescence spectra at 370–390 nm (Table II). The maxima at 310–320 nm of the corrected excitation spectra correspond to the maxima of the n,π^*_{CO} absorptions. As a typical example, the fluorescence and absorption spectra of **16** are shown in Figure 1. The quantum yield (ϕ_f) for fluorescence (Table II) was determined by comparing the total intensity of the corrected emission spectrum of each compound with that of a standard by using solutions of identical optical density at the excitation wavelength. The singlet lifetimes (τ_s, Table II) were measured by single-photon counting[37-39] using a computer-assisted iterative convolution technique similar to that described by Zimmerman et al.[39] Lifetimes as short as 0.1 ns were obtained reproducibly within ±0.05 ns by this technique. The convoluted results were then reproduced graphically together with the lamp profiles measured in each run and the experimental fluorescence decay data. Figure 2 shows the results for compounds **15** and **29**.



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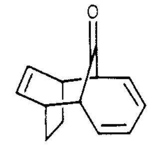

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Theoretical Calculations.[40] Methods. A CNDO/S computer program available from the Quantum Chemistry Program Exchange possessed two undesirable properties: (a) the program was designed to calculate 0–0 transitions which are difficult to verify experimentally, especially for pure n → π^* transitions, and (b) the CNDO/S model predicts no singlet–triplet energy splitting for n → π^* transitions, in clear disagreement with experimental observations. Together with Dr. K. Krogh-Jespersen,[41] we applied a modified INDO model[42] reparameterized[19a] for prediction of Franck–Condon maxima and correct singlet–triplet energy splittings. Since this model (INDO/S) has been described in detail elsewhere,[19,40,41] only the results and conclusions obtained from these calculations are presented here. Excited-state calculations on **1**, **7**, **11**, and **16** were performed in the singly excited configuration-interaction approximation by including a large number (~70) of configurations to obtain excited-state energies and oscillator strengths for the transitions. Calculations were done only on geometries representing the lowest energy conformations of the ground state of these systems. Bond lengths and bond angles were carefully chosen from appropriate model systems.[41,43]

Table II. Fluorescence Data and Singlet Lifetimes of 3,5-Cycloheptadienones[a]

compd	ex max,[b] nm	em max,[c] nm	$10^4\phi_f$	τ_s,[d] ns	10^6k_f, s^{-1}
1	310	390	12.5	1.05 ± 0.05	1.2
16	310	388	3.2	0.11 ± 0.05	2.9
15	320	370	6.7	0.82 ± 0.05	0.82
29	320	386	6.7	1.29 ± 0.05	0.52

[a] In cyclohexane (10^{-2} M) at room temperature. [b] Maximum of corrected fluorescence excitation spectrum. [c] Maximum of corrected fluorescence emission spectrum. [d] Singlet lifetime measured by single photon counting and iterative convolution.

Results of INDO/S Calculations on 1 and 16 (Table I). The results of calculations on the twisted dienones **1** and **16** have been reported previously.[19] Due to the C_2 symmetry, the molecular orbitals show contributions from many atoms and several orbitals from each atom, but it was nevertheless possible to identify molecular orbitals which were localized mainly in the carbonyl group (n and π_{CO}) or in the diene moiety (ψ_1–ψ_4). The following results and conclusions emerged.

(a) The fair agreement between observed and calculated values for transition energies and oscillator strengths suggests that these calculations are reliable for values not easily obtained experimentally.

(b) The four methyl groups in **16** have very minor effects on transition energies, oscillator strengths, and configurational compositions. This is in apparent disagreement with results of CNDO/S calculations on **1** and **16** reported by Houk and co-workers,[17a,44] who found that T_1 was π,π^* in **1** and n,π^* (or CT) in **16** and that the relative energies of the states of these systems were "extremely sensitive" to symmetry and substitutions. These calculations[17a,44] were used to rationalize the observed variations in singlet and triplet photochemistry and intersystem crossing efficiencies in 3,5-cycloheptadienones, including the report[18] of the photochemistry of **16**, which has not been shown to be erroneous in several respects.

(c) Our calculations indicate that the lowest excited singlet (S_1) is largely n,π^*_{CO} with some mixing of ψ_2,π^*_{CO} and n,ψ_3. This mixing accounts for the enhanced UV absorption of these β,γ-unsaturated ketones relative to their saturated analogues.

(d) The S_2 state is almost exclusively (95%) localized in the diene moiety (ψ_2,ψ_3). Since the excitation in S_1 and S_2 is localized in different regions of these molecules and since the excited states may have different relaxed geometries, the usually facile internal conversion $S_2 \rightarrow S_1$ may be retarded in **1** and **16**, allowing reaction from S_2 to compete effectively with internal conversion.

(e) The lowest triplet (T_1) is calculated to be largely a diene π,π^* state, corresponding to S_2. The calculated energies are somewhat higher than those estimated[19] from sensitization and quenching experiments. However, experimental values are obtained for equilibrated states, i.e., in their lowest vibrational levels, while the calculated energies represent Franck–Condon maxima.

(f) No less than three triplets are located below the lowest singlet state. The enegry gap between the singlet

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(35) D. I. Schuster, J. Eriksen, P. S. Engel, and M. A. Schexnayder, *J. Am. Chem. Soc.*, **98**, 5025 (1976).

(36) J. Eriksen, Ph.D. Thesis, New York University, 1976.

(37) W. R. Ware, *Creat. Detect. Excited State*, **1A**, 213 (1971).

(38) L. J. Cline Love and L. A. Shaver, *Anal. Chem.*, **48**, 365A (1976).

(39) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974); H. E. Zimmerman and T. P. Cutler, *J. Chem. Soc., Chem. Commun.*, 598 (1975).

(40) The INDO/S calculations were performed in collaboration with Dr. K. Krogh-Jespersen and Professor Mark Ratner of this department. A more detailed description of these calculations can be found elsewhere.[19,36,41]

(41) K. Krogh-Jespersen, Ph.D. Thesis, New York University, Jan 1976; K. Krogh-Jespersen and M. A. Ratner, *J. Chem. Phys.*, **65**, 1305 (1976); K. Krogh-Jespersen and M. A. Ratner, *Theor. Chim. Acta*, **47**, 283 (1978).

(42) J. A. Pople and D. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

(43) *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

(44) K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *J. Am. Chem. Soc.*, **94**, 6233 (1972).

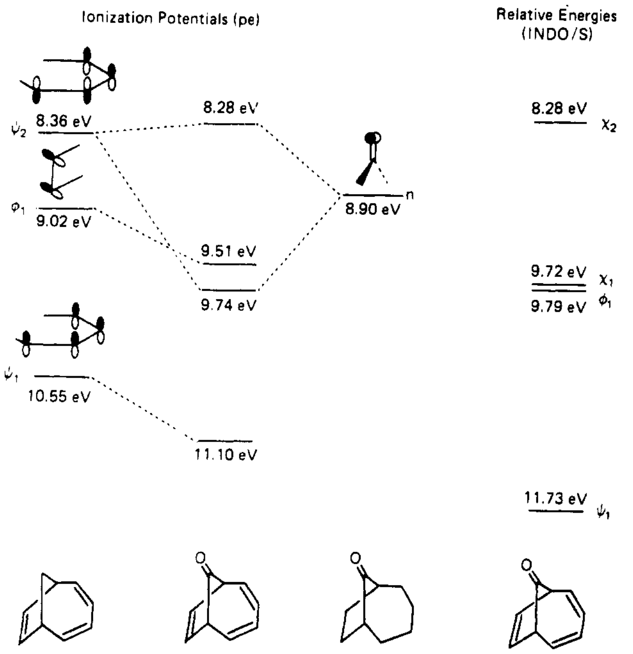


Figure 3. Relative energies and assignments of the four highest occupied molecular orbitals of **11** as determined by photoelectron spectroscopy[45] and INDO/S calculations.

and triplet n,π^*_{CO} states (S_1 and T_3) is calculated to be 0.4 eV, in good agreement with commonly accepted values for ketones.[29]

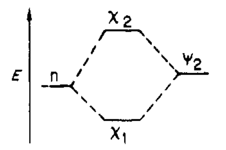
(g) No triplets are energetically located between S_1 and S_2, suggesting that intersystem crossing from S_2 should be relatively unimportant. Thus, the reactions seen on excitation into S_2 are concluded to occur from S_2 and not from an upper triplet state populated by intersystem crossing from S_2.

(h) The observed wavelength-dependent photochemistry of **1** and **16** is in agreement with the results of these calculations, as discussed earlier.

Results of INDO/S Calculations on 7 and 11. Results of calculations on **7** and **11**, which contain a planar diene moiety (C_s symmetry), are shown in Table I. The important conclusions emerging from these calculations are summarized below.

(a) Calculated and observed transition energies are in fair agreement.

(b) Both **7** and **11** show a strong interaction in the ground state between the oxygen lone pair (n) and the highest occupied molecular orbital (ψ_2) of the diene moiety, which have the same symmetry. This interaction leads to two molecular orbitals, χ_1 and χ_2. The calculations reveal no interaction between the alkene and diene moieties in the ground state of **11**, in excellent agreement with experimental photoelectron (pe) spectroscopy data[45] on **11**. The assignment of the close-lying second and third orbitals was not possible from pe data and was based on CNDO calculations.[45] The relative energy levels and assignments of the four highest occupied molecular orbitals of the ground state of **11** determined by the pe study and our calculations are shown in Figure 3.



$$\chi_1 = n + \lambda\psi_2$$

$$\chi_2 = \psi_2 - \lambda n$$

(c) Due to mixing of the n and ψ_2 orbitals in the ground states of **7** and **11**, the two lowest singlet excited states (S_1 and S_2) are very similar with respect to configurational composition of the electronic states, thus predicting photochemical behavior insensitive to excitation wavelength in the region 250–300 nm, as found experimentally.

(d) In **11**, S_3 is calculated to be an almost pure ($\sim$98%) charge-transfer state arising by a transition from χ_2 to the unoccupied alkene molecular orbital. There is the possibility of some interesting photochemical behavior upon direct population of this state by using short-wavelength UV excitation.

(e) Four triplets are located energetically below the lowest singlet in **11**, but no triplets are located between S_1 and S_2 in either **7** or **11**.

(f) Since excitation of both the carbonyl group and the diene moiety is involved in the S_1 state of **7** and **11**, it is not surprising that the reaction pathways from this state include both decarbonylation and cyclobutene formation.

Discussion

Fluorescence. Since 3,5-cycloheptadienones[19b] as well as other β,γ-unsaturated ketones[35,36] fluoresce in dilute solution at room temperature, their singlet excited-state lifetimes can be measured directly, providing a powerful tool in mechanistic and photophysical studies of these ketones. The singlet lifetime (τ_s) is governed by the rate constants for fluorescence (k_f), radiationless decay to the ground state (k_{ds}), intersystem crossing to the triplet manifold (k_{ST}), and reaction (k_r^S), according to eq 6. The

$$\tau_s^{-1} = \sum_i k_i = k_f + k_{ds} + k_{ST} + k_r^S \tag{6}$$

$$k_i = \phi_i \tau_s^{-1} \tag{7}$$

rate constant (k_i) for any singlet-derived process with quantum efficiency ϕ_i is given by eq 7. For chemical reactions, eq 7 is not valid if an intermediate is generated which can revert to starting material in competition with progress to product. In such a case, and in the absence of data concerning the magnitude of the partitioning ratio R, eq 7 yields minimum values of k_r^S (see below). Thus, from the measured lifetimes and fluorescence quantum yields, the rate constants for fluorescence (k_f) could be calculated. Values of $\sim 10^6$ s^{-1} for these rate constants (Table II) are very similar to those obtained for a large variety of β,γ-unsaturated ketones and are quite insensitive to changes in molecular structure in these systems.[35,36] Additional fluorescence data (quenching efficiency by oxygen, natural fluorescence lifetimes, Stokes' shifts, average fluorescence wavelengths, fluorescence centers of gravity, and fluorescence bandwidths) were obtained for some twenty-odd β,γ-unsaturated ketones and will be reported elsewhere.[46]

Decarbonylation. Extrusion of carbon monoxide has been observed as a major photoreaction on direct irradiation of all 3,5-cycloheptadienones studied to date.[3] Since this reaction has not been observed with triplet sensitization, and since it is not quenched by typical triplet quenchers, it has been concluded that it occurs directly from the singlet excited state S_1.[3,7,8] On the basis of this description and the additional assumption that decarbonylation is a concerted process, rate constants for decarbonylation of **1** and **16** were calculated from quantum

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(45) W. Schafer, H. Schmidt, A. Schweig, R. W. Hoffmann, and H. Kunz, *Tetrahedron Lett.*, 1953 (1974).

(46) J. Eriksen, *J. Phys. Chem.*, in press.

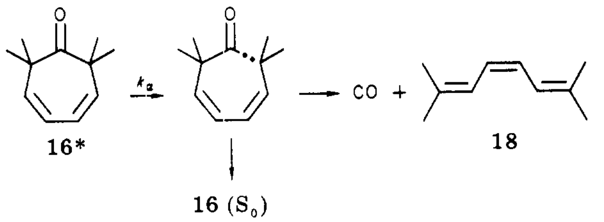
Table III. Reactivity Data for Decarbonylation and Intersystem Crossing of 3,5-Cycloheptadienones

compd	τ_s,[a] ns	ϕ_{-CO}	$10^8 k_{-CO}$, s^{-1}	ϕ_{ST}	$10^8 k_{ST}$, s^{-1}
1	1.05 ± 0.05	0.74[b]	7.0	⩽0.02	⩽0.2
16	0.11 ± 0.05	0.11	10.0	0.36	33
7		0.66[b]		⩽0.015	
11		(80%)[c,d]			
15	0.82 ± 0.05	(25%)[c,e]		0.24[f]	2.9
30		(10%)[c,e]			

[a] In nitrogen-saturated cyclohexane. [b] Reference 7. [c] Chemical yield. [d] Reference 13. [e] Reference 16. [f] Reference 3, p 30.

yields and fluorescence lifetimes by using eq 7 and are given in Table III along with reactivity data for other cycloheptadienones.

The assumption as to concertedness and the singlet assignment must both be examined. An alternative decarbonylation mechanism in the case of 16 involves initial α cleavage to a diradical which then loses CO in a second step, competitive with reversion of the diradical to starting material. This stepwise mechanism has support in the work of Engel and Schexnayder[47] on acyclic β,γ-enones in which intermediate acyl–alkyl radical pairs, which go on to give decarbonylation and coupling products, were intercepted by radical traps (nitroxyls).[48] The analogous radical-pair decarbonylation mechanism for the cycloheptadienones cannot be rigorously excluded, although a concerted cheleotropic extrusion of CO is both theoretically attractive[12] and structurally favorable (see below). In the case of 7 where the total quantum efficiency for reaction on direct irradiation is 0.94 ±0.09,[7] such energy wastage by diradical reversion according to a stepwise mechanism is minimal in any event. In the case of 16, however, where ϕ_{-CO} is only 0.11, such reversion is a more distinct possibility, while 1 occupies a middle position (ϕ_{-CO} = 0.74). We are in the course of experiments involving the use of radical traps and studies of CIDNP effects[49] which may resolve this issue. If the diradical mechanism prevails, the rate constants for loss of CO in Table III will have to be adjusted upward to accurately reflect the rates of α cleavage. Presently, however, we still favor the concerted mechanism in these systems in the absence of evidence *requiring* a stepwise pathway.



16*

18

16 (S_0)

While the evidence is consistent with decarbonylation arising directly from S_1 ($^1n,\pi^*$), an alternative mechanism involving reaction via the n,π^* triplet state (T_3) following intersystem crossing cannnot be ignored. One must then postulate that in those cases (1, 7, 11) where products of sensitized photolysis are not seen on direct excitation into S_1 (a) intersystem crossing occurs to T_3 but not to T_1, in apparent violation of El-Sayed's rules,[50] and (b) reaction from T_3 occurs to the complete exclusion (partial in the case of 16) of internal conversion to T_1. The suggestion was made recently[51,52] that reactions (e.g., [1,3]-sigmatropic acyl migrations) of electronically excited β,γ-enones involving α cleavage proceed via the n,π^* triplet (T_2) rather than the n,π^* singlet (S_1) and that the experimental facts may even compel the assignment of the triplet pathway.[52] Attempts to distinguish the alternatives through correlation of fluorescence lifetimes and reaction quantum yields were inconclusive,[35,52] but very recently a study comparing the course of a thermal dioxetane decomposition with direct and triplet-sensitized photolyses of a cyclopentenyl ketone established that in this system the T_2 (n,π^*) state is definitely reactive with respect to α cleavage.[53,53a] However, product ratios reveal that α cleavage on direct photolysis occurs mainly in this system from S_1.[53] By analogy, it is likely that the T_3 state of the cycloheptadienones possesses α-cleavage reactivity; the question is whether or not this state is populated or not on excitation into S_1 and if it reacts prior to decay to lower triplets. Unlike the situation with several simple β,γ-enones,[3,5,53,54] there is no evidence for α cleavage of any cycloheptadienones under conditions of triplet sensitization. In the absence of experimental evidence which would compel us to adopt an interpretation involving decarbonylation from $^3n,\pi^*$ (T_3) in these systems, we find the alternative singlet mechanism more attractive.

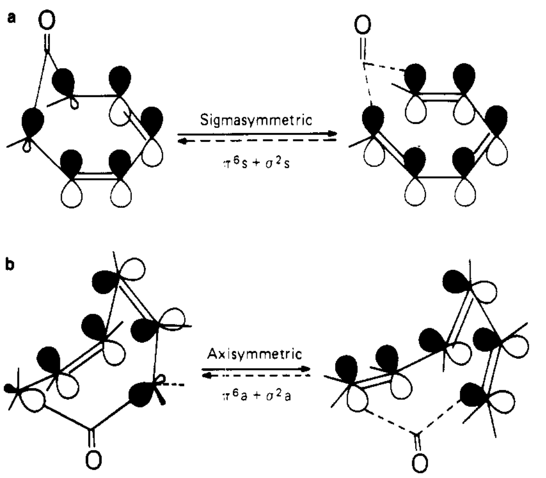


Figure 4. Concerted mechanisms for decarbonylation of photoexcited 3,5-cycloheptadienones: (a) sigmasymmetric extrusion of CO from dienones of C_s symmetry; (b) axisymmetric extrusion of CO from dienones of C_2 symmetry.

If it is a linear concerted singlet process, decarbonylation is predicted theoretically[7,12] to occur in a disrotatory fashion by sigmasymmetric ($_\pi 6_s + _\sigma 2_s$) expulsion of CO in 3,5-cycloheptadienones possessing a planar diene moiety (7, 11, 15, 30), requiring very little orbital reorganization, as

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(47) M. A. Schexnayder and P. S. Engel, *J. Am. Chem. Soc.*, **97**, 4825 (1975).

(48) See also A. J. A. van der Weerdt and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1357 (1977).

(49) See A. J. A. van der Weerdt, H. Cerfontain, J. P. W. van der Ploeg, and J. A. den Hollander, *J. Chem. Soc., Perkin Trans. 2*, 155 (1978); A. Henne and K. Schaffner, private communication of unpublished results.

(50) M. A. El-Sayed, *Acc. Chem. Res.*, 1, 8 (1968); see also ref 29(b), p 165 ff, and ref 50a. (a) A referee claims that the El-Sayed rules do not require that in a β,γ-enone $^1n,\pi^* \rightarrow {}^3n,\pi^*$ is necessarily slower than $^1n,\pi^* \rightarrow {}^3\pi,\pi^*$ (alkene). Furthermore, he notes that the low value of k_{ST} for 1 in Table III is hardly consistent with an "allowed" singlet → triplet transition.

(51) K. Schaffner, *Tetrahedron*, **32**, 641 (1976).

(52) J. C. Dalton, M. Shen, and J. J. Snyder, *J. Am. Chem. Soc.*, **98**, 5023 (1976).

(53) M. J. Mirbach, A. Henne and K. Schaffner, *J. Am. Chem. Soc.*, **100**, 7127 (1978). (a) This conclusion is supported by photo-CIDNP studies: A. Henne, N. P. Y. Siew, and K. Schaffner, *J. Am. Chem. Soc.*, **101**, 3671 (1979).

(54) See, for example, P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.*, **97**, 145 (1975).

Table IV. GLC Columns

column	width, in.	length, cm	substrate	support	mesh size
1	1/8	300	5% SE-30	Chromosorb W	60-80
2	1/8	180	10% Carbowax 20M	Chromosorb P	60-100
3	1/4	300	20% PDEAS	Chromosorb P	80-100
4	1/4	200	20% Apiezon L	Chromosorb W	60-80
5	1/4	100	20% Apiezon L	Chromosorb W	60-80
6	1/8	120	10% Carbowax 20M	Chromosorb P	60-80
7	1/8	50	10% UC-W 98	WAW-DMCS	80-100

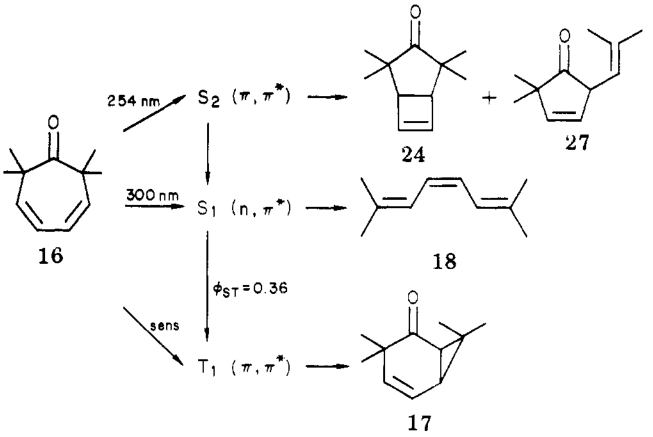
shown in Figure 4a. In the case of twisted dienones such as **1**, **2**, and **16**, we suggest that a concerted axisymmetric (${}_{\pi}6_a + {}_{\sigma}2_a$) decarbonylation is operative (see Figure 4b). A concerted sigmasymmetric expulsion of CO from **16**, as assumed by Paquette et al.,[18] would bring two methyl groups into close proximity, introducing repulsive steric forces which would presumably raise the energy of activation and reduce the rate constant (k_{-CO}) for sigmasymmetric CO extrusion of **16** compared with **1**. This is not observed (see Table III). However, the data are consistent with an axisymmetric extrusion of CO, in which the methyl groups in **16** would be sufficiently separated to minimize such steric interference. Lemal and McGregor[55] predicted that an axisymmetric expulsion of CO should be possible for compounds of suitable geometry.

Intersystem Crossing. Assuming the validity of the singlet mechanism for decarbonylation, quantum yields (ϕ_{ST}) for intersystem crossing (or upper limits in cases where the process could not be detected) were determined for compounds **1**, **7**, and **16** by using eq 3-5. These are listed in Table III, together with the rate constants (k_{ST}) for intersystem crossing as calculated by using eq 7. It is noteworthy that the presence of the four methyl groups in **16** leads to a >100-fold increase in k_{ST} compared to **1**. This result was not anticipated[19a] on the basis of our INDO/S calculations, which indicated that the methyl groups in **16** had only minor effects on transition energies, oscillator strengths, and orbital configurational compositions. The effect is consistent, however, with Houk's CNDO/S calculations[17a,56] which suggested that the lowest triplet in **1** is π,π^* and in **16** is n,π^* or charge-transfer in nature. The source of the discrepancy in the two sets of calculations remains to be resolved.

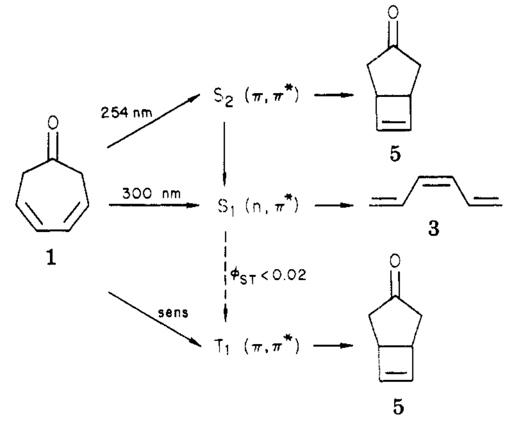
Turro, Yang, and their co-workers[57,58] have shown that α alkylation caused a slight decrease in k_{ST} for alkanones (e.g., acetone, $k_{ST} = (4.5–5.0) \times 10^8\ s^{-1}$; 2-pentanone, $k_{ST} = 3.1 \times 10^8\ s^{-1}$)[53] and for some 3-cyclopentenones.[59] In 3,5-cycloheptadienones, however, assuming a singlet decarbonylation pathway, α methylation leads to a greater than 100-fold *increase* in k_{ST} (compare **1** and **16**, Table III). We therefore conclude that at the present time there is no general correlation between experimental values of k_{ST} and molecular structure for ketones of different structural types and that alkanones are not necessarily good models for predictions of the effect of substituents on values of k_{ST} in other types of systems. The *experimental* determination of the effect of molecular structure on k_{ST} in a wide variety of ketones urgently needs the attention of photochemists.

Summary. The course of the photochemistry of **1** and **16** is best depicted as in Schemes I and II, on the basis of the data, calculations, and arguments given above.

Scheme I



Scheme II



Experimental Section

All melting points and boiling points are uncorrected. Ultraviolet spectra were recorded on a Perkin-Elmer Coleman 124D double-beam spectrophotometer equipped with a digital display of absorbance or transmittance. Infrared spectra were recorded on a Perkin-Elmer Model 735 infrared spectrophotometer. A polystyrene film was used for calibration on all spectra. Proton magnetic resonance spectra were recorded on Hitachi Perkin-Elmer Model R-24 or R-20B high-resolution NMR spectrometers. Tetramethylsilane (Me_4Si) was used as internal standard for all spectra. Carbon-13 magnetic resonance spectra were recorded by Mr. C. Strom on a Varian Associates Model XL-100 spectrometer equipped with a Nicolet Fourier transform accessory. Solutions in chloroform-*d* were used, and reported δ values are relative to Me_4Si. Mass spectra were recorded by Mr. C. Strom on a Varian Associates M-66 double-focusing cycloidal-path mass spectrometer or a Du Pont Model 21-492B mass spectrometer.

Gas-Liquid Partition Chromatography. Analytical GLC analyses were carried out on a Hewlett-Packard Model 5710A gas chromatograph equipped with a Model 5702A oven temperature programmer, a strip chart recorder, Model 7123A, and an electronic integrator, Model 3373B. Preparative separations were carried out by using a Varian Aerograph Model 920 chromatograph equipped with a thermal conductivity detector. Sample collections were made in U-tubes submerged in dry ice-acetone. The GLC

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(55) D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1325 (1966).

(56) Reference 3, p 65.

(57) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 2564 (1970).

(58) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Am. Chem. Soc.*, **92**, 6974 (1970).

(59) T. R. Darling, J. Pouliquen, and N. J. Turro, *J. Am. Chem. Soc.*, **96**, 1247 (1974).

columns used in analytical ($^1/_8$ in.) and preparative ($^1/_4$ in.) scale work are listed in Table IV.

Instrumentation for Photochemical Studies. A Rayonet photochemical chamber reactor, Model RPR-100, was used for all analytical-scale photolyses. The instrument was equipped with a Rayonet merry-go-round, Model MGR-100, supporting up to eight test tubes and providing the same light intensity for each tube. The cylindrical chamber of the reactor housed exchangeable lamps, and the inside wall was coated with a reflective material. A fan at the bottom circulated air for cooling during the irradiation. This study involved the use of three sets of low-pressure mercury lamps with output centered at 254, 300, and 350 nm, respectively. Matched quartz (for 254-nm irradiation) or Pyrex (for 300- and 350-nm irradiation) test tubes of 15-mL capacity were used in the reactor. For preparative-scale photolyses a Rayonet Model RPR-204 preparative reactor was used.

Procedure for Direct Irradiation. In a typical experiment, 5 mL of a 0.01 M solution of the sample under investigation was purged with nitrogen or argon for 10 min prior to photolysis. In exploratory experiments, aliquots were taken from the test tube and analyzed by GLC. In preparative runs the crude photolysates were initially analyzed by GLC and by spectroscopy to assure that no isomerization or decomposition had taken place during the subsequent separation or purification procedures.

Procedure for Sensitized Photolyses. In these irradiations the concentrations of the sample under investigation and the sensitizer were adjusted so that the sensitizer absorbed >99% of the incident light. The solutions were purged with nitrogen for 10 min prior to irradiation. The sensitizers used were acetone (J. T. Baker, reagent grade, freshly distilled, bp 56 °C, E_T = 78 kcal/mol[26]), used as solvent with irradiation at 300 nm, and benzophenone (J. T. Baker, recrystallized from ethanol, mp 49 °C, E_T = 68.5 kcal/mol[26]), used with irradiation at 350 nm.

Procedure for Quenching Experiments. All quenching experiments were carried out in the merry-go-round apparatus. In the standard procedure, 2-mL portions of a stock solution of a sample to be studied were pipetted into 5-mL volumetric flasks. The appropriate amount of quencher (liquid or solid) was added to each flask, and the solutions were diluted to the 5-mL mark. The mixtures were then transferred to Pyrex test tubes, covered with rubber septa, and purged with nitrogen for 15 min. Four to six tubes were run along with duplicates of the solution without added quencher. The solutions were irradiated until the conversion of starting material was about 10%. One milliliter of a stock solution of a GLC standard was added to each tube after irradiation, and the photolysates were analyzed by GLC. At least two injections from each tube were made. The ratios of the photoproducts to the standard were calculated and the ratios (P_0/P_Q) of a product in the absence (P_0) to the product in the presence (P_Q) of quencher were determined. The data were then analyzed according to eq 1. When 1,3-cyclohexadiene (CHD) was used as a quencher, the tubes were also analyzed for CHD dimers. An authentic sample of CHD dimers obtained from Dr. G. C. Barile was used for coinjections in the GLC analyses. The following quenchers were used: naphthalene (J. T. Baker, recrystallized from 2-propanol, mp 80 °C, E_T = 61 kcal/mol[26]), CHD (Chemical Samples Co., fractionally distilled immediately before use, bp 80 °C, E_T = 53 kcal/mol[26]), and 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide (**22**, synthesis described below, E_T = 35–42 kcal/mol[28]).

Quantum yields were measured on an optical bench by using a split-beam technique described earlier.[7] Chemical actinometry using potassium ferrioxalate[60] was used, and the procedure was in all respects analogous to that described by Calvert and Pitts.[61] The quantum yields were measured at 313 nm at 25 °C, and conversions of starting materials were kept below 5%. Product appearances were determined by GLC analysis. Each quantum yield measurement was performed twice, and the experimental error in the measurements was estimated to be ±10%.

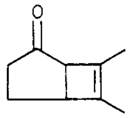
Fluorescence Measurements. (a) Instrumentation. Fluorescence spectra were recorded on a Hitachi/Perkin-Elmer Model MPF-2A spectrofluorimeter which allows for scanning of a grating emission monochromator at constant excitation wavelength for obtaining fluorescence emission spectra and for scanning of a grating excitation monochromator at constant emission wavelength for measuring fluorescence excitation spectra. The sample holder was a 1-cm quartz cuvette with four polished sides.

(b) Purity Considerations. Each solute was carefully purified by appropriate techniques (distillation, crystallization, liquid chromatography, preparative-scale GLC) until a single peak in a GLC analysis was observed on two different columns, corresponding to a purity of >99.9% in most cases. UV absorption spectra of the purified samples were in good agreement with published data where available. Several samples were purified and repurified, resulting in quantitatively reproducible spectra. If an impurity was responsible for the observed luminescence, some measurable change in emission maximum or intensity would have been expected. It is virtually impossible that more than 20 β,γ-unsaturated ketones (including the 3,5-cycloheptadienones in this report) synthesized by entirely different routes from different chemicals could contain a common type of fluorescent impurity which escaped all purification methods. Furthermore, compound **2** was obtained by two different synthetic schemes involving no overlapping reagents or solvents.[62] The fluorescence of the product from each synthesis was quantitatively identical. It should also be noted that fluorescence from β,γ-unsaturated ketones has been reported simultaneously from our[7,19] and other[52,63] laboratories. Cyclohexane (Aldrich, spectrophotometric Gold Label) was used in all fluorescence measurements. This solvent was found to be of excellent quality, showing only end absorption in the UV and no detectable fluorescence in the excitation range 250–350 nm. Thus, this solvent could be used without further purification. However, a Raman scattering band of cyclohexane due to the C–H vibrations was observed at a frequency shift of -2880 cm^{-1} relative to the excitation frequency.[64] Hence, excitation at 300 nm led to a Raman band at 328 nm.

(c) Optical densities of 1.0–2.0 at the excitation wavelength were used to obtain maximum fluorescence intensities. Due to the large Stokes' shifts observed[36,46] for β,γ-unsaturated ketones, reabsorption of emitted light was unimportant.

(d) Correction of Emission and Excitation Spectra. An emission-sensitivity curve was obtained for the spectrofluorimeter by a photodiode calibration technique.[65] All emission spectra were corrected according to this curve. A calibration curve for wavelength-dependent excitation factors was obtained from the fluorescence excitation spectrum of a uniform layer[66] of sodium salicylate on a microscope slide which has a wavelength-independent fluorescence quantum yield (ϕ_f = 0.99 ± 0.03) in the desired excitation range, 250–350 nm.[67]

(e) Fluorescence quantum yields (ϕ_f) were measured by comparing the area under the corrected emission curve plotted vs. a linear wavenumber scale of a standard of known ϕ_f with that of a sample of unknown ϕ_f. The solvent, excitation wavelength (313 nm), slit widths, and optical densities at the excitation wavelength were identical. The standard used was 6,7-dimethylbicyclo[3.2.0]hept-6-en-2-one (**31**), obtained from Mr. S. Hussain in this laboratory. The ϕ_f (7.23×10^{-3}) of **31** was determined by comparing its emission with that of the primary



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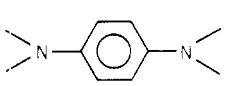

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[60] C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

[61] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966, pp 783–6.

[62] We are grateful to Mr. Oscar Roberto and Ms. Lidia Teresa Calcaterra for supplying samples of **2**.

[63] S. R. Kurowsky and H. Morrison, *J. Am. Chem. Soc.*, **94**, 507 (1972); K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 4281 (1971).

[64] C. A. Parker, "Photoluminescence of Solutions", Elsevier, New York, 1968, p 66.

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[66] F. S. Johnson, K. Watanabe, and R. Tousey, *J. Opt. Soc. Am.*, **41**, 702 (1951).

[67] R. Allison, J. Burns, and A. J. Tuzzolino, *J. Opt. Soc. Am.*, **54**, 747 (1964).

standard *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (**32**; ϕ_f = 0.18 at 313 nm in cyclohexane[68]).

(f) Data Treatment. A computer program was developed for calculating corrected fluorescence spectra and maxima of corrected spectra and for plotting absorption and corrected fluorescence spectra vs. a linear wavenumber abscissa (see Figure 2). The observed absorption and uncorrected fluorescence spectra were read into permanent files point by point. On the average, 80 points were used for an absorption spectrum and 60 points for a fluorescence spectrum. In addition, the computer program calculated natural lifetimes, Stokes' shifts, fluorescence center of gravity, average fluorescence wavelengths, fluorescence bandwidths, and oscillator strengths of absorption bands. The results of these calculations will be published elsewhere.[46]

Lifetime Measurements. Singlet excited-state lifetimes were measured by single-proton counting.[37-39] Since the lifetimes were of the same order or shorter than the pulse width of the flash lamp, a convolution technique was required to extract the correct lifetimes from the observed fluorescence decays.[39] An excitation filter consisting of a Corning glass filter no. 7-54 (2 mm) plus a solution of $NiSO_4 \cdot 6H_2O$ (50 g) and $KCr(SO_4)_2 \cdot 12H_2O$ (15 g) in 100 mL of H_2O (2 cm) was used to isolate the absorption bands of the ketones at ~300 nm. This filter had no transmittance above 350 nm. The emission filter consisting of a Corning glass filter no. 4-70 (2 mm) and a solution of $NaNO_2$ (75 g) in 100 mL of H_2O (1 cm) showed transmittance in the 400–600-nm region.

In a typical run, a sample OD of 1–2 at 300 nm was used, corresponding for most 3,5-cycloheptadienones to a concentration of ~0.01 M. The sample holder was a 1-cm quartz cuvette with four polished sides. The sample was purged with N_2 for 10 min. The photon counting was continued until 10 000–20 000 counts were collected in the peak channel. For most samples, this required 30–60 min. The emission filter was removed, and the lamp profile was measured by replacing the sample cuvette with a 4-mm tube containing MgO powder, which was known to have about 100% reflectivity.[69] Thus, the counting experiment was usually finished within 1 h. In about 100 experiments made over a period of many months using this procedure, changes in the lamp profile during an experiment could only be detected in two or three cases. Such runs were discarded, and the experiment was repeated.

The sample decay and lamp profile values were read into a computer program which performed iterative convolution in a manner similar to that described by Zimmerman and co-workers.[39] The computer program allowed for (a) plotting the lamp profile and sample decay in normal and semilogarithmic plots on an X–Y recorder, (b) calculating a convoluted decay from the lamp profile and a trial value of the decay lifetime, (c) performing iterative convolution until an optimum fit to the sample decay was obtained, and (d) plotting the optimal convoluted decay. Results of this are shown in Figure 2.

The lifetimes obtained with this technique were reproducible to ±0.05 ns, and lifetimes as short as 0.1 ns could be measured. A few model compounds were tested. Thus, with reported values in parentheses, the lifetimes determined in cyclohexane were as follows: **32**, 4.28 ± 0.05 ns (4.3 ns[70]); *p*-terphenyl, 0.96 ± 0.05 ns (0.96 ns[70]).

Cycloheptanone ethylene ketal (33) was synthesized by the route used to prepare the corresponding cyclohexanone derivative.[71] The resulting material was distilled through a short Vigreux column to give 66.0 g (84.6%) of **33**: bp 63 °C (3.3 mm) [lit.[71] bp 51 °C (1.3 mm)]; ν (neat) 2920, 2850, 2460, 1375, 1220, 1170, 1125, 1100, 1080, 1040, 1015, 950, 890, 850, 780 cm^{-1}.

2,6-Cycloheptadienone ethylene ketal (34) was synthesized from **33** according to the procedure described by Garbisch[72] in 61% yield: bp 63–64 °C (1.7 mm) [lit.[72] bp 58 °C (0.75 mm)]; ν (neat) 3010, 2925, 2865, 1660, 1405, 1220, 1100 (s), 980, 835, 820, 700 cm^{-1}.

2,6-Cycloheptadienone (35) was obtained in 48% yield via **34** according to the procedure of Garbisch:[72] bp 61–63 °C (3 mm) [lit.[72] bp 50.5–51 °C (1.0 mm)]; ν (neat) 3010, 2920, 1645 (s), 1610, 1410, 1300, 1200, 860 cm^{-1} (lit.[67] ν 1647 (s)).

2,2,7,7-Tetramethyl-3,5-cycloheptadienone (16) was prepared by the procedure of Paquette et al.[18] The crude material was distilled and redistilled through a short Vigreux column to give **16** in 51% yield; bp 55–56 °C (3 mm) [lit.[18] bp 48–51 °C (1.5 mm)]. The compound was purified by spinning-band distillation on a Perkin-Elmer Model 151 annular still to give a fraction [bp 75 °C (7 mm)] of >99% purity as determined by GLC: ν (neat) 3000, 2950, 2920, 2850, 1695 (s), 1660, 1610, 1475, 1400, 1380, 1050, 1020, 900, 790, 710 cm^{-1}; λ_{max} (MeOH) 243 nm (ϵ 4700), 290 (635); ^1H NMR (CCl_4) δ 5.76 (complex m, 4 H), 1.23 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 212.4 (C=O), 137.4 and 125.4 (C=C), 50.1, 25.4 (Me); *m/e* 164 (M^+), 149 (M^+ – Me), 137, 136 (100%, M^+ – CO), 121 (M^+ – CO – Me), 107, 105, 93, 91, 79, 77.

3,5-Cycloheptadienone (1) was synthesized in 15% yield from tropone[73] by using the procedure described earlier;[74] bp 52–57 °C (12 mm) [lit.[74] bp 52–54 °C (9.5 mm)]. Purification by column chromatography (silica gel, 40 cm × 1.3 cm, 9:1 hexane/ether) gave **1** in >99.8% purity according to analytical GLC: ν (CCl_4), 3000, 2950, 2850, 1710 (s), 1590, 1410, 1240, 1040, 900, 790 cm^{-1}; λ_{max} (C_6H_{12}) 231 nm (ϵ 6000), 290 sh (240); ^1H NMR (CCl_4) δ 5.5–6.5 (m, 4 H), 2.98 (d, 4 H, *J* = 12 Hz); ^{13}C NMR ($CDCl_3$) δ 213.2 (C=O), 128.0, 123.0 (C=C), 45.2; *m/e* 108 (M^+), 107, 106, 80 (M^+ – CO), 79 (100%), 78, 77, 66, 65, 63, 54, 53, 52, 51, 50, 41, 39.

Bicyclo[4.2.1]nona-2,4-dien-9-one (7) was a sample prepared by C. W. Kim[7] and was purified by preparative GLC.

2-Butenedial (19) was prepared from 2,5-dihydro-2,5-dimethoxyfuran[75] in 12% yield by the procedure of Alder et al.:[23] mp 40–42 °C; ν (CCl_4) 3350, 2950, 2800, 2720, 1695 (s), 1250, 860 cm^{-1}; ^1H NMR (CCl_4) δ 6.80 (dd, 2 H), 9.90 (dd, 2 H).

Isopropyltriphenylphosphonium iodide (20) was prepared from 2-iodopropane[76] and triphenylphosphine (Aldrich) in 93% yield by using the procedure of Wittig and Wittenberg;[24] mp 195–196 °C (lit.[24] mp 195–196 °C).

2,7-Dimethyl-2,4,6-octatriene (18). A sample of 4.8 g (0.1 mol) of a 52% mineral oil dispersion of sodium hydride (Alfa) was washed five times with pentane and placed in a 500-mL three-necked round-bottomed flask equipped with a mechanical stirrer, pressure-equalizing dropping funnel, condenser, and two stopcocks connected to a water aspirator and a nitrogen tank. The system was evacuated and refilled with nitrogen until the sodium hydride was finely powdered. The tube to the water aspirator was then connected to a mercury-filled U-tube, and a slightly positive pressure of nitrogen was maintained during the reaction. From the dropping funnel was added 50 mL of dimethyl sulfoxide (freshly distilled at 5 mm from calcium hydride), and the flask was heated in a water bath at 75 °C until the evolution of hydrogen ceased (30 min). To the cooled solution of the dimsyl anion was then added 43.2 g (0.2 mol) of **20** in 100 mL of warm dimethyl sulfoxide. The blood-red solution was stirred for an additional 30 min, after which 4.2 g (0.05 mol) of **19** in 10 mL of dimethyl sulfoxide was added. Stirring of the dark brown solution was continued at room temperature for 2 h and at 60 °C for an additional 2 h. The reaction mixture was poured into 200 mL of water and extracted with five 100-mL portions of pentane. The combined pentane extracts were washed twice with water and dried over anhydrous sodium sulfate. The pentane was evaporated, and part of the residue was purified by preparative GLC (column 3, Table IV) to give **18** as a white solid, mp 36–37 °C. This material was in all respects identical with the photoproduct obtained from irradiation of **16** at 300 nm.

2,3-Dimethyl-2,3-dinitrobutane (37) was prepared in 65% yield from 2-nitropropane (Aldrich) by the procedure of Sayre:[77] mp 207–208 °C (lit.[77] mp 208–209 °C); ν (CCl_4) 2980, 1460, 1380, 1350, 1340 cm^{-1}; ^1H NMR (CCl_4) δ 1.72 (s).

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(69) Reference 64, p 253.

(70) Reference 68, pp 168, 220.

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***N,N'*-Dihydroxy-2,3-diamino-2,3-dimethylbutane (38)** was synthesized from **37** in 35% yield according to the procedure of Lamchen and Mittag:[78] mp 149–150 °C (lit.[78] mp 157–159 °C); ^{1}H NMR (Me$_2$SO-d_6) δ 1.1 (s, 12 H), 1.8–3.1 (v br, 4 H).

3,3,4,4-Tetramethyl-1,2-diazetine 1,2-Dioxide (22).[28,79] To a stirred solution of 5.0 g (0.034 mol) of **38** in 100 mL of water was added dropwise 10.9 g (0.068 mol) of bromine (Baker). A water bath was used to keep the reaction mixture at room temperature. The solution was stirred for 1 h and extracted with four 50-mL portions of chloroform. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Recrystallization from methanol gave 2.0 g (35%) of **22**: mp 184–185 °C dec (lit.[28] mp 190–192 °C dec); ν (CHCl$_3$) 3000, 1555, 1465, 1380, 1220 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.62 (s).

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Synthesis of the Isomeric Phenols of Benz[*a*]anthracene from Benz[*a*]anthracene

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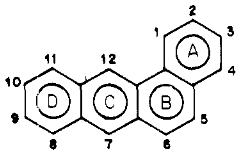
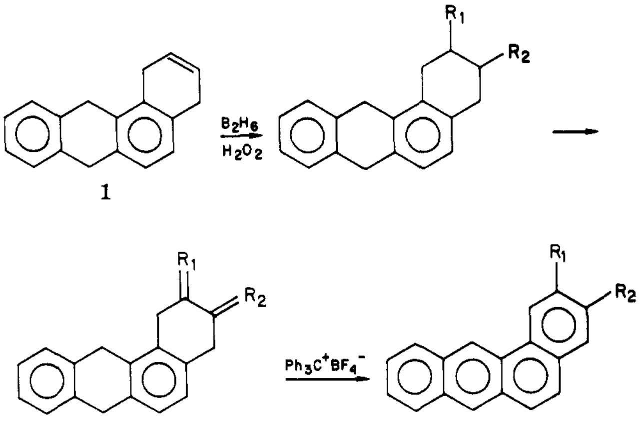
Novel and convenient syntheses of seven isomeric phenols of benz[*a*]anthracene (1-, 2-, 3-, 8-, 9-, 10-, and 11-HO-BA) from the parent polycyclic hydrocarbon are described. These syntheses demonstrate the feasibility of introduction of functional groups into polycyclic arene ring positions not prone to direct substitution through initial regioselective hydrogenation (or metal–ammonia reduction), followed by appropriate synthetic operations to introduce carbonyl or other desired functional groups into benzylic or olefinic ring positions and finally dehydrogenation. Fewer synthetic steps are generally required, and overall yields are superior to those obtained via the conventional synthetic approaches which entail total synthesis of each isomeric derivative from appropriately substituted smaller molecular units. Conversion of the aryl ketonic intermediates to phenols is accomplished by a new general method involving dehydrogenation of the corresponding enol acetate derivatives with *o*-chloranil.

Benz[*a*]anthracene (BA) is an ubiquitous environmental contaminant formed through incomplete combustion of organic matter. It is present in variable concentration in the atmosphere, soil, automobile exhaust, cigarette smoke, and foods.[2] In contrast to structurally related hydrocarbons, such as 7-methyl-BA, 7,12-dimethyl-BA, dibenz[*a,h*]anthracene, and benzo[*a*]pyrene, which are potent carcinogens, BA exhibits only borderline activity as a tumor initiator.[2,3] Despite many years of investigation, the reason for this difference remains uncertain. However, recent evidence suggests that differences in the patterns of metabolism and the reactivity of diolepoxide metabolites with DNA may be critically involved.[3,4]



BA

Chart I. Synthesis of 2- and 3-HO-BA



3a, R$_1$ = O; R$_2$ = H$_2$
b, R$_1$ = H$_2$; R$_2$ = O

4a, R$_1$ = OH; R$_2$ = H
b, R$_1$ = H; R$_2$ = OH
c, R$_1$ = OAc; R$_2$ = H
d, R$_1$ = H; R$_2$ = OAc

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