

- (14) G. Schröder and W. Martin, *Angew. Chem., Int. Ed. Engl.*, **5**, 130 (1966).  
 (15) A sample of **14** and its infrared spectrum were kindly provided by Professors A. Padwa and G. L. Lange, respectively. See (a) A. Padwa, W. Koehn, J. Masaracchia, C. L. Osborn, and D. J. Trecker, *J. Amer. Chem. Soc.*, **93**, 3633 (1971); (b) G. L. Lange and E. Neidert, *Tetrahedron Lett.*, 4215 (1971).  
 (16) Compound **15** has not been previously observed but has been suggested as an intermediate: A. Krebs and D. Byrd, *Justus Liebigs Ann. Chem.*, **707**, 66 (1967).  
 (17) S. W. Staley, L. A. Grezzo, and A. W. Orvedal, manuscript in preparation.  
 (18) The chemical shifts are given relative to tetramethylsilane. We are most grateful to Professor J. B. Grutzner for obtaining these spectra.  
 (19) (a) Chemical shifts are given in ppm downfield from internal TMS in 3:1 CCl<sub>4</sub>-CDCl<sub>3</sub>: H. Günther, G. Jlkeli, H. Schmickler, and J. Prestien, *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973); see also (b) A. J. Jones, P. J. Garratt, and K. P. C. Vollhardt, *ibid.*, **12**, 241 (1973); (c) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, D. Jordan, and W. Kitching, *J. Amer. Chem. Soc.*, **96**, 1595 (1974); (d) E. L. Motell, D. Lauer, and G. E. Maciel, *J. Phys. Chem.*, **77**, 1865 (1973).  
 (20) J. B. Stothers, "Carbon-13 Nmr Spectrometry," Academic Press, New York, N.Y., 1972, p 27.  
 (21) For <sup>13</sup>C spectra of methyl-substituted cyclopentadienyl anions, see W. T. Ford and J. B. Grutzner, *J. Org. Chem.*, **37**, 2561 (1972).  
 (22) S. W. Staley and A. W. Orvedal, unpublished results.  
 (23) (a) H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, **No. 21**, 109 (1967); (b) G. Binsch, "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," E. D. Bergman and B. Pullman, Ed., The Israel Academy of Sciences and Humanities, Jerusalem, 1971, p 25.  
 (24) Reference 20, p 49.  
 (25) Cyclooctatetraene dianion has also been oxidized with metal salts (T. Antkowiak and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5361 (1972)), with the tropylium ion (R. W. Murray and M. L. Kaplan, *J. Org. Chem.*, **31**, 962 (1966)), and with other organic compounds (E. E. Gol'teuzen, Z. V. Todres, A. Ya. Kaminskii, S. S. Gitis, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1083 (1972), and references cited therein).

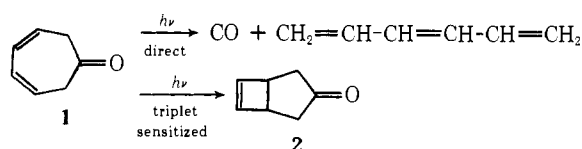
## Photochemistry of Bicyclo[4.2.1]nona-2,4-dien-9-one, a Bridged 3,5-Cycloheptadienone<sup>1</sup>

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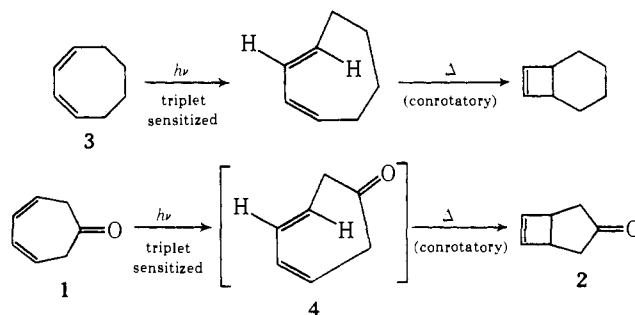
**Abstract:** The direct and triplet-sensitized photochemistry of the title compound **7** has been studied and is compared with similar investigations of simple 3,5-cycloheptadienones and other 2,7-bridged derivatives to assess the control of molecular geometry on singlet and triplet photochemistry in these systems. Direct photolysis of **7** gives cyclooctatriene **10** by decarbonylation ( $\Phi = 0.66$ ), the *endo*-cyclobutene derivative **11** ( $\Phi = 0.14$ ), and a third labile unidentified product. Photolysis of **7** sensitized by acetone, benzophenone, Michler's ketone, or triphenylene gives a new ketone, dihydrobarbaralone **18**, by an oxa-di- $\pi$ -methane rearrangement. Products **10** and **11** are seen only in the case of acetone sensitization, suggesting either some singlet transfer to **7** or competitive light absorption by **7**. Products were identified on the basis of spectral data and chemical transformations. Fluorescence emission from **7** can be observed at room temperature and 77°K, and similar emission is seen from all of the other 3,5-cycloheptadienones studied. It is concluded that the singlet-derived photodecarbonylation, which occurs from systems in which the diene moiety is either twisted or constrained to be planar, is probably a concerted chelotropic reaction. Deactivation to the ground state of **7** from S<sub>1</sub> is relatively inefficient and unimportant, as is intersystem crossing to T<sub>1</sub>. Electrocyclic closure of the excited singlet to the cyclobutene **11**, which is not observed with twisted 3,5-cycloheptadienones, suggests that such singlet reactivity is seen only when the diene moiety is planar and is probably a simple concerted disrotatory cyclization. When the diene moiety is twisted, cyclobutene formation can be observed but only on sensitized photolysis *via* T<sub>1</sub>, supporting the earlier hypothesis that the reaction in such cases involves further twisting toward a *cis-trans* geometry, followed by thermal conrotatory ring closure. These reactions support Dauben's concept of ground state conformational control of photochemical reactions. The 1,2-acyl shift (oxa-di- $\pi$ -methane rearrangement) is seen only on triplet sensitization and is shown for the first time to be highly efficient ( $\Phi = 0.89$  using Michler's ketone in benzene). The mechanism of the transformation is discussed and comparison is made with some anomalous results reported previously.

The photochemistry of 3,5-cycloheptadienone (**1**) and related compounds has been a subject of continuing interest for well over a decade. In the original study of Chapman and his coworkers,<sup>4</sup> it was found that **1** underwent efficient photofragmentation to carbon monoxide and a mixture of acyclic hexatrienes, a reaction which could not be quenched by either piperylene or naphthalene. Schuster and coworkers later found that triplet-sensitized photolysis of **1** followed an entirely different course, leading to the valence tautomer bicyclo[3.2.0]hept-6-en-3-one (**2**).<sup>5</sup> Since none of

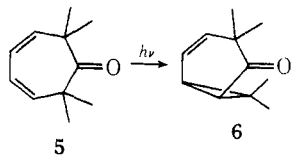


**2** was formed on direct photolysis of **1**,<sup>4,5</sup> it was unambiguous in this case that the photodecarbonylation occurred exclusively *via* a singlet excited state to the exclusion of in-

tersystem crossing to the triplet manifold, from which in turn only valence tautomerization occurs. *Cis,cis*-diene triplets with favorable geometries (such as 1,3-cyclooctadiene **3**)<sup>6</sup> had been shown to undergo photoisomerization to a *cis-trans* diene followed by an orbital symmetry-allowed thermal electrocyclic ring closure to a *cis*-fused cyclobutene derivative. However, attempts to trap the analogous intermediate *cis,trans*-3,5-cycloheptadienone (**4**) derived from **1**

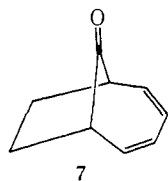


were unsuccessful,<sup>7</sup> indicating either that **4** was not formed, or that it was too short lived to be trapped by the reagents utilized. The most reasonable interpretation seemed to be that the triplet state of **1** begins to twist so as to form **4**, but crossover to the ground state potential surface, which leads directly to **2**, occurs before the potential minimum corresponding to **4** is reached. It is likely that the ground state surface has a maximum in the region corresponding to **4**, facilitating deactivation from T<sub>1</sub> to S<sub>0</sub> as the geometry of the triplet approaches that of **4**.<sup>8</sup> Paquette and coworkers<sup>9</sup>

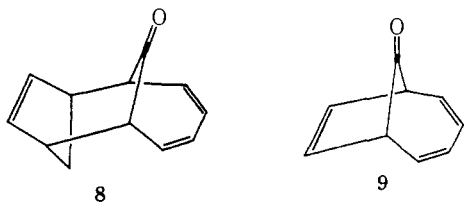


reported that the tetramethyl-3,5-cycloheptadienone **5** underwent rearrangement to the same product **6** on both direct and triplet-sensitized photolysis. The absence of any quenching effect in the direct photolysis on addition of piperylene or naphthalene<sup>9</sup> suggested either that the singlet was the reactive state under these conditions, or that the triplet state which formed after intersystem crossing reacted very rapidly, precluding transfer of triplet excitation. The failure of **5** to undergo either photodecarbonylation or closure to a cyclobutene derivative was rationalized on the basis of the geometric requirements of these reactions (see Discussion). However, the possibility of rearrangement to **6**, formally a 1,2-acyl shift, from both singlet and triplet excited states is most unusual. In a large number of cases, it has been found that the photochemical 1,2-acyl shift of  $\beta,\gamma$ -unsaturated ketones to give cyclopropyl ketones (oxa-di- $\pi$ -methane rearrangement) originates exclusively from triplet excited states.<sup>10</sup>

In order to better understand the role of molecular geometry in regulating the course of photochemical reactions of  $\beta,\gamma$ -unsaturated ketones in general and 3,5-cycloheptadienones in particular, we began some years ago a study of the photochemistry of the title compound **7**, a 2,7-bridged 3,5-cycloheptadienone. The diene moiety in **7** is necessarily



planar, in contrast to **1** and **5** where molecular models and spectroscopy indicate that the dihedral angle between the planes defined by the double bonds is about 45°.<sup>4,5,11</sup> The specific molecular motions suggested<sup>5</sup> for the singlet and triplet reactions of photoexcited **1** should be either substantially modified or are impossible with **7**. Thus, the photochemical behavior of **7** *vis-à-vis* **1** serves as a test of the mechanistic postulates proposed earlier.<sup>4,5,7,9</sup> These results will be compared with recently published parallel studies of the photochemistry of systems related to **7**, which involve the tropone-cyclopentadiene adduct **8**,<sup>12,13</sup> and bicyclo[4.2.1]nona-2,4,7-trien-9-one (**9**).<sup>14-16</sup> Also, this is the only

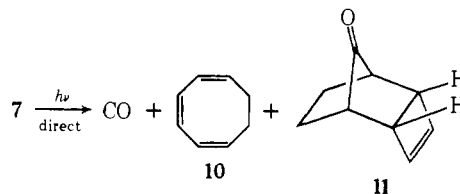


study to date reporting quantitative as well as qualitative measurements of photochemical reactivity of 3,5-cycloheptadienones.

## Results

Bicyclo[4.2.1]nona-2,4-dien-9-one (**7**) was prepared from ketone **9**<sup>16</sup> by the indirect reduction methods discussed elsewhere.<sup>17</sup>

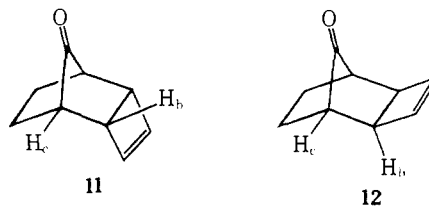
**Direct Photolysis of 7.** Irradiation of **7** through Pyrex using a high-pressure mercury lamp was carried out in ethyl ether, cyclohexane, and methanol at concentrations of **7** from  $1 \times 10^{-4}$  to 0.12 M, at 25, 0, and  $-77^\circ$ . Under all conditions, three photoproducts were formed, two of which were identified. These were 1,3,5-cyclooctatriene (**10**) and the valence tautomer of **7**, tricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-9-one (**11**). The third product, whose yield never exceeded 10% in any photolysis, was thermally unstable, and its isolation and identification were not achieved.



The major product of these photolyses was triene **10**, which was isolated by preparative gas-liquid partition chromatography (glpc), and compared directly by glpc and spectrally with an authentic sample of **10**.<sup>18</sup> The chemical yield of **10** was 40–70%, as the material formed rapidly at first but then decreased as photolysis was continued owing to formation of secondary photoproducts,<sup>19</sup> which were observed in the later stages of reaction. Quantum yields for formation of **10** in ethyl ether at 313 nm determined on an optical bench were 0.66 after 20 min of irradiation and 0.60 after 40 min.<sup>20</sup>

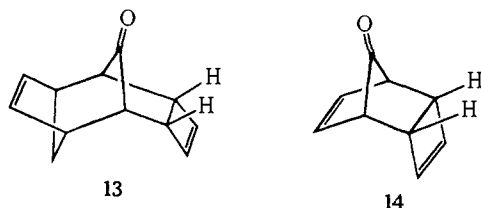
The tricyclic ketone **11** was isolated from photolysates by preparative glpc, and identified on the basis of spectral properties and an alternative synthesis. Mass spectroscopy indicated **11** was an isomer of starting material, and the absence of appreciable absorption in the ultraviolet spectrum (end absorption with a shoulder at 280 nm) indicated lack of conjugation. The carbonyl stretch in the infrared at 1770  $\text{cm}^{-1}$ , shifted from that in **7** at 1750  $\text{cm}^{-1}$ ,<sup>17</sup> indicated a more strained ring system. The nmr spectrum showed two vinyl hydrogens ( $H_a$ ) as a sharp singlet at  $\delta$  6.30, bridgehead hydrogens on the cyclobutene ( $H_b$ ) at 3.12, bridgehead hydrogens adjacent to the carbonyl ( $H_c$ ) at 2.17, and four aliphatic protons ( $H_d$ ) at 1.59 ppm. These assignments are consistent with those of a number of related compounds.<sup>12,16,21</sup>

The stereochemistry of the cyclobutene ring (*i.e.*, endo as in **11** or exo as in **12**) can be assigned as *endo*-(**11**) on the basis of the coupling constant  $J_{bc} = 4.7$  Hz. From the geometries of **11** and **12**, values of  $J_{bc}$  of 5 and 1 Hz, re-



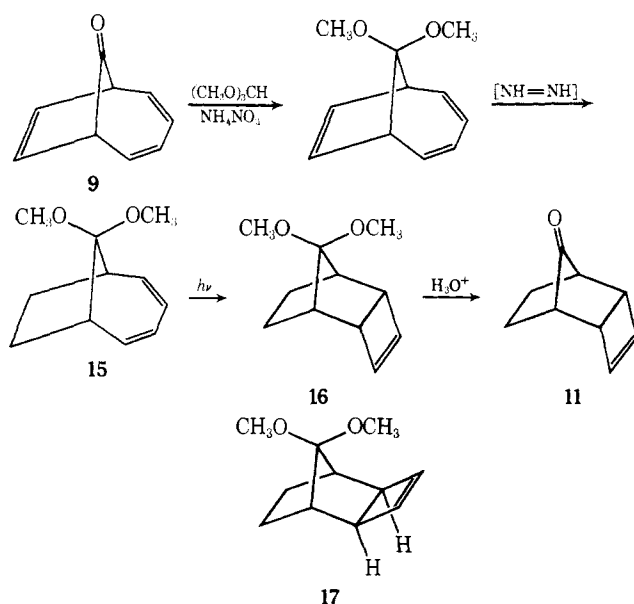
spectively, are predicted from the Karplus relationship.<sup>22</sup> The value  $J_{bc} = 4.7$  Hz found for **11** agrees with that found for a number of related compounds assigned *endo* configu-

rations, including the valence tautomers **13** and **14** derived photochemically from ketones **8** and **9**, respectively.<sup>12,16</sup>



An independent synthesis of **11**, involving photolysis of ketal **15**,<sup>17</sup> is outlined in Scheme I. Since the only chromophore in **15** is a *cis*-butadiene moiety, electrocyclic ring closure from the excited state to a cyclobutene is the expected reaction,<sup>23</sup> and formation of the *endo* isomer **16** rather than *exo*-**17** was anticipated on the basis of steric hindrance by the neighboring methoxyl group. Indeed, hydrolysis of **16** gave ketone **11** with exactly the same glpc retention time and nmr, ir, and uv spectra as the material obtained directly from **7**.

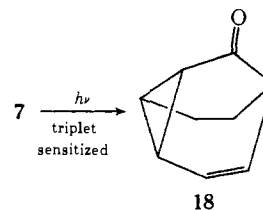
Scheme I



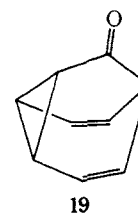
The quantum yield for formation of **11** from  $10^{-2}$  M **7** in ethyl ether at 313 nm was 0.14 after 20 min of irradiation and 0.096 after 40 min.<sup>20</sup> Chemical yields of **11** were as high as 30–40% when **7** was irradiated at Dry Ice temperatures. At low temperature, the third unidentified product (see above) was not formed. At room temperature, values of  $\Phi$  for formation of the unknown product under the conditions given above were 0.14 and 0.093,<sup>20</sup> making the assumption that it is also an isomer of **7**.

**Triplet-Sensitized Photolysis of 7.** Reactions were carried out in acetone, cyclohexane, and benzene at 0 and 25° using benzophenone, triphenylene, Michler's ketone (MK), and acetone as sensitizers. Degassing of solutions was necessary because of quenching of reaction by dissolved oxygen. A single photoproduct **18** was formed in runs with MK and triphenylene. With benzophenone, in addition to **18** another minor product with a very long glpc retention time was observed, which could be an adduct of benzophenone with **7** or **18**. Using acetone as the sensitizer and solvent, small amounts of **10** and **11** were observed in addition to **18**. MK was the ideal sensitizer in that relatively small amounts of MK were required because of its high absorbance in the 300–400-nm region, and also because of easy extractibility

from photolysates with dilute acid, facilitating product isolation.

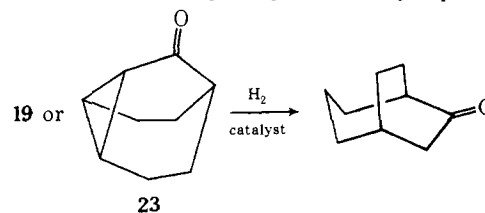


The ketone photoproduct **18** was isolated and purified by glpc. The compound, mp 47–47.5°, is an isomer of starting material according to its mass spectrum and is unconjugated according to its uv spectrum (no maxima above 210 nm; shoulder 260–280 nm). The carbonyl stretch in the infrared at  $1700\text{ cm}^{-1}$  (with a shoulder at  $1750\text{ cm}^{-1}$ ) indicates the carbonyl is in a less strained ring than in **7**. The nmr spectrum of **18** showed only a multiplet for two vinyl hydrogens at  $\delta$  5.83, a one-proton multiplet at 2.63 (presumably the allylic proton  $\alpha$  to the carbonyl), and the balance as a broadened singlet at 2.06 ppm. However, in the presence of the shift reagent  $\text{Eu}(\text{fod})_3$  at least six different resonances could be detected over a range of 11.3 ppm. The spectral data for **18** can be compared with that of barbaralone **19**,



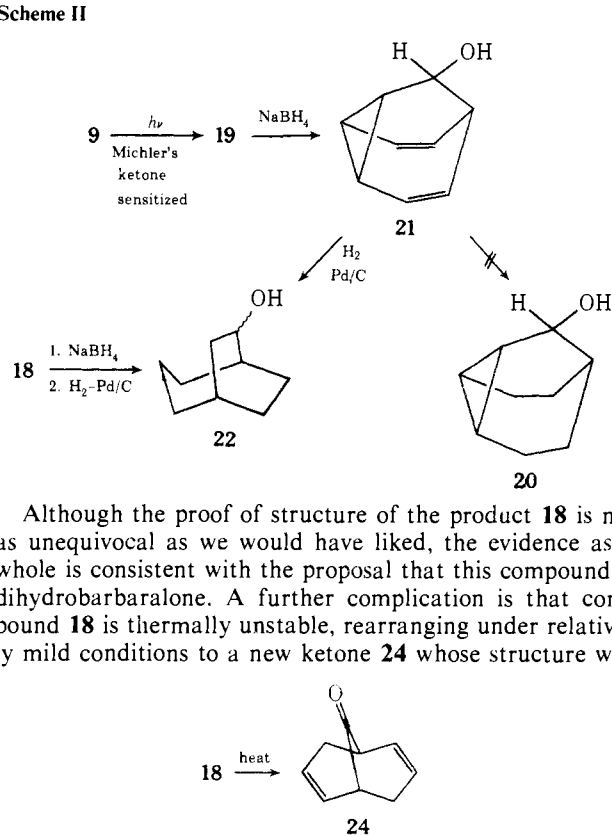
mp 50–51°,<sup>16</sup> which shows a carbonyl stretch at  $1700\text{ cm}^{-1}$  and nmr resonances at  $\delta$  5.92 (4 H), 2.91 (3 H), and 2.46 (1 H) at  $-70^\circ$  under conditions where the degenerate Cope rearrangement of **19** is slow on the nmr time scale.<sup>24</sup>

An independent proof of structure was planned involving reduction to the saturated alcohol **20**, which was to be prepared independently from the known<sup>24</sup> ketone **19** as shown in Scheme II. The actual reactions took a different course. The formation of barbaralone by sensitized photolysis of **9**<sup>15,16</sup> followed by reduction with sodium borohydride in methanol gave barbaralol **21**, whose properties including the nmr spectrum agreed generally with those reported for this compound<sup>24,25</sup> (see Experimental Section). Catalytic hydrogenation of **21** gave 80% of a product, purified by glpc (mp  $190^\circ$  with sublimation), *m/e* (parent peak) 122, which can not be tetrahydrobarbaralol **20** (mp 206–207°)<sup>26</sup> but is tentatively suggested to be bicyclo[3.2.2]nonan-6-ol (**22**) (mp  $191$ – $192^\circ$  with sublimation).<sup>27</sup> Consistent with this assignment is the report that catalytic hydrogenation of barbaralone **19** and tetrahydrobarbaralone **23** gives bicyclo[3.2.2]nonan-6-one as a principal and major product, re-



spectively.<sup>24,28</sup> Sodium borohydride reduction of **18** followed by catalytic hydrogenation gave a mixture of four compounds, the major component having the same glpc retention time as the product of reduction of **21**. The mass spectrum of the mixture derived from **18** showed a peak at *m/e* 138 which might indicate the presence of **20** in the reduction mixture.

## Scheme II



Although the proof of structure of the product **18** is not as unequivocal as we would have liked, the evidence as a whole is consistent with the proposal that this compound is dihydrobarbaralone. A further complication is that compound **18** is thermally unstable, rearranging under relatively mild conditions to a new ketone **24** whose structure was

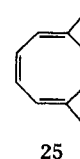
assigned on the basis of spectral properties (see Experimental Section for details), and whose retention time under our glpc conditions was the same as the starting dienone **7**. While no dimers have been isolated in this investigation in either direct or sensitized photolysis, we cannot exclude the possibility that they might have been formed and escaped our analytical and isolation methods.

The quantum yield for formation of **18** at 370 nm in benzene using MK as the sensitizer ( $10^{-3} M$ ) and  $0.01 M$  **7** is 0.89 after 10 min of irradiation and 0.61 after 25 min.<sup>20</sup> The result suggests **18** undergoes sensitized photolysis to other products, but lack of material prevented further studies along these lines.

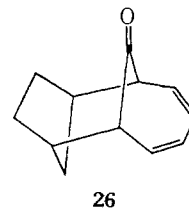
The report<sup>14-16</sup> that triplet-sensitized photolysis of the parent trienone **9** gives barbaralone **19** in high yields is totally consistent with our observations and further supports the assignment of structure to **18**.

**Miscellaneous Results on 1 and 5.** Using an improved procedure for determining quantum yields,<sup>29</sup> the photolysis of dienone **1** was reinvestigated. For the direct photolysis of  $0.01 M$  **1** in ether, a value of 0.74 was found for disappearance of **1** at 313 nm.<sup>30</sup>

Because of numerous questions arising from earlier work,<sup>9</sup> a quantity of the tetramethyl dienone **5** was prepared, and quantum yields for disappearance on direct and sensitized photolysis were measured. In the direct photolysis of  $0.01 M$  **5** in ether,  $\Phi$  for disappearance of **5** at 290 nm was 0.69, while in acetone ( $0.01 M$ ) at 313 nm,  $\Phi$  for disappearance of **5** was 0.81. The direct photolysis of **5** afforded two major products in about equal amounts, according to glpc analysis, which were isolated by column chromatography.<sup>31a</sup> One of these was shown to be the ketone **6**, isolated and identified earlier by Paquette, *et al.*<sup>9</sup> The other was the previously undiscovered decarbonylation product 2,7-dimethyl-2,4,6-octatriene (**25**), identified spectrally and by direct comparison with an authentic sample.<sup>31b</sup> The formation of neither product could be quenched by up to  $2.0 M$  naphthalene in tetrahydrofuran,<sup>31a</sup> consistent with the ear-



lier results.<sup>9</sup> However, 1,3-cyclohexadiene (CHD) in high concentrations (up to  $8.4 M$ ) was able to quench the formation of **6** but not of triene **25**; the quenching of **6** is accompanied by the formation of the CHD dimers in characteristic ratio, confirming the occurrence of triplet energy transfer.<sup>31c</sup> The Stern-Volmer quenching slope was only  $0.094 M^{-1}$ , indicating a low value for  $k_q$  (perhaps because the triplet excitation energy  $E_T$  of **5** is even less than that of CHD,  $\sim 53 \text{ kcal/mol}$ <sup>31d</sup>) and/or a short lifetime of the lowest triplet state of **5**.<sup>31e</sup> Acetone- or benzophenone-sensitized photolysis of **5** gives only ketone **6** and none of triene **25**, substantiating the conclusion that decarbonylation of **5** as **1** occurs only from excited singlet states.<sup>31a</sup>



**Emission Spectra.** Emission from **1**, **5**, **7**, **8**, and **26** was observed at room temperature in degassed ethanol and ether solutions. In the case of **7**, the emission of a thoroughly degassed sample was identical with that of a solution which had been saturated with oxygen, suggesting that the emission is fluorescence. Broad emission spectra of all these compounds with maxima at 410–430 nm are seen at room temperature. Emission from **7** is enhanced in an ethanol glass at  $77^\circ K$ , and the excitation spectrum (uncorrected) is very similar to the uv absorption of **7**. The emission and excitation spectra overlap at 340 nm, further evidence that the emission is fluorescence and not phosphorescence. The fact that all the compounds studied show such similar emission spectra makes it unlikely that impurities are responsible.

Hancock and Grider<sup>32</sup> have observed emission from eleven  $\beta,\gamma$ -saturated ketones at  $77^\circ K$  in ethanol and isopentane which they have characterized as phosphorescence on the basis of lifetimes in the 5–200 msec range. Since we have not as yet determined the lifetimes of the emission from the 3,5-cycloheptadienones at room temperature and  $77^\circ$ , the conclusion that the emission in all cases is fluorescence must be regarded as tentative. However, (1) the lack of an oxygen effect seen with **7** (above) and (2) the fact that **1** and **7** do not give products at room temperature derived from triplets support our contention that the emission from at least these ketones at room temperature must be singlet derived, *i.e.*, fluorescence. Further work should clarify these points.

### Discussion

Since the products of direct and triplet-sensitized photolysis of **7** are completely different, it can be concluded that the decarbonylation product **10** and the valence tautomer **11** are derived exclusively from the lowest singlet excited state of **7**, while dihydrobarbaralone **18** is derived exclusively from a triplet excited state of **7**. In the case of acetone, it is likely that a small amount of singlet energy transfer to **7** from the relatively long-lived acetone singlets competes with intersystem crossing of the sensitizer ( $k_{st} = 5 \times 10^8$  for acetone<sup>33</sup> and  $2 \times 10^{11} \text{ sec}^{-1}$  for benzophenone),<sup>34</sup> affording the usual singlet-derived products **10** and **11** in

**Table I.** Multiplicity of Reaction Pathways of 3,5-Cycloheptadienones

Compd	Occurrence of $S_1^* \rightarrow T_1^*$	Decarbonylation <sup>a</sup>	Cyclobutene formation <sup>a</sup>	Oxa-di- $\pi$ -methane rearrangement <sup>a</sup>	Dimerization
<b>1</b> <sup>b</sup>	No	Singlet $\Phi = 0.74$	Triplet $\Phi \geq 0.11$	Not obsd	Not obsd
<b>5</b> <sup>c, d</sup>	Yes <sup>e</sup>	Singlet $\Phi_{dir}^{-K} = 0.69$	Not obsd	Triplet <sup>e</sup> $\Phi_{sens} = 0.81$	Not obsd
<b>7</b> <sup>d</sup>	No	Singlet $\Phi = 0.66$	Singlet $\Phi = 0.14$	Triplet $\Phi = 0.89$	Not obsd
<b>8</b> <sup>c</sup>	Yes	Singlet	Singlet	Triplet	Triplet
<b>9</b> <sup>f</sup>	No	Singlet	Singlet	Triplet	Not obsd

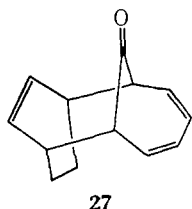
<sup>a</sup> Quantum yields measured in this study. <sup>b</sup> References 4 and 5. <sup>c</sup> Reference 9. <sup>d</sup> This work. See also ref 31a. <sup>e</sup> References 12 and 13. <sup>f</sup> References 14, 15, and 16. <sup>g</sup> See text for discussion on this point.

small yield. Thus, as in the case of **1**,<sup>5</sup> intersystem crossing to triplets of **7** does not demonstrably compete with chemical reaction of the singlets. The total quantum yield for product formation from the singlet was found to be  $0.94 \pm 0.09$  at short reaction time in ethyl ether using 313-nm excitation, indicating deactivation of the singlet by radiative and nonradiative pathways is relatively unimportant under these conditions.

The triplets of **7** are converted efficiently into dihydrobarbaralone **18**, with  $\Phi = 0.89 \pm 0.09$  at 370 nm using Michler's ketone as the sensitizer in benzene. Again, deactivation of the triplets of **7** by radiative and nonradiative pathways is relatively unimportant. Any residual inefficiency may even be ascribed to inefficiency in triplet energy transfer owing to self-quenching of the MK triplets.<sup>35</sup> The conversion to **18** is another example of the 1,2-acyl shift or oxa-di- $\pi$ -methane rearrangement.

The course of the photochemical reactions of compounds **1**, **5**, **7**, **8**, and **9** is summarized in Table I. All these compounds are formally 3,5-cycloheptadienones. In the table, the source (*i.e.*, singlet or triplet state) of each type of product observed is indicated, as well as the occurrence (or lack) of intersystem crossing from singlets to triplets.

**Decarbonylation.** This reaction is exclusively a singlet excited state process. It is the dominant singlet process in the cases of **1**, **5**, **7**, and **9**, although the quantum efficiency has not been measured for **9**.<sup>16</sup> Irradiation of **8** and **27** in hex-



ane at 300 nm gave 25 and 10% decarbonylation, respectively.<sup>12</sup> In the case of **9**, the chemical yield of cyclooctatetraene, the decarbonylation product, was 82% in tetrahydrofuran solution at 300 nm,<sup>14</sup> and 70% in ether at 254 nm.<sup>16</sup> The high quantum efficiency seen for this reaction with **1** and **7** would suggest, although it does not require, that decarbonylation is a concerted disrotatory chelotropic reaction,<sup>36</sup> as previously postulated.<sup>5</sup> As a linear concerted process,<sup>36</sup> the reaction is predicted theoretically<sup>5,36</sup> to occur in a disrotatory fashion, which must be the case with the constrained dienones **7**, **8**, and **9**. It is interesting that the reaction seems to occur equally well with dienones which possess  $C_2$  symmetry, such as **1** and **5**, and those with a mirror plane, such as **7**, **8**, and **9**. The precise stereochemistry of ring-opening (*i.e.*, conrotatory or disrotatory) of the monocyclic systems has yet to be determined. The supposed absence of decarbonylation in the case of the tetramethyl dienone **5** noted by Paquette, *et al.*,<sup>9</sup> was blamed on secon-

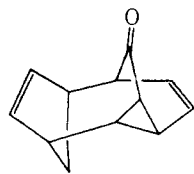
dary steric effects caused by interaction of methyls brought into proximity by the rotations required for concerted CO expulsion.<sup>36</sup> Contrary to the earlier study,<sup>9</sup> however, we have now demonstrated<sup>31a</sup> that decarbonylation does indeed occur on direct photolysis of **5**, although intersystem crossing from  $S_1$  to  $T_1$  is competitive with decarbonylation, unlike the situation with **1**.<sup>5</sup> It appears that the energy barrier for concerted CO expulsion is raised in **5** to a level which forces the molecule into alternative reaction and deactivation pathways.<sup>37</sup>

**Cyclobutene Formation.** It is significant that the 2,7-bridged cycloheptadienones **7**, **8**, **9**, and **27** all show cyclobutene formation from their excited singlets, while the monocyclic dienones **1** and **5** do not. This suggests that a planar *cis*-butadiene unit is a necessary requirement for the reaction, which probably simply involves a concerted symmetry-allowed<sup>38</sup> disrotatory ring closure. In **1** and **5**, the skew conformation of the diene moiety effectively prevents concerted cyclobutene formation in the singlet. In addition, cyclobutene ring closure in **5** which would result in increased steric interference of the methyls is inhibited.<sup>9</sup>

The observation of a typical diene reaction<sup>23</sup> on irradiation of dienones **7**, **8**, **9**, and **27** in the  $n \rightarrow \pi^*$  absorption band indicates that the excitation is not localized on the carbonyl group. The enhanced intensity of  $n \rightarrow \pi^*$  transitions for these compounds, as for most  $\beta,\gamma$ -unsaturated ketones, has been ascribed<sup>10b,39</sup> to mixing with  $\pi \rightarrow \pi^*$  and charge transfer transitions involving the diene. Thus, reaction of the excited singlet in the diene portion of the molecule is not surprising.

The fact that only in the case of **1** is cyclobutene formation observed from the triplet manifold supports our original contention<sup>5</sup> that the mechanism involves further twisting of the already twisted triplet in the direction of formation of the *cis,trans*-dienone **4**, followed by conrotatory thermal ring closure to **2**.<sup>5,7</sup> This illustrates ground state conformational control of photochemical reactions, as stressed by Dauben.<sup>38b</sup> Although the *cis,trans*-dienone **4** has resisted detection thus far, it is possible that studies at very low temperature using matrix isolation techniques, as so successfully employed by Chapman and his coworkers,<sup>40</sup> may allow detection of this unstable and elusive species.

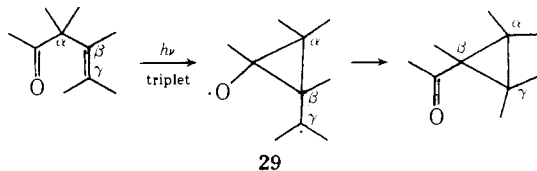
**Oxa-di- $\pi$ -methane Rearrangements. 1,2-Acyl Shifts.** In the cases of dienones **7** and **9**, the rearrangements to **18** and **19**, respectively, are seen *only* on triplet sensitization and occur in high chemical yield and, in the case of **7**  $\rightarrow$  **18**, high quantum yield. In these cases, it is clear that the reaction originates exclusively in the triplet manifold. The analogous compound **28** is formed from **8** on direct photolysis in methanol or acetonitrile, a reaction on which triplet quenchers had "very little effect,"<sup>13</sup> and in benzene on direct or triplet-sensitized photolysis. It is not completely clear from the published data<sup>13</sup> whether the formation of **28** is exclusively a triplet process, or whether there may be a



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singlet component to the reaction in some solvents. Houk and Worthington<sup>13</sup> suggest that the reaction in polar solvents proceeds *via* a  $^3n,\pi^*$  or  $^3CT$  state following intersystem crossing from the singlet, and presumably the same is true in benzene solution, although this has not been established on the basis of the published data. The situation in the case  $5 \rightarrow 6$  has been clarified to a great extent. We have substantiated that the triplet state of **5** can rearrange to **6**,<sup>9</sup> and our new quenching data indicate that the formation of **6** on direct photolysis of **5** derives from a barely quenchable (by CHD) triplet state after intersystem crossing from  $S_1$ . Thus, triplet yields on direct photolysis of **5** must be substantial in contrast to **1**, where such triplet yields are negligible. The methyls in **5** could facilitate intersystem crossing (rate constant  $k_{st}$ ) by increasing  $k_{st}$  or decreasing the rate constant  $k_{-CO}$  for decarbonylation of  $S_1$ .<sup>41,42</sup> We favor the latter interpretation. A definitive solution to the problem is possible from determination of fluorescence lifetimes and quantum yields including  $\Phi_{st}$  for **1** and **5**. Studies along these lines are in progress.<sup>31a</sup>

Thus far, four 3,5-cycloheptadienones have been demonstrated to undergo the oxa-di- $\pi$ -methane rearrangement from the triplet manifold, while no corresponding singlet reactivity has been established. This parallels the behavior of many other  $\beta,\gamma$ -unsaturated ketones which undergo 1,2-acyl shifts<sup>43</sup> in contrast to other modes of reaction of singlets (*e.g.*, 1,3-acyl shifts).<sup>10</sup> The dichotomy in behavior was initially rationalized by Schuster, Underwood, and Knudsen on the basis of a difference in spin density distributions in the singlet and triplet states, which affects the nature of orbital interactions leading to bonding.<sup>10a</sup> Implicit in this discussion<sup>10a</sup> was the assumption that the relevant singlet and triplet states of these ketones have  $^3n,\pi^*$  configurations. Houk, *et al.*, have presented theoretical arguments which suggest, however, that the lowest triplet of simple  $\beta,\gamma$ -unsaturated ketones is largely  $\pi,\pi^*$  in nature. This assertion is supported by observations of phosphorescence from a number of such ketones at 77°K in polar and nonpolar glasses.<sup>32</sup> Solvent shifts, vibrational spacings, and lifetimes characteristic of emission from  $^3\pi,\pi^*$  states are seen. Houk, *et al.*,<sup>10b</sup> rationalize the triplet reactivity of these ketones by proposing (on the basis of calculations) that the lowest triplet would show little weakening of the bond between the carbonyl carbon and the  $\alpha$ -carbon (in contrast to the singlet), and that the occupied antibonding orbital would be bonding between  $C_{CO}$  and  $C_\beta$ . Thus, it is proposed that the diradical **29** is either an intermediate or a



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species on the reaction surface for the concerted reaction.<sup>10b</sup> The same intermediate, first proposed by Dauben, *et al.*,<sup>44</sup> has also been invoked by Michl using a general principle that in triplet reactions the unpaired spins will tend to be as far apart and as noninteracting as possible.<sup>8</sup> It should be noted that involvement of **29** is by no means excluded by the original spin density explanation.<sup>10a</sup> Furthermore, even if

the  $\pi,\pi^*$  triplet is of lower energy, the reaction could be taking place *via* thermally populated  $n,\pi^*$  triplets of higher energy and greater reactivity. The one thing that is *not* expected or predicted on the basis of any of these mechanistic rationalizations is the occurrence of 1,2-acyl shifts from singlet  $n,\pi^*$  states.<sup>45</sup>

## Experimental Section

All melting points are uncorrected. Proton magnetic resonance spectra were recorded with Varian Model A-60 and Perkin-Elmer Models R-20 and R-24 spectrometers, with tetramethylsilane as internal standard in most instances. Mass spectra were obtained at 70 V by Mr. Charles Strom on a Varian M-66 double-focusing cycloidal path mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 Grating Infracord spectrophotometer, with a polystyrene film used for calibration. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer. The emission spectra were obtained with the assistance of Professor Charles Marzocco on a Baird-Atomic Model SF-1 fluorescence spectrophotometer.

**Gas-Liquid Partition Chromatography.** Analytical studies were made using an F & M Model 5750 research chromatograph with flame ionization detection. In most studies, a 6 ft  $\times$   $\frac{1}{8}$  in. column of 15% Carbowax 20M on 80-100 mesh Chromosorb W was used, designated column A. When other columns were utilized, this is indicated specifically. Preparative separations were carried out using an Aerograph A-90-P chromatograph, using a 15 ft  $\times$  0.25 in. column of 30% Carbowax 20M on Chromosorb W (column B). Collections were made using a U-tube in a Dry Ice-acetone bath. In quantitative analyses, areas under the peaks in the chromatogram were measured using either the cut-and-weigh method, disc integration, or with a K and E Model 4236M planimeter. Appropriate compounds were used as internal standards, and the relative detector response of the standard and the compound under study were determined from mixtures of known quantities of the compounds.

**Photolytic Apparatus. (a) Immersion Well Apparatus.** This consists of a water-jacketed Pyrex immersion well containing a 450-W Hanovia high-pressure mercury lamp. The immersion well fits into a Pyrex reaction vessel which has a gas inlet and an outlet at the bottom for removing samples for analysis during the photolysis.

**(b) Rayonet Reactor.** This apparatus, supplied by the Southern New England Ultraviolet Co., Inc., consists of a circular array of lamps inside a reflecting surface. In these studies, lamps with output concentrated around 3500 Å were utilized. Generally, a cylindrical Pyrex vessel containing the solution to be photolyzed was placed at the center of the apparatus. In some runs, a motor-powered turntable containing samples in Pyrex test tubes was placed inside the reactor.

**(c) Merry-Go-Round.**<sup>46</sup> This apparatus, supplied by the Moses Co., Newark, Del., consists of a precision-made turntable with 30 sample positions, with a central opening for a Pyrex immersion well containing a 550-W Hanovia lamp. Filters were placed in the four positions surrounding the immersion wells. Photolyses were carried out at ambient temperatures in Pyrex tubes. Rotation of the turntable by a motor during photolysis assures equal light exposure of each test tube.

**Bicyclo[4.2.1]nona-2,4-dien-9-one (7)** was prepared by the procedures described elsewhere.<sup>17</sup> This material was usually freshly prepared before each photolytic experiment.

**Direct Photolysis of Bicyclo[4.2.1]nona-2,4-dien-9-one.** The direct irradiation of ketone **7** was done in ethyl ether, cyclohexane, or methanol at 0° in Pyrex tubes using the merry-go-round apparatus, equipped with a 550-W Hanovia lamp surrounded by Pyrex filter sleeves. In a typical run, a solution of 1.5 g of dienone **7** in 100 ml of ethyl ether (0.11 M) was divided among 30 Pyrex tubes, which were irradiated in an ice-water bath for 10 hr. The solutions had been purged with nitrogen for 30 min prior to irradiation. Aliquots were withdrawn periodically and analyzed by glpc (column A). The combined photolysate after irradiation was concentrated by removal of solvent through a short fractionation column using a water aspirator. Three photoproducts in addition to starting material were separated and isolated using preparative glpc (column B) at a column temperature of 180° and injection port temperature of 280°. The major product was identified as **1,3,5-cyclooctatriene (10)** by spectral and glpc comparison with an authentic sample.

The next product was identified as *endo*-tricyclo[4.2.1.0<sup>2,5</sup>]non-3-ene-9-one (**11**) on the basis of spectral data and independent synthesis (see below). The nmr spectrum of **11** is given in the text. The compound has an ir spectrum (neat) with peaks at 3005, 2960, 2885, 1815, 1770, 1450, 1300, 1225, 1115, 850, 780, 615, and 525 cm<sup>-1</sup>. The uv spectrum (methanol) has a shoulder from 280 to 300 nm ( $\epsilon$  300). The mass spectrum shows *m/e* 134, 106, 105, 91, 79, 78 (base), and 77. There was an additional product formed in trace amounts. Attempts were made to collect this compound from a scaled-up photolysis using 3.0 g of dienone **7**, but this new material polymerized rapidly at the injection port of the glpc to form a white powder which did not melt up to 205°, was insoluble in ether, and showed no definable structure in its nmr and ir spectra.

The direct irradiation of **7** was carried out also in a Dry Ice-methanol bath at -70° in Pyrex tubes within a larger dewar with a Pyrex glass window. A 550-W high-pressure mercury lamp in a water-jacketed well was placed 1 in. from the window of the dewar. After 1.5-hr photolysis, the starting material was completely consumed. The photoproducts **10** and **11** were formed, but the unidentified product (see above) was not detectable in even trace amounts in the photolysate by glpc.

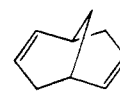
**Sensitized Photolysis of Dienone 7.** Irradiation of dienone **7** was carried out in acetone, as well as in benzene or cyclohexane in the presence of benzophenone, triphenylene, or Michler's ketone as sensitizers. The apparatus and experimental conditions were essentially the same as in the direct photolysis of **7**. In a typical run, 500 mg of **7** in 100 g of acetone was irradiated at ice-water temperature for 3.5 hr with a 450-W Hanovia lamp. Under these conditions, 97% of the light should be absorbed by acetone, according to the uv spectra of the solutions. The glpc analysis of the photolysate showed about 60% of a new product, in addition to the products previously isolated from direct photolysis of **7**. In a run using 3 mg of dienone **7** and 400 mg of benzophenone in 15 ml of benzene, with benzophenone absorbing 97% of the light from a 550-W Hanovia lamp and the solution in four Pyrex test tubes in a merry-go-round in a water bath, the starting material was totally consumed after 80 min. Glpc analysis of the photolysate indicated there was only a trace of ketone **11** present, and a single major product with the same glpc retention time as the major product of the acetone photolyses. Similar results were obtained using 400 mg of **7** and 3.8 g of triphenylene in 150 ml of benzene, with triphenylene absorbing about 80% of the incident light. The starting material was present in only trace amounts (glpc) after 3 hr, and the reaction was stopped after 4.5 hr. The photolysate was analyzed by glpc and shown to contain about 10% **10**, 10% **11**, and 80% of the same new product as obtained above. The solvent and sensitizer were removed, and the new photoproduct was collected and purified using preparative glpc (column B) and identified as dihydrobarbaralone (**18**) on the basis of spectral data and the other data and analogies given in the Results section. The material, mp 47–47.5°, had an ir spectrum (CHCl<sub>3</sub>) with peaks at 3030, 2970, 2895, 1750, 1700, 1450, 1310, 1235, 1150, 910, 885, 700, and 450 cm<sup>-1</sup>. The mass spectrum had *m/e* 134, 106, 91, 85, 83, and 78 (base). The uv and nmr spectral data are given in the Results.

**Photolysis of 9,9-Dimethoxybicyclo[4.2.1]nona-2,4-diene (15).** A solution of 500 mg of ketal **15**<sup>17</sup> in 100 ml of ether was divided among 27 Pyrex tubes, which were irradiated at ice-water temperature in the merry-go-round with a 450-W Hanovia lamp. The solutions were purged with nitrogen for 30 min prior to irradiation. Aliquots were withdrawn periodically and examined by glpc. After 30 hr of photolysis, the solutions consisted of a single photoproduct according to glpc analysis. Photolysis of **15** in acetone under similar conditions also afforded the same photoproduct, but at a much slower rate. After removal of solvent using a short fractionation column, the product was isolated and purified by preparative glpc on a 12 ft × 0.25 in. column of 25% Carbowax 20M on 80–100 mesh Chromosorb W. The liquid product was identified as 9,9-dimethoxytricyclo[4.2.1.0<sup>2,5</sup>]non-3-ene (**16**) on the basis of spectral data:  $\nu_{\max}$  (neat) 3040, 2960, 2940, 2830, 1450, 1325, 1315, 1305, 1290, 1220, 1137, 1108, and 1050 cm<sup>-1</sup>;  $\lambda_{\max}$  (CH<sub>3</sub>OH) shoulder extending to 320 nm;  $\delta_{\text{TMS}}$  (CDCl<sub>3</sub>) 6.20 (2 H, s), 3.23 (6 H, d), 3.03 (2 H, br s), 2.12 (2 H, br s), and 1.41 ppm (4 H, m); *m/e* 180, 165, 150, 149, 133, 114, 105 (base), 101, and 91.

**Hydrolysis of ketal 16** was accomplished by stirring the ketal with 3 *N* HCl at 0° for 20 min. The product was about 95% pure, according to glpc, and had the same nmr, ir, and uv spectra and

glpc retention time as the ketone **11** obtained from direct photolysis of dienone **7**.

**Thermal Stability of Photoproducts.** The thermal stability of each of the photoproducts isolated above was tested by injecting pure samples of **11** and **18** onto column A in the gas chromatograph and increasing the temperature of the column from 150 to 230° and the injection port from 180 to 280°. The compounds were also individually dissolved in small amounts of analytical grade xylene in capillary tubes which were sealed and heated for 2 hr in an oil bath at 200–230°. It was shown spectroscopically and by glpc that **11** was quantitatively converted back to dienone **7**, while **18** resulted in approximately 90% of a new ketone **24**. This new ketone had the same glpc retention time as **7** on column A but had different spectroscopic properties:  $\delta_{\text{TMS}}$  (CDCl<sub>3</sub>) 5.85 (m, 4 H), 3.13 (br s, 2 H), and 2.75 ppm (br s, 4 H);  $\nu$  (neat) 3050, 2950, 2910, 2850, 1735, 1440, 1280, 1240, 1115, 1050, 810, 730, 710, and 670 cm<sup>-1</sup>;  $\lambda$  (CH<sub>3</sub>OH) shoulder to 320 nm. The ketone was assigned the structure bicyclo[3.3.1]nona-2,6-dien-9-one (**24**) on the basis of the lack of diene conjugation in the uv spectrum, the relative simplicity of the nmr spectrum, and comparison with the nmr spectrum of bicyclo[3.3.1]nona-2,6-diene (**30**):<sup>47</sup>  $\delta$  5.7 (m, 4 H), 2.5 (br m, 2 H), 2.1 (m, 4 H), and 1.7 (tr, 2 H) ppm.



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Tricyclo[3.3.1.0<sup>2,8</sup>]nona-3,6-dien-9-one (barbaralone, **19**) was prepared by the method of Paquette, *et al.*<sup>15</sup> Michler's ketone (32.2 g, 0.12 mol) was dissolved in 1 l. of benzene (insoluble material was separated by filtration), and 5.0 g (0.038 mol) of trienone **1** was added to the solution, which was purged with nitrogen for 30 min and irradiated in the Rayonet reactor using 11 350-nm lamps. Aliquots were periodically withdrawn and analyzed by glpc. There was 90% conversion to a single photoproduct after 32 hr. The benzene solution was diluted with 300 ml of ethyl ether and washed three times with 100 ml of 3 *N* H<sub>2</sub>SO<sub>4</sub>, once with 100 ml of saturated carbonate solution, and three times with 100 ml of saturated salt solution. The organic layer was dried over MgSO<sub>4</sub> and then concentrated. The residue was taken up in 50 ml of ether, leaving a small amount of insoluble Michler's ketone. The product crystallized from the solution at Dry Ice-acetone temperatures. Recrystallization gave 2.1 g of barbaralone (**19**), mp 46–48° (lit.<sup>15</sup> mp 47–49°), with the carbonyl stretch in the infrared at 1705 cm<sup>-1</sup> (lit.<sup>24</sup> 1700 cm<sup>-1</sup>).

Tricyclo[3.3.1.0<sup>2,8</sup>]nona-3,6-dien-9-ol (barbaralol, **21**) was prepared by slow addition of barbaralone (1.5 g, 0.011 mol) in 10 ml of methanol to a stirred methanol solution of 1.11 g (0.03 mol) of sodium borohydride and a drop of 50% KOH solution at ice temperature. The mixture was stirred overnight at room temperature. It was acidified with 40 ml of 5% HCl and then extracted with 3 × 100 ml of ethyl ether. The ethereal solution was washed with 4 × 50 ml of saturated salt solution, dried over MgSO<sub>4</sub>, and concentrated, affording 1.2 g of a yellow product. This material was recrystallized with difficulty from pentane, giving white crystals of barbaralol (**21**), mp 78–85° (lit.<sup>24</sup> mp 88–89°). The nmr spectrum agreed well with that reported previously,<sup>24</sup> showing  $\delta_{\text{TMS}}$  (CDCl<sub>3</sub>) 5.85 (tr, 1 H), 5.51 (tr, 1 H), 4.04–3.94 (m, 4 H), 3.59 (m, 1 H), 2.43 (m, 2 H), and 1.43 ppm (br s, 1 H).

**Hydrogenation of Barbaralol** (100 mg) in 20 ml of methanol was carried out at atmospheric pressure and room temperature over 10% palladium/charcoal catalyst by stirring overnight. The catalyst was removed by filtration, the solution was concentrated, and the crude product was crystallized from hexane at Dry Ice-acetone temperature. Pure product was obtained by preparative glpc and had mp 190° with sublimation. The material was volatile with a camphorous odor. The compound had the following spectral properties:  $\delta_{\text{TMS}}$  (CDCl<sub>3</sub>) 1.1–2.3 (complex multiplet, 13 H) and 3.75 ppm (d, 1 H);  $\nu$  (CDCl<sub>3</sub>) 3615, 3000, 2940, 2900, 1450, 1120, and 1065 cm<sup>-1</sup>; *m/e* 122 (base), 109, 107, 94, 93, and 81. The data are consistent with the structure bicyclo[3.2.2]nonan-6-ol (**22**). One report on this compound<sup>27</sup> cites mp 191–192° with sublimation, high volatility, and a strong camphorous odor.

**Quantum yields** were determined by a split-beam technique developed in our laboratory by Liu.<sup>29</sup> The light beam from a Bausch



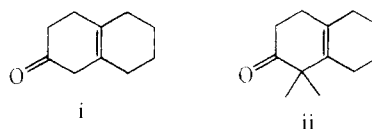
and Lomb grating monochromator with a 200-W super pressure Osram lamp was split by a fused silica disc held at 45° to the light beam into two beams at 90° to each other. The ratio of light intensity in the beams was determined using ferrioxalate actinometer<sup>48</sup> solutions in cells in each path and was varied from 11.2 to 16.5. Then the solution of the substrate was placed in the cell position along the major light path, and a fresh actinometer solution in the minor path, and the solutions were irradiated for periods of 10–90 min, depending on the requirements of the individual run. The total amount of light absorbed by the actinometer during the entire irradiation was determined in the usual manner,<sup>48</sup> and the total amount of light absorbed by the sample could then be precisely calculated using the predetermined splitting ratio, above, and the optical densities of the sample solution measured before and after photolysis. The per cent conversions were kept as low as possible consistent with the analytical requirements, generally less than 10%. The amount of product formed in the sample cell was determined in all cases by glpc with internal standards, using detector response factors determined from mixtures of precisely weighed samples of the product of interest and the internal standard.

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## References and Notes

- (1) Part XLI of a series on the photochemistry of ketones in solution. Portions of this work were presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1–5, 1974, Abstract ORGN-109. Part XL: D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **6**, 69 (1974).
- (2) Address correspondence regarding this paper to this author at the Department of Chemistry, New York University, Washington Square, New York, N.Y. 10003.
- (3) This paper is based largely on the Ph.D. dissertation of C. W. Kim, New York University, Feb. 1973.
- (4) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).
- (5) D. I. Schuster, B. R. Scolnick, and F.-T. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968).
- (6) R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).
- (7) D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, **35**, 3190 (1970).
- (8) J. Michl, *Mol. Photochem.*, **4**, 243, 257 (1972).
- (9) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, **90**, 5153 (1968).
- (10) For leading references and possible explanations of the differences in behavior of singlets and triplets in these systems, see (a) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4304 (1971); (b) K. N. Houk, D. J. Northington, and R. E. Duke, *ibid.*, **94**, 6233 (1972); and (c) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
- (11) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Amer. Chem. Soc.*, **87**, 321 (1965).
- (12) T. Mukai, Y. Akasaki, and T. Hagiwara, *J. Amer. Chem. Soc.*, **94**, 675 (1972).
- (13) K. N. Houk and D. J. Northington, **94**, 1387 (1972).
- (14) K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972).
- (15) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 2155 (1972).
- (16) T. A. Antkowiak, D. C. Sanders, G. B. Timitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972).
- (17) D. I. Schuster and C. W. Kim, *J. Org. Chem.*, in press.
- (18) Available from the studies of F.-T. H. Lee, Ph.D., New York University, 1966.
- (19) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964); W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); J. Zirner and S. Winstein, *Proc. Chem. Soc., London*, 235 (1964).
- (20) The fact that quantum yields were time dependent indicates that the primary photoproducts are destroyed by secondary reactions to some extent.
- (21) C. W. Jefford and F. Delay, *J. Amer. Chem. Soc.*, **94**, 4794 (1972); L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966).
- (22) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1969).
- (23) For a review and references, see G. J. Fonken in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N.Y., 1967.
- (24) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).
- (25) M. J. Goldstein and B. J. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).
- (26) M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970). The method of synthesis of **20** was not given in this paper.

- (27) V. Ioan, M. Popovici, E. Mosanu, M. Elean, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **10**, 185 (1965); *Chem. Abstr.*, **63**, 4181f (1965).
- (28) K. Alder, S. Hartung, and G. Hausmann, *Chem. Ber.*, **89**, 1972 (1956); W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).
- (29) K. Liu, Ph.D. Dissertation, New York University, 1973.
- (30) A less reliable value of 0.11 was found for formation of **2** on sensitized isomerization of 0.01 M **1** in acetone at 313 nm using a sample of **1** which was only 75% pure according to glpc.
- (31) (a) J. Eriksen, unpublished results from this laboratory. Details of these and other recent studies of **5** will be reported separately. (b) R. M. Coates and W. H. Robinson, *J. Amer. Chem. Soc.*, **94**, 5920 (1972). We are grateful to Dr. Coates for sending us spectra of triene **25** for direct comparison with our material. (c) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964); (d) R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965). (e) NOTE ADDED IN PROOF: Recent experiments by J. Eriksen establish that quenching of **5** → **6** by 3,3,4,4-tetramethyl-1,2-diazetidene 1,2-dioxide ( $E_T = 35\text{--}42$  kcal/mol)<sup>31f</sup> is efficient in acetonitrile,  $k_q\tau = 30$ . This suggests  $E_T$  for **5** is probably ~40–50 kcal/mol. (f) E. F. Ullman and P. Singh, *J. Amer. Chem. Soc.*, **94**, 5077 (1972).
- (32) (a) K. G. Hancock and R. O. Grider, *J. Chem. Soc., Chem. Commun.*, 581 (1972). (b) We have also seen room-temperature emission from 2,2-dimethylcyclohept-3-en-1-one, similar in appearance to that of the 3,5-cycloheptadienones. Hancock and Grider have observed emission from this compound at 77°K with a lifetime of 44 msec.
- (33) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970); F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).
- (34) P. M. Rentzepis, *Science*, **16**, 239 (1970).
- (35) D. I. Schuster and M. D. Goldstein, *J. Amer. Chem. Soc.*, **95**, 986 (1973).
- (36) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970, p 152f.
- (37) These results do not rigorously exclude a two-step decarbonylation mechanism involving  $\alpha$ -cleavage as the initial step, although the high quantum efficiencies for **1** and **7** made such a mechanism appear unlikely in these cases. The fact that decarbonylation is a singlet state reaction, which competes effectively with intersystem crossing and decay to ground state, both of which must occur at fast rates, suggests that spin pairing is an important feature in facilitating the reaction. This is easier to understand in terms of a concerted rather than a stepwise process. In the absence of any evidence to the contrary, the concerted decarbonylation mechanism seems the most reasonable at the present time, and we will therefore assume that it is this mechanism which operates. See also the discussion in ref 5, particularly footnote 34. For a case of linear sigmatropic extrusion of CO from ketone triplets, see T. R. Darling, J. Pouliquen, and N. J. Turro, *J. Amer. Chem. Soc.*, **96**, 1247 (1974).
- (38) (a) Reference 36, p 38ff; (b) see also W. G. Dauben, R. G. Williams, and R. D. McKelvey, *J. Amer. Chem. Soc.*, **95**, 3932 (1973), and references cited therein.
- (39) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); A. Moscovitz, K. Mislou, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).
- (40) As a dramatic example, see O. L. Chapman, C. L. McIntosh, and J. Paicansky, *J. Amer. Chem. Soc.*, **95**, 614 (1973).
- (41) An interesting effect of  $\alpha$ -methyl groups on the photochemistry of  $\beta,\gamma$ -unsaturated ketones has recently been reported.<sup>42</sup> In the case of **i**, only



- the triplet-derived oxa-di- $\pi$ -methane rearrangement is observed on direct photolysis. With **ii**, only the singlet-derived [1,3]acyl shift is seen on direct photolysis, while the oxa-di- $\pi$ -methane reaction occurs on acetone sensitization. The authors conclude that it is the variation in singlet reaction rate constant, not  $k_{SI}$ , which is principally affected by methyl substitution. Engel has also found examples of [1,3]-acyl shifts originating in triplet states: P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972), as well as some unpublished cases.
- (42) P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Amer. Chem. Soc.*, **96**, 924 (1974).
  - (43) The reaction can also be viewed formally as a [ $\pi_2s + \pi_2a$ ] cycloaddition; see ref 36, p 89ff.
  - (44) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).
  - (45) On the basis of his orbital description of excited states in these systems, Houk<sup>13</sup> rationalized the inefficiency of intersystem crossing in 3,5-cycloheptadienones with a  $C_2$  conformation, such as **1**. However, he likewise predicted<sup>13</sup> that intersystem crossing in  $C_s$  3,5-cycloheptadienones, such as **7** and **9** would be rapid, although this process is not observed in these cases. Whether the rates of intersystem crossing are different or not can be determined from singlet lifetimes, fluorescence yields, etc.
  - (46) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).
  - (47) H. Musso and U. Biethan, *Chem. Ber.*, **100**, 119 (1967).
  - (48) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).