Trans Intermediates in Benzocycloheptadienone Photochemistry[1]

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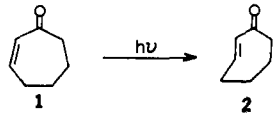
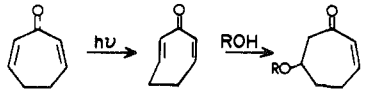
Abstract: Six different 2,4-cycloheptadienones in which the 2,3-double bond is incorporated in an aromatic ring (**4**, **11**, **16**, **29**, **30**, and **31**) gave photoproducts with a trans-4,5 double bond, as shown by trapping with furan. However, these six dienones behaved quite differently from one another when irradiated without a trapping agent present. In cyclohexane, irradiation of **4** gave dimers **5** and **6**, whereas **29** gave (among other products) the remarkable dimer **35**. These dimers have structures which clearly show that they arise from ($4\pi + 2\pi$) cycloaddition of a trans intermediate to the styrene moiety of the starting ketone, followed by further rearrangement. The predominant products from the irradiation of **11**, **16**, and **29** in cyclohexane were head-to-head cyclobutane dimers in which one moiety was trans and the other cis (at the sites of the original C(4)–C(5) double bond). Under the same irradiation conditions, **30** and **31** were recovered unchanged. The unusual stereochemistry of the cyclobutane dimers may be accounted for by a concerted thermal dimerization of two ground state trans intermediates. Alternatively, the cyclobutane dimers may arise from rearrangement of an initial ($4\pi + 2\pi$) adduct of the trans intermediate to the styrene moiety of the starting ketone, a mechanism which would explain the lack of dimer formation from **30** and **31**. Irradiation of **11** in methanol resulted in stereospecific transannular addition of methanol to a trans intermediate, to give **15**.

Little is known about the chemistry of *trans*-cycloheptenones. Corey[2] and Eaton[3] prepared *trans*-2-cycloheptenone (**2**) by irradiating the cis ketone, and its IR spectrum was observed at low temperatures. The difference in $\nu_{C=O}$ (1665 cm^{-1} in **1**, 1715 cm^{-1} in **2**) showed that geometric constraints in **2**



1 **2**

cause deconjugation of the C=C and C=O double bonds. On warming, **2** formed dimers of as yet unknown constitution. Compound **2** readily gave trans adducts with cyclopentadiene[2] and furan.[2,3] It was later shown that **2** also rapidly adds ROH (R = H, alkyl, Ac)[4,5] and amines[5] in what is formally a Michael addition, under conditions where the cis isomer **1** does not react with these nucleophiles. *trans*-2,6-Cycloheptadienone (**3**) reacts similarly with nucleophiles.[6] As far as we are aware,



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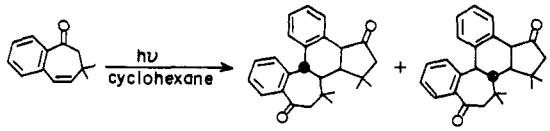
2 and **3** are the only *trans*-cycloheptenones for which there is reasonable evidence.

We first became interested in strained cycloalkenones of this type as a consequence of studies on the photochemistry of cycloheptadienones.[7] In particular, we observed[8] that irradiation of **4** in cyclohexane gave two dimers, **5** and **6**. Despite the

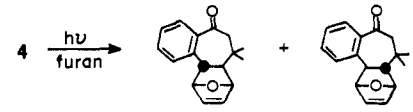


4 **5** **6**

presence of four different chiral centers in these dimers, only the two stereoisomers shown were formed. The trans ring juncture between the six- and seven-membered rings suggested that the dimerization might proceed via the trans isomer of **4**. We report here evidence that this is the case. We also report here on the synthesis and photochemistry of analogues of **4** which either have the *gem*-dimethyl group relocated α to the carbonyl group or lack methyl substituents altogether. These relatively minor structural changes alter markedly the types of photoproducts isolated, although all of the reactions appear to proceed via trans intermediates. The same is true of naphtho analogues of **4**. Our results show that *trans*-cycloheptenones, though highly reactive, are capable of a rather broad range of reactivity depending upon details of structure.

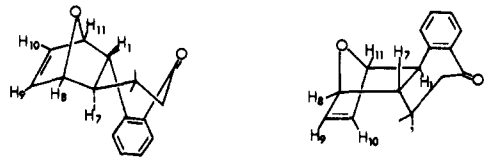
Results and Discussion

Irradiation of 4 in Furan. When **4** was irradiated in furan,



7 (52%) **8** (20%)

dimers **5** and **6** were not formed. Instead, two crystalline trans furan adducts, **7** and **8**, were isolated. The trans geometry of



7 **8**

these adducts was clear from their NMR spectra. Three-dimensional structures drawn below approximate the most favored conformations of the adducts.[9] Table I shows the chemical shifts, coupling constants, and approximate dihedral angles for the pertinent protons.

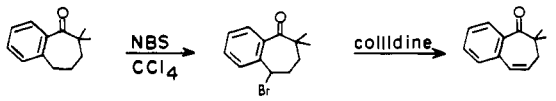
Key features of the spectra are these. In each isomer only one of the two ring juncture protons was coupled to an adjacent bridgehead proton ($J_{1,11}$ and $J_{7,8}$). It is known[3,10,11] that only exo protons in adducts of this type couple with the adjacent bridgehead protons, since the dihedral angle between the endo and bridgehead protons is approximately 90°. Since only one coupling constant of this type was observed, each adduct can have only one exo proton, either at C(1) or C(7). Each adduct must therefore have trans geometry. It is also known that in these systems exo protons are deshielded relative to endo protons.[3,10] This permits us to assign specific structures to the two adducts. H(1) appears at lower field in **7** than in **8**, and H(7) appears at lower field in **8** than in **7**. Therefore, H(1) must be exo (and H(7) endo) in **7**, and the converse must be true in **8**. Other features of the NMR spectra (for example $J_{1,7}$, which certainly would have been >6 Hz if the ring juncture

Table I. NMR Data for Furan Adducts 7 and 8

	δ, ppm		J, Hz			Dihedral angle, deg	
	7	8		7	8	7	8
H(1)	3.42	2.78	1,7	6	6	150	150
H(7)	1.23	2.08	1,11	4	0	55	100
H(11)	5.43	5.43	7,8	0	4	90	55
H(8)	4.67	4.85	8,9	2.0	1.5	20-30	15-20
H(10)	6.20	6.53	9,10	6	6	0	0
H(9)	6.35	6.27	10,11	1.5	2.0	20-30	15-20
CH_3(exo)	1.18	1.22					
CH_3(endo)	1.12	0.82					

were cis[3,12]) are consistent with the assignment.

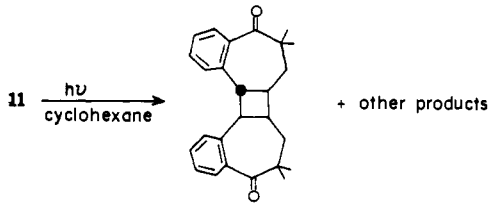
Irradiation of 7,7-Dimethyl-2,3-benzo-2,4-cycloheptadienone (11). In order to explore the generality of the photochemistry of **4**, and also to determine whether α cleavage might compete with double bond isomerization, we synthesized **11** and irradiated it in several solvents. Synthesis of **11** from the known **9**[13] by bromination and dehydrobromination was



9 **10** **11**

unexceptional, and the structure of **11** was clear from its method of synthesis and spectra (see Experimental Section).

Irradiation of **11** in cyclohexane gave mainly the cyclobutane dimer **12.** Small amounts (10–15%) of other cyclobutane

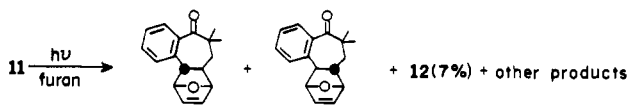


12 (59%)

dimers were also formed, and about 5–10% of **11** was recovered. No product analogous to **5** or **6** was formed.

The gross structure of **12** was clear from its spectra. For example, the mass spectrum showed a weak M^+ peak and a base peak at $(M/2)^+$, characteristic of the cleavage in halves of cyclobutane dimers.[14] The NMR spectrum of **12** showed four separate methyl singlets and two different benzylic methine protons, clearly establishing the absence of a symmetry plane or axis. The head-to-head orientation and exact stereochemistry of **12** was determined by x-ray irradiation of a single crystal.[15]

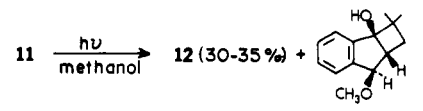
Irradiation of **11** in furan gave mainly two trans furan ad-



13 (33%) **14** (15%)

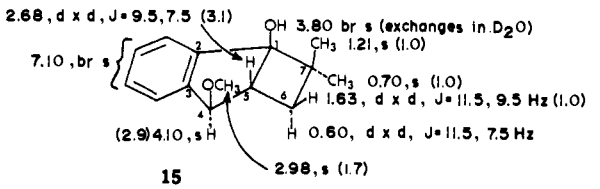
ducts **13** and **14**. Some **12** and other cyclobutane (4%) and furan (4%) dimers were also formed, in addition to recovered **11** (5%). The same NMR criteria used to establish the structures of **7** and **8** were used to assign structures to **13** and **1**.[16]

Irradiation of **11** in methanol gave, in addition to the cyclobutane dimer **12,** a methanol adduct to which we assign structure **15**.[17] The structure of **15** was deduced from its spectra. The IR spectrum showed a hydroxyl group and the mass spectrum showed, in addition to M^+, peaks corresponding to the loss of water, methanol, and isobutylene. It was possible,



15 (55-65%)

with the aid of decoupling and shift reagent, to analyze the NMR spectrum of **15** in detail and to clearly establish the stereochemistry shown. Dreiding models show that the H(4)–H(5) dihedral angle is 90°; consequently, $J_{4,5}$ is zero and H(4) appears as a singlet. Models also give 10 and 150° for the H(5)–H(6) (exo) and H(5)–H(6) (endo) dihedral angles, respectively. Irradiation at H(5) gave the geminal coupling constant for the H(6) protons as 11.5 Hz, permitting the two $J_{5,6}$ values to be assigned. These assignments were verified by irradiation at δ 1.63 and 0.60. The unusually high field positions of the endo C(6) proton and endo C(7) methyl are undoubtedly due to shielding by the aromatic ring.



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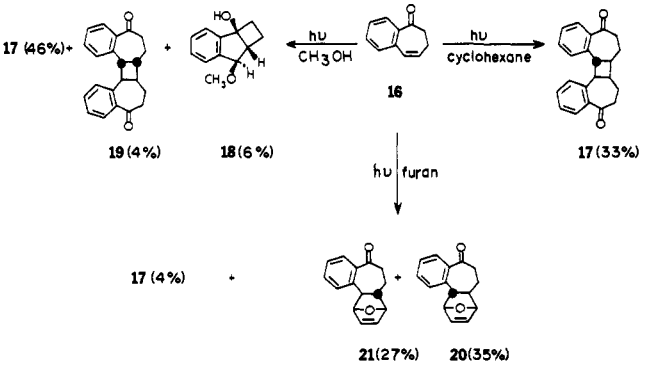
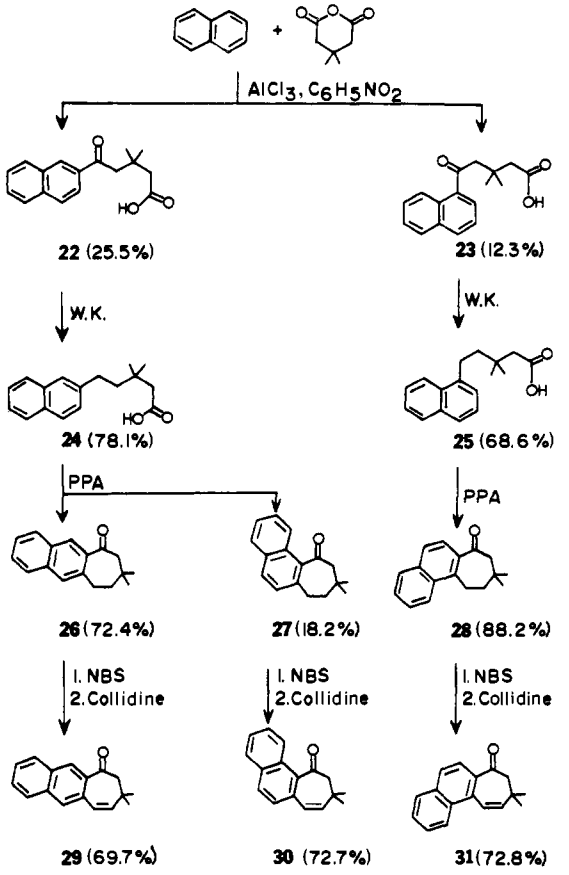
No compound corresponding to **15** was isolated when **4** was irradiated in methanol, the products again being mainly dimers **5** and **6**.

Irradiation of 2,3-Benzo-2,4-cycloheptadienone (16). Despite their similar structures and chromophores, **4** and **11** gave structurally different types of photoproducts, both in cyclohexane and in methanol (although they gave similar adducts in furan). Since the methyl substituents obviously affected product structure, we decided to prepare and irradiate **16,** the parent compound without methyl substituents. We prepared **16**[18] from benzosuberone by a route analogous to the preparation of **11** (see Experimental Section). Irradiation of **16** in



cyclohexane gave as the major product a cyclobutane dimer which is probably **17** (by analogy with **12**). The NMR spectrum of **17** showed that it did not have a symmetry plane or

Scheme I



axis. The same dimer was formed in even higher yield in methanol, but low yields of a symmetric dimer **19**[19] and a methanol adduct **18**[20] (analogous to **15**) were also formed. In furan, **16** gave mainly the trans adducts **20** and **21**, in addition to a little cyclobutane dimer **17**. The structural assignment for **20** and **21** is based on their NMR spectra.[21]

Synthesis and Irradiation of the Three Naphtho Analogues of 4. The synthesis of **29, 30,** and **31** was accomplished according to Scheme I. The reactions are patterned after the synthesis of **4**,[8] and the structures follow directly from the synthetic route and spectral properties. Only two features of Scheme I are worth special comment. Keto acids **22** and **23** were distinguished by their UV spectra[22] and by the fact that, after reduction, **22** gave two cyclization products (**26** and **27**), whereas **23** gave only one (**28**). Ketones **26** and **27** were distinguished by their UV[23] and NMR[24] spectra.

Irradiation of **29** in cyclohexane gave four crystalline dimers to which we assign structures **32–35**. The mass spectra of **32–34** showed that they were cyclobutane dimers, with low

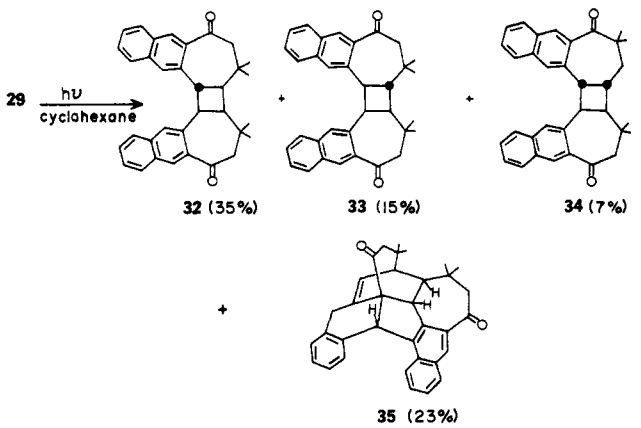
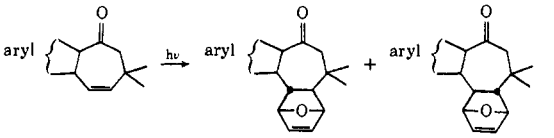


Table II. Furan Adducts from **29**, **30**, and **31**



	Mp, °C	%	Mp, °C	%
29	36 129–130	59	37 171–172	21
30	38 167–168	59	39 179–180	19
31	40 163–164	41	41 186–187	28

Table III. Partial NMR Spectra of Furan Adducts **36–41**[9]

	H(1) (exo), H(7) (endo)			H(1) (endo), H(7) (exo)		
	36	38	40	37	39	41
H(1)	3.50	3.48	3.83	2.85	2.80	3.33
H(7)	1.30	1.43	1.47	2.17	2.33	2.52
H(8)	4.67	4.68	4.70	4.87	4.90	4.85
H(9)	6.28	6.37	6.18	6.27	6.23	6.28
H(10)	6.28	6.22	5.83	6.52	6.47	6.87
H(11)	5.52	5.47	6.12	5.53	5.40	5.58
$J_{1,7}$	6	6	5	6	7	7
$J_{1,11}$	4	4	5	0	0	0
$J_{7,8}$	0	0	0	4	4	3.5
$J_{8,9}$	~1	1.5	2	1.5	1.5	1.5
$J_{9,10}$		5	6	6	5.5	6
$J_{10,11}$	~0–1	1	1.5	2	2	2

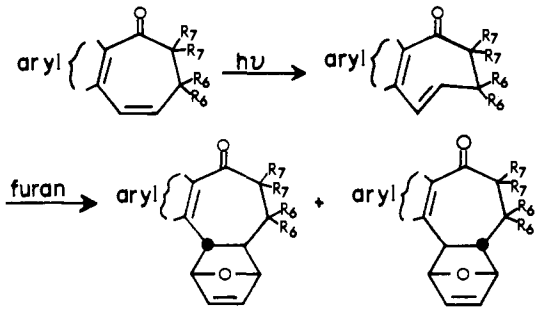
intensity (<5%) M^+ peaks at *m/e* 472 and base peaks at $(M/2)^+$. For dimer **35**, on the other hand, the M^+ peak was the base peak, and the peak at $(M/2)^+$ was very weak (7%). The detailed structures of **32–35** were determined by single crystal x-ray analysis.[25] Consistent with these assignments, **32, 33,** and **35** each showed four separate methyl singlets in their NMR spectra, whereas **34** showed two six-proton singlets for the methyl groups. Also, **34** showed two-proton doublets at δ 2.38 and 3.87 (cyclobutane methine protons, J = 8 Hz) and at δ 2.78 and 3.42 (methylene protons, J = 20 Hz), consistent with its symmetry. Irradiation of **29** in methanol gave **32** (16%), **33** (29%), and **35** (33%); no **34** was present in the crude reaction mixture (NMR) nor was any methanol adduct isolated.

Irradiation of **30** or **31** in cyclohexane under the same conditions used with **29** gave only recovered starting material in nearly quantitative yield.

Irradiation of **29, 30,** or **31** in furan gave, in each case, two trans adducts. The adducts were crystalline and their structures, including stereochemistry, were readily assigned from their NMR spectra. In each case, the isomer with the benzylic proton exo predominated (Table II). Important features of the NMR spectra of the adducts are summarized in Table III.[9] The most significant of these are that H(1) appears at lower field in **36, 38,** and **40** (where it is exo) than it does in **37, 39,** or **41** (where it is endo).[3,10] The converse is true for H(7). Also, $J_{1,11}$ is 4–5 Hz when H(1) is exo (**36, 38, 40**), but 0 when H(1) is endo (**37, 39, 41**) and the converse is true for $J_{7,8}$.[3,11,12] The chemical shifts of H(1), H(10), and H(11) are somewhat exceptional in **40** and **41** because the second aryl ring comes close in space to those three protons.

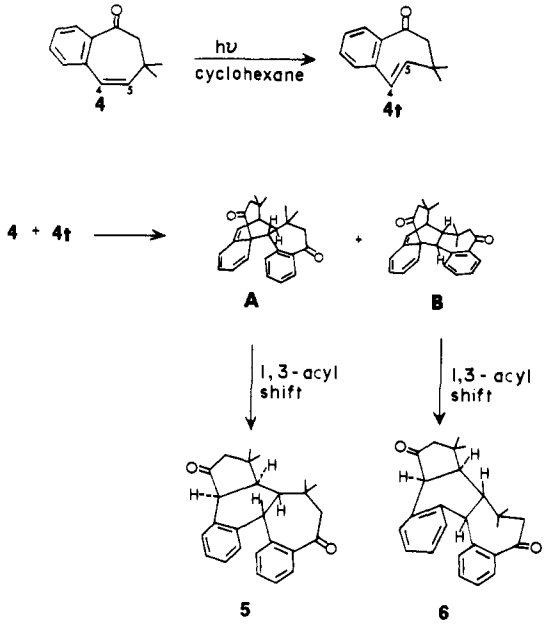
Mechanistic Considerations. Each of the cycloheptadienones which we studied (**4, 11, 16, 29, 30,** and **31**) gave a good yield of two trans adducts when irradiated in furan. It seems clear, therefore, that as with **1** the photoreaction in each case is a cis → trans isomerization of the carbon–carbon double bond.

Although each of the trans intermediates reacted similarly toward furan, they reacted very differently from one another when the irradiations were carried out in cyclohexane or



methanol. We consider first plausible mechanisms which rationalize the observed products in each case. We will then return to the question of how substituents affect the reactivities of the trans intermediates.

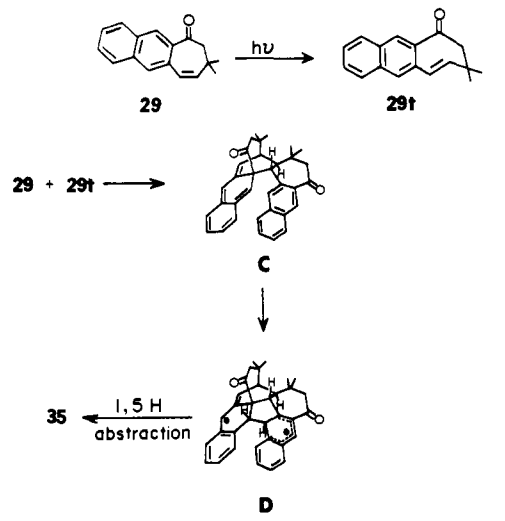
The formation of **5** and **6** from **4** can be rationalized as follows. Photoisomerization of **4** gives **4t,** which then cycloadds



to the styrene moiety of **4**. The proposed intermediates A and B which arise in this way undergo a 1,3-suprafacial acyl shift to give the observed products, **5** and **6,** respectively.

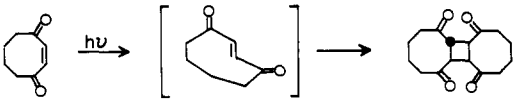
Each product is formed as a consequence of C(5)-C(5) bonding between **4** and **4t**. No products were observed as a consequence of C(4)-C(5) bonding. The polarities of the C(4)-C(5) double bonds in **4** and **4t** are reversed. In **4,** C(5) is δ^+ as a consequence of conjugation through the benzene ring with the carbonyl group. In **4t** there is probably direct transannular interaction between the double bond and the carbonyl group such that C(5) is δ^- and C(4) is δ^+ (the direction of methanol addition to **11t** to form **15** supports this idea). Therefore only C(5)-C(5) bonding between **4** and **4t** occurs.[26] As to the preference for A over B (i.e., **5** over **6**), interference between the *gem*-dimethyl groups would actually seem to favor B. However in the formation of B there is a highly unfavorable interaction between the three-carbon carbonyl-containing bridge of **4** and the aryl ring of **4t,** best seen with models, and this effect apparently predominates.

The formation of **35** from **29** can be similarly rationalized. The trans intermediate **29t** adds to the styrene moiety of **29** to give C (analogous to A from **4** and **4t**). Unlike A, C is an *o*-quinonedimethide. Any diradical character in this moiety could lead to attack on the nearby aryl ring to give D which, from models, can easily undergo intramolecular 1,5-hydrogen abstraction to give the observed product **35**. We have no good explanation why 1,3-acyl migration does not occur in C to form products analogous to **5** and **6** from A.

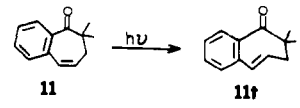


The predominant products from the irradiation of **11, 16,** and **29** in cyclohexane were cyclobutane dimers in which one moiety was trans and the other cis. Only the head-to-head orientation with C(5)-C(5) bonding was observed. The formation of **32** as the principal cyclobutane dimer of **29** is particularly striking, since in this dimer two adjacent *gem*-dimethyl bearing carbons are cis to one another on the cyclobutane ring. The absence or very minor formation of the usual cyclobutane dimers in which both moieties have cis geometry is also noteworthy. Finally, the absence of dimer formation, cyclobutane or otherwise, from **30** and **31** is an important fact to which we shall return.

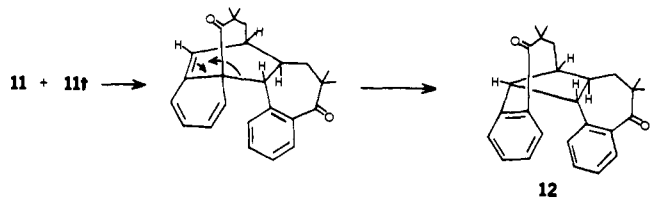
The stereochemistry observed in the cyclobutane dimers **12, 17, 32,** and **33** rules out an excited state allowed concerted process ($_\pi 2_s + _\pi 2_s$) for their formation. The high stereoselectivity, and the obvious unimportance of thermodynamics in controlling product stereochemistry (see especially **32**) also rules out the stepwise diradical dimerization mechanism frequently observed with cyclohexenones.[27] The observed stereochemistry would, however, be consistent with expectation for a *concerted ground state dimerization of two trans-cycloalkenone molecules* ($_\pi 2_s + _\pi 2_a$).[28] Similar stereochemistry has been observed recently in the photodimerization of 2-cyclooctene-1,4-dione.[28b] Such a mechanism requires that the trans isomer react with itself much faster than it reacts with the cis isomer, since the latter is present in larger concentration (and by a concerted reaction, would give dimer with different stereochemistry than was observed).[28c]



One unsatisfactory aspect of this mechanism is that it does not explain why cyclobutane dimers are readily formed from **29,** but not from the closely related **30** and **31**. We suggest, therefore, an alternative mechanism. It is possible that dimerization begins by the cycloaddition of ground state, highly reactive *trans*-cycloalkenone (formed by irradiation of the cis isomer) to the styrene moiety of the cis ketone, as in the formation of A and B from **4** or C from **29**. The resulting adduct can rearomatize through a 1,3-acyl shift (as with A and B) or through a 1,3-shift of the benzylic carbon, as illustrated for the formation of **12** from **11**. This proposal provides a rationalization for the remarkable absence of dimer formation from **30** and **31**. We know, through trapping with furan, that **30** and **31** form reactive trans intermediates. There is no obvious reason from the examination of models why **30,** for example, could not form cyclobutane dimers analogous to **32** and **33**. But if the cyclobutane dimers are formed by an initial ($4\pi + 2\pi$)



11 11t



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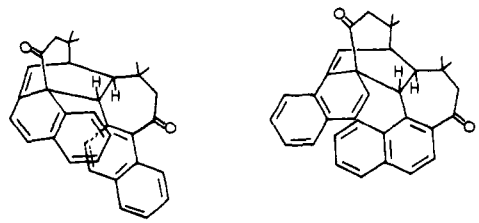
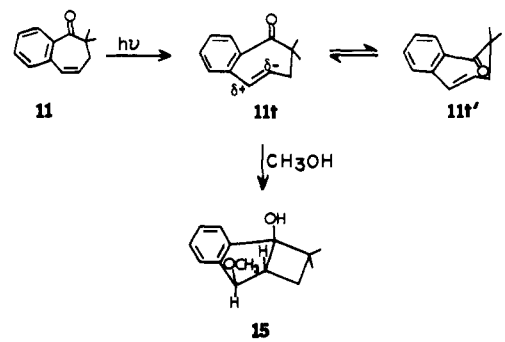
cycloaddition of trans ketone to cis ketone followed by a 1,3-shift, then an explanation becomes apparent. Intermediates analogous to C (from **29**) would be difficult or impossible to form from **30** (+ **30t**) or **31** (+ **31t**) because of steric interference between the aryl rings.



from **30** + **30t** from **31** + **31t**

We cannot at present distinguish between these alternatives, although in principle it should be possible to do so, since the mechanism which involves a reaction between two trans intermediates requires two photons for every cyclobutane dimer molecule formed, and the latter mechanism requires only one photon.

Finally, the transannular addition of methanol (**15** from **11**, **18** from **16**) deserves brief comment. The complete stereospecificity of the addition, leading only to product with the methoxyl and hydroxyl groups cis, is noteworthy. The reaction undoubtedly involves addition to the *trans*-cycloalkenone. Two conformations of the trans ketone are possible, but reaction from one of these (**11t'**) would lead to a trans ring juncture between the four- and five-membered rings. Addition of methanol and ring closure from **11t** gives the observed product. The double bond in **11t** is probably polarized as shown because of through-space interaction with the carbonyl group. If the addition of methanol to **11t** were a stepwise process two stereoisomers of **15** could be formed (i.e., a cis fusion of the 4/5



11 11t 11t'

15

rings, but with methoxyl either cis or trans to the hydroxyl). Since only one isomer is formed, we regard the addition and ring closure as being concerted.[29] We have no explanation why methanol addition is a major reaction pathway with **11**, but only a minor path in other cases.

In summary, the principal photoreaction of 2,3-benzo- or 2,3-naphtho-2,4-cycloheptadienones is cis → trans isomerization of the C(4)-C(5) double bond. The resulting trans intermediates form cycloadducts with furan. They also form various types of dimers whose detailed structure depends on subtle and as yet poorly understood substituent effects. The first step in certain of these dimerizations involves a $4\pi + 2\pi$ cycloaddition of the trans intermediate to the styrene moiety of the cis ketone. The stereochemistry of the cyclobutane dimers can be rationalized by a concerted dimerization of two ground state trans intermediates. Certain of the trans intermediates also add methanol stereospecifically.

Experimental Section[30]

Irradiation of 6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone (4) in Furan. A solution (0.061 M) containing 800 mg (4.30 mmol) of 6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone[8] in 70 mL of furan was irradiated through Pyrex for 2 h. The yellow reaction mixture was concentrated under reduced pressure, and the residue was chromatographed. The first eluate was concentrated and the residue was recrystallized from hexanes to give 415 mg (52%) of pure adduct **7**, mp 160–161 °C (colorless needles): IR (Nujol) $\nu_{C=O}$ 1652 cm^{-1}; λ_{max}^{MeOH} 286 nm (ϵ 2290), 246 (12 070); NMR[9,31,32] ($CDCl_3$) δ 1.12 (s, 3 H, methyl, 1.47), 1.18 (s, 3 H, methyl, 1.00), 1.23 (d, 1 H, J = 6 Hz, H(7), 1.94), 2.43 (d, 1 H, J = 11 Hz, methylene, 1.35), 2.83 (d, 1 H, J = 11 Hz, methylene, 1.35), 3.42 (dd, 1 H, J = 4, 6 Hz, H(1), 2.94), 4.67 (br d, 1 H, J = 2 Hz, H(9), 3.71), 5.43 (dd, 1 H, J = 1.5, 4 Hz, H(8), 2.71), 6.20 (dd, 1 H, J = 1.5, 6 Hz, H(10), 1.12), 6.35 (dd, 1 H, J = 2, 6 Hz, H(11), 1.18), 6.88–7.35 (m, 3 H, arom), 7.53–7.75 (m, 1 H, arom, 1.12); mass spectrum, *m/e* (rel intensity) 254 (0.2), 186 (77), 171 (100), 144 (73), 143 (44), 141 (38), 128 (57), 115 (71), 39 (41).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.26; H, 7.11.

The second eluate was concentrated and the residue was recrystallized from hexanes to give 140 mg (20%) of pure adduct **8**, mp 171–172 °C (colorless needles): IR (Nujol) $\nu_{C=O}$ 1662 cm^{-1}; λ_{max}^{MeOH} 286 nm (ϵ 2390), 247 (12 880); NMR ($CDCl_3$) δ 0.82 (s, 3 H, methyl, 1.00), 1.22 (s, 3 H, methyl, 1.25), 2.08 (dd, 1 H, J = 4, 6 Hz, H(7), 1.25), 2.33 (d, 1 H, J = 11 Hz, methylene, 2.75), 2.68 (d, 1 H, J = 11 Hz, methylene, 2.50), 2.78 (br d, 1 H, J = 6 Hz, H(1), 2.50), 4.85 (dd, 1 H, J = 1.5, 4 Hz, H(9), 6.50), 5.43 (br d, 1 H, J = 2 Hz, H(8), 4.50), 6.27 (dd, 1 H, J = 1.5, 6 Hz, H(11), 1.00), 6.53 (dd, 1 H, J = 2, 6 Hz, H(10), 1.50), 6.93–7.52 (m, 3 H, arom), 7.57–7.80 (m, 1 H, arom, 2.00); mass spectrum, *m/e* (rel intensity) 254 (0.5), 186 (75), 171 (100), 144 (72), 143 (41), 141 (46), 128 (57), 115 (73), 81 (47), 39 (33).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.33; H, 7.20.

A similar irradiation of **4** (186 mg, 1.0 mmol) in 15 mL of spectrograde cyclohexane containing 204 mg (3.0 mmol) of furan (Rikosha 400 W lamp, Pyrex, 4 h) gave on similar workup 85 mg (33%) of pure adduct **7** and 31 mg (12%) of pure adduct **8**.

7,7-Dimethyl-2,3-benzo-2-cycloheptenone (9). To a suspension of sodium amide (3.4 g, 0.085 mol) in 15 mL of toluene at 40–60 °C was added dropwise with stirring a solution of 12 g (0.075 mol) of benzosuberone in 30 mL of toluene. The red mixture was refluxed for 30 min, cooled to room temperature, and 12 mL (0.19 mol) of methyl iodide in 15 mL of toluene was added dropwise. The mixture was refluxed for 2 h, cooled, and poured into 150 mL of saturated salt solution. Workup gave a crude product which was resubmitted to the same procedure. Distillation of the resulting product with a short-path Vigreux column gave 8.1 g (58%) of **9**, bp 80–81 °C (0.5 Torr) [lit. value[13] 140 °C (16 Torr)]: IR (neat) $\nu_{C=O}$ 1680 cm^{-1}; NMR (CCl_4) δ 1.10 (s, 6 H, *gem*-dimethyl), 1.00–2.00 (m, 4 H, C(5) and C(6) methylenes), 2.69 (t, 2 H, J = 6 Hz, C(4) methylene), 6.80–7.18 (m, 4 H, arom).

7,7-Dimethyl-2,3-benzo-2,4-cycloheptadienone (11). To a solution of **9** (8 g, 0.042 mol) in 150 mL of carbon tetrachloride was added 0.3–0.4 g of benzoyl peroxide and 10 g (0.055 mol) of *N*-bromosuccinimide. The mixture was refluxed until the NBS was consumed (6–7 h). The succinimide was filtered and the solvent was evaporated to give 12 g of crude 4-bromo-7,7-dimethyl-2,3-benzo-2-cycloheptenone (**10**). 2,4,6-Collidine (12 mL) was added to this crude residue and the mixture was heated overnight at 115 °C. The semisolid reaction mixture was triturated with 200 mL of hexane, and the hexane layer was washed with 10% hydrochloric acid and water and dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue through a short Vigreux column gave 4.5 g (57%) of **11**, bp 93–96 °C (1 Torr): IR (neat) $\nu_{C=O}$ 1675 cm^{-1}; λ_{max} (cyclohexane) 310 nm (ϵ

1970), 277 (sh, 2930), 261 (5730), 236 (12 600); NMR (CCl_4) δ 1.15 (s, 6 H, *gem*-dimethyl), 2.30 (dd, 2 H, J = 1, 5 Hz, methylene), 5.80 (dt, 1 H, J = 11, 5 Hz, C(5) vinyl), 6.33 (br d, 1 H, J = 11 Hz, C(4) vinyl), 6.85–7.60 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 186 (70), 171 (22), 158 (9), 144 (43), 130 (100), 115 (45). An analytical sample was prepared by GLC (6 ft × 0.25 in. column, 10% XF 1150 on Chromosorb, 180 °C).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.55. Found: C, 83.79; H, 7.44.

Irradiation of 11 in Cyclohexane. A solution (0.05 M) containing 186 mg (1 mmol) of **11** in 20 mL of spectrograde cyclohexane was irradiated (Uranium glass filter) for 4 h. The reaction was monitored by TLC. Some precipitate forms during the irradiation. The reaction mixture was concentrated to dryness and the residue was triturated with hexane. The solid product was filtered to yield 110 mg (59%) of dimer **12**, mp 278–280 °C (acetone): IR (Nujol) $\nu_{C=O}$ 1690, 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (s, 3 H, methyl), 1.10 (s, 3 H, methyl), 1.22 (s, 3 H, methyl), 1.25 (s, 3 H, methyl), 1.50–2.20 (m, 4 H, C(6) and C(6′) methylenes), 2.50–3.00 (m, 2 H, C(5) and C(5′) methines), 3.45 (t, 1 H, J = 10 Hz, C(4) methine), 3.80–4.10 (m, 1 H, C(4′) methine), 6.95–7.31 (m, 8 H, arom); mass spectrum, *m/e* (rel intensity) 372 (3.5), 186 (100). An analytical sample, mp 282–283 °C, was prepared by two recrystallizations from acetone.

Anal. Calcd for $(C_{13}H_{14}O)_2$: C, 83.83; H, 7.55. Found: C, 83.87; H, 7.58.

The hexane filtrate was concentrated and subjected to preparative TLC (silica gel, 2 mm, methylene chloride). Two fractions were isolated, 28 mg (15%) of a cyclobutane dimer **42** and 18 mg (9%) of recovered **11**. The dimer (dimers?) **42** was not obtained pure, but the sample isolated had a mass spectrum with peaks at *m/e* 372 (3) and 186 (100).

Irradiation of 11 in Furan. A solution (0.06 M) containing 558 mg (3 mmol) of **11** in 50 mL of furan (freshly distilled from lithium aluminum hydride) was irradiated (Uranium glass filter) for 3 h. The solvent was removed and the residue was chromatographed on 35 g of silica gel. The first fraction (28 mg, 5%) was recovered **11**. The second fraction (40 mg, 7%) was dimer **12**. The third fraction (23 mg, 4%) was mainly dimer **42**. The fourth fraction (30 mg, 4%) was a mixture of unidentified furan adducts (mass spectrum). The fifth fraction (115 mg, 15%) was the furan adduct **14**, mp 127–128 °C (hexane): IR (Nujol) $\nu_{C=O}$ 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (s, 3 H, endo C(5) methyl), 1.15 (s, 3 H, exo C(5) methyl), 1.40–2.45 (m, 4 H, C(1), C(6), and C(7) protons), 4.72–4.89 (m, 1 H, C(8) methine), 5.20 (br d, 1 H, J = 1.5 Hz, C(11) methine), 6.18 (dd, 1 H, J = 1.5, 6 Hz, C(10) vinyl), 6.50 (dd, 1 H, J = 2, 6 Hz, C(9) vinyl), 7.00–7.22 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 254 (1), 186 (100), 171 (31), 68 (19).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.18; H, 7.09.

The sixth fraction (250 mg, 33%) was the furan adduct **13**, mp 123–124 °C (hexane; eluted as an oil, but later crystallized): IR (neat) $\nu_{C=O}$ 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.11 (s, 3 H, endo C(5) methyl), 1.23 (s, 3 H, exo C(5) methyl), 1.50–2.18 (m, 3 H, C(6) and C(7) protons), 3.08 (dd, 1 H, J = 4, 5 Hz, C(1) methine), 4.50 (d, 1 H, J = 2 Hz, C(8) methine), 5.13 (dd, 1 H, J = 1.5, 4 Hz, C(11) methine), 6.30 (dd, 1 H, J = 1.5, 6. Hz, C(10) vinyl), 6.52 (dd, 1 H, J = 2, 6 Hz, C(9) vinyl), 6.70–7.22 (m, 4 H, arom); mass spectrum. *m/e* (rel intensity) 254 (1), 186 (100), 171 (27), 68 (15).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.21; H, 7.11.

Irradiation of 11 in Methanol. A solution (0.05 M) containing 558 mg (3 mmol) of **11** in 60 mL of methanol was irradiated (Uranium glass filter) for 3 h. The solvent was evaporated and the residue was triturated with hexane. the solid fraction which remained (185 mg, 33%) was dimer **12** and the oily fraction isolated after evaporation of the hexane (435 mg, 66%) was *cis*-4-methoxy-7,7-dimethyl-2,3-benzobicyclo[3.2.0]hept-2-en-1-ol (**15**). Attempts to obtain an analytical sample of **15** by chromatography on silica gel or Florisil failed because the compound was too strongly adsorbed and tended to lose water or methanol. Chromatography on 25 g of Florisil with methylene chloride/methanol (9:1) eluent gave 302 mg (46%) of an NMR-pure sample (in some experiments, up to 5% of dimer **42** was also isolated). For **15**: IR (neat) ν_{OH} 3390 cm^{-1}; NMR ($CDCl_3$) δ 0.60 (dd, 1 H, J = 7.5, 11.5 Hz, endo C(6) methylene), 0.70 (s, 3 H, endo C(7) methyl), 1.21 (s, 3 H, exo C(7) methyl), 1.63 (dd, 1 H, J = 9.5, 11.5 Hz, exo C(6) methylene), 2.68 (dd, 1 H, J = 7.5, 9.5 Hz, C(5) methine), 2.98 (s, 3 H, methoxyl), 3.80 (br s, 1 H, hydroxyl, exchanges in D_2O), 4.20 (s, 1 H, C(4) methine), 7.00–7.30 (m, 4 H, arom); for decoupling and $Eu(fod)_3$ shift data on **15**, see text; mass spectrum, *m/e* (rel intensity) 218 (0.5), 200 (1), 186 (10), 162 (57), 147 (100).

2,3-Benzo-2,4-cycloheptadienone (16). The procedure was similar to that described for the preparation of **11**. Benzosuberone (5 g, 0.031 mol) was brominated with 7 g (0.043 mol) of *N*-bromosuccinimide in 100 mL of carbon tetrachloride using 0.35 g of benzoyl peroxide as catalyst. The resulting bromo ketone was dehydrobrominated using 9 mL of 2,4,6-collidine (120 °C, overnight). Distillation gave 2.2 g (44%) of **16**, bp 82–85 °C (0.5 Torr) [lit. value[18] 146 °C (75 Torr)]: IR (neat) $\nu_{C=O}$ 1680 cm^{-1}; λ_{max} (cyclohexane) 315 nm (ϵ 2190), 277 (sh, 3350), 268 (5660), 259 (5400), 230 (23 400); NMR (CCl_4) δ 2.20–2.60 (m, 2 H, C(7) methylene), 2.70–2.98 (m, 2 H, C(6) methylene), 5.96 (dt, 1 H, J = 11, 5 Hz, C(5) vinyl), 6.32 (d, 1 H, J = 11 Hz, C(4) vinyl), 6.90–7.80 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 158 (91), 130 (79), 129 (100), 128 (51), 115 (70). An analytical sample was purified by GLC, 6 ft × 0.25 in. column, 10% XF 1150 on Chromosorb W, 180 °C.

Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.46; H, 6.40.

Irradiation of 16 in Cyclohexane. A solution (0.05 M) containing 474 mg (3 mmol) of **16** in 60 mL of spectrograde cyclohexane was irradiated (Uranium glass filter) for 8 h. The reaction mixture was concentrated and chromatographed on 50 g of silica gel. After several unidentified, minor fractions there was obtained 150 mg (33%) of the cyclobutane dimer **17** as an oil which solidified on standing, mp 129–131 °C (ethanol–hexane; difficult to recrystallize). For **17**: IR (neat) $\nu_{C=O}$ 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.65–2.20 (m, 4 H, C(6) and C(6′) methylenes), 2.60–3.10 (m, 6 H, C(5) and C(5′) methines and C(7) and C(7′) methylenes), 3.50–3.90 (m, 2 H, C(4) and C(4′) methines), 7.00–7.60 (m, 8 H, arom); mass spectrum, *m/e* (rel intensity) 316 (0.8), 158 (100).

Anal. Calcd. for $(C_{11}H_{10}O)_2$: C, 83.51; H, 6.37. Found: C, 83.38; H, 6.31.

Irradiation of 16 in Methanol. A solution (0.043 M) containing 474 mg (3 mmol) of **16** in 70 mL of analytical grade methanol was irradiated (Uranium glass filter) for 5.5 h. The residue obtained on concentration of the reaction mixture was chromatographed on 50 g of silica gel to give 216 mg (46%) of **17** followed by 20 mg (4%) of another cyclobutane dimer **19** as an oil: IR (neat) $\nu_{C=O}$ 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.76–2.25 (m, 4 H, C(6) and C(6′) methylenes), 2.40–2.80 (m, 2 H, C(5) and C(5′) methines), 2.80–3.00 (m, 4 H, C(7) and C(7′) methylenes), 3.88 (d, 2 H, J = 8 Hz, C(4) and C(4′) methines), 6.90–7.50 (m, 8 H, arom); mass spectrum, *m/e* (rel intensity) 316 (1.4), 158 (100).

Further elution with methylene chloride containing 1% of methanol gave 100 mg of a brown fraction containing about 30% (NMR) of bicyclic adduct **18** (estimated yield 6%): IR (neat) ν_{OH} 3400 cm^{-1}, $\nu_{C=O}$ from other products, 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.60–3.00 (m, 6 H), 3.18 (s, 3 H, methoxyl), 4.25 (s, 1 H, benzyl), 6.90–7.55 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 190 (weak), 172 (weak), 158 (strong).

Irradiation of 16 in Furan. A solution (0.055 M) containing 395 mg (2.5 mmol) of **16** in 45 mL of furan (freshly distilled from lithium aluminum hydride) was irradiated (Uranium glass filter) for 6 h. Chromatography on 50 g of silica gel gave 16 mg (4%) of dimer **17** followed by 60 mg of pure furan adduct **21**, mp 156–157 (hexane) or 154–155 °C (sublimation at 120–130 °C and 0.4 Torr), then 232 mg of a mixture of **21** and **20** (40:60 by NMR), and finally 57 mg of pure furan adduct **20**, mp 174–175 (hexane) or 171–172 °C (sublimation at 120–130 °C and 0.3 Torr). The mixture of **20** and **21** could be partially separated by fractional crystallization from hexane (adduct **21** is the more soluble isomer). The total yield of **21** was 27%, and of **20** was 35%. For **21**: IR (Nujol) $\nu_{C=O}$ 1665 cm^{-1}; NMR ($CDCl_3$) δ 1.10–1.70 (m, 1 H, C(7) methine), 1.90–2.40 (m, 2 H, C(6) methylene), 2.70–3.00 (m, 3 H, C(1) methine and C(5) methylene). 4.78–4.90 (m, 1 H, C(8) methine), 5.43 (br s, 1 H. C(1) methine), 6.28 (dd, 1 H, J = 1.5, 6 Hz, C(10) vinyl), 6.57 (dd, 1 H, J = 1.5, 6 Hz, C(9) vinyl), 7.00–7.80 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 226 (0.25), 158 (100), 68 (12).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.62; H, 6.30.

For **20**: IR (Nujol) $\nu_{C=O}$ 1665 cm^{-1}; NMR ($CDCl_3$) 1.20–2.50 (m, 3 H, C(6) methylene and C(7) methine), 2.60–3.00 (m, 2 H, C(5)

methylene), 3.40 (dd, 1 H, J = 4, 6 Hz, C(1) methine), 4.60 (d, 1 H, J = 1.5 Hz, C(8) methine), 5.40 (dd, 1 H, J = 1.5, 4 Hz, C(11) methine), 6.25 (dd, 1 H, J = 1.5, 5.5 Hz, C(10) vinyl), 6.40 (dd, 1 H, J = 1.5, 5.5 Hz, C(9) vinyl), 6.90–7.80 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 226 (0.5), 158 (100), 68 (10).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.68; H, 6.20.

3,3-Dimethyl-4-(2′-naphthoyl)butanoic acid (22) and 3,3-Dimethyl-4-(1′-naphthoyl)butanoic acid (23). To a solution of 19.2 g (0.15 mol) of naphthalene and 14.2 g (0.1 mol) of 3,3-dimethylglutaric anhydride in 80 mL of nitrobenzene was added 26.7 g (0.2 mol) of aluminum chloride in small portions. The mixture was stirred at 0–5 °C for 12 h, then treated with 20 mL of concentrated hydrochloric acid. The solvent was removed by steam distillation and the product was triturated with chloroform. The chloroform layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The oily residue was subjected to silica gel chromatography to give 12.4 g (46%) of a crystalline product containing **22** and **23** (2:1 by NMR; the C(2) methylene peaks at δ 2.63 in **22** and 2.67 in **23** were used). Repeated fractional crystallization (**22** separated first) from hexanes gave 7.0 g (26%) of pure **22**, mp 95–96 °C (colorless needles), and 3.2 g (12%) of pure **23**, mp 84–85 °C (pale yellow prisms).

For **22**: IR (Nujol) $\nu_{C=O}$ 1688, 1672 cm^{-1}; λ_{max}^{MeOH} 340 nm (ϵ 2160), 326 (sh, 1890), 291 (sh, 6210), 280 (9990), 270 (sh, 7020), 247 (32 290), 240 (sh, 30 190);[22] NMR ($CDCl_3$) δ 1.22 (s, 6 H, *gem*-dimethyl), 2.63 (s, 2 H, C(2) methylene), 3.25 (s, 2 H, C(4) methylene), 7.43–8.20 (m, 6 H, arom), 8.48 (br s, 1 H, C(1′) arom), 11.56 (br s, 1 H, CO_2H); mass spectrum, *m/e* (rel intensity) 270 (23), 252 (10), 237 (19), 170 (56), 155 (100), 127 (46).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.71; H, 6.50.

For **23**: IR (Nujol) $\nu_{C=O}$ 1686, 1655 cm^{-1}; λ_{max}^{MeOH} 295 nm (ϵ 6000), 238 (sh, 13 800), 221 (sh, 37 330), 214 (42 000);[22] NMR ($CDCl_3$) δ 1.22 (s, 6 H, *gem*-dimethyl), 2.67 (s, 2 H, C(2) methylene), 3.22 (s, 2 H, C(4) methylene), 7.27–8.17 (m, 6 H, arom), 8.37–8.72 (m, 1 H, C(2′) arom), 11.13 (br s, 1 H, CO_2H); mass spectrum, *m/e* (rel intensity) 270 (9), 252 (49), 237 (67), 210 (15), 195 (21), 156 (29), 155 (100), 127 (46).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.41; H, 6.69.

3,3-Dimethyl-5-(2′-naphthyl)pentanoic Acid (24). to a solution of 2.4 g (0.043 mol) of potassium hydroxide in 4 mL of ethylene glycol was added a solution of 2.7 g (0.01 mol) of **22** in 6 mL of the same solvent. The solution was cooled to room temperature and hydrazine hydrate (2 mL, 0.04 mol) was slowly added. The solution was stirred and slowly heated to 200 °C, all volatile components boiling below 200 °C being removed by distillation. The mixture was refluxed for 10 h, cooled to room temperature, and poured into ice water containing 65 mL of concentrated hydrochloric acid, affording **24** as an off-white solid which was recrystallized from hexanes to give 2.0 g (78%) of **24**, mp 72–73 °C (colorless prisms): IR (Nujol) $\nu_{C=O}$ 1686 cm^{-1}; λ_{max}^{MeOH} 285 nm (ϵ 3260, sh), 275 (4780), 265 (sh, 4190); NMR ($CDCl_3$) δ 1.13 (s, 6 H, *gem*-dimethyl), 1.52–1.95 (m, 2 H, C(4) methylene), 2.35 (s, 2 H, C(2) methylene), 2.57–2.98 (m, 2 H, C(5) methylene), 7.18–7.93 (m, 7 H, arom), 11.55 (br s, 1 H, CO_2H); mass spectrum, *m/e* (rel intensity) 256 (55), 155 (100), 141 (97), 115 (17), 57 (20), 56 (17), 43 (17), 41 (21).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.69; H, 7.83.

8,9,10,11-Tetrahydro-9,9-dimethyl-7-oxocyclohepta[*a*]naphthalene (27) and 8,9,10,11-Tetrahydro-9,9-dimethyl-7-oxocyclohepta[*b*]naphthalene (26). To a freshly prepared solution of phosphoric anhydride (11 g) in 7 mL of phosphoric acid was added 1.2 g (4.6 mmol) of **24**, and the mixture was heated on the steam bath for 2 h, and poured while hot into ice water, affording 1.1 g of a semisolid (containing **27** and **26**, 7:3 by GLC) which was recrystallized from hexanes to give 0.54 g of **26** as colorless plates, mp 105–106 °C. The hexanes filtrate was subjected to silica gel chromatography to give as the first fraction 0.2 g (19%) of nearly pure **27** as a pale yellow oil which was further purified to a colorless oil by gas–liquid chromatography (5 ft × 0.25 in. 20% SE-30 on Chromosorb W, 80–100 mesh, 210 °C). The second fraction gave 0.26 g of **26** for a combined yield of 0.80 g (72%).

For **27**: IR (neat) $\nu_{C=O}$ 1672 cm^{-1}; λ_{max}^{EtOH} 299 nm (ϵ 5450), 242 (sh, 14 070); NMR ($CDCl_3$) δ 1.13 (s, 6 H, *gem*-dimethyl), 1.62–1.90 (m, 2 H, C(10) methylene), 2.68 (s, 2 H, C(8) methylene), 2.88–3.22 (m, 2 H, C(11) methylene), 7.23–7.93 (m, 3 H, arom), 7.25 (d, 1 H, J = 8.5 Hz, C(1) arom), 7.88 (d, 1 H, J = 8.5 Hz, C(2) arom), 8.10–8.42 (m, 1 H, C(6) arom); mass spectrum, *m/e* (rel intensity) 238 (100), 223 (4), 210 (14), 195 (31), 182 (41), 181 (63), 169 (33), 155 (20), 154 (87), 153 (43), 152 (33), 141 (29), 140 (23), 139 (25).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.47; H, 7.53.

For **26**: IR (Nujol) $\nu_{C=O}$ 1664 cm^{-1}; λ_{max}^{EtOH} 347 nm (ϵ 2600), 298 (sh, 7090), 286 (9450), 275 (sh, 7560), 251 (50 100), 246 (47 730), 235 (sh, 31 660); NMR ($CDCl_3$) δ 1.12 (s, 6 H, *gem*-dimethyl), 1.63–1.90 (m, 2 H, C(10) methylene), 2.70 (s, 2 H, C(8) methylene), 3.02–3.30 (m, 2 H, C(11) methylene), 7.10–8.08 (m, 5 H, arom), 8.40 (s, 1 H, C(6) arom); mass spectrum, *m/e* (rel intensity) 238 (100), 223 (5), 210 (7), 195 (21), 182 (18), 181 (20), 169 (61), 165 (13), 154 (55), 153 (25), 152 (22), 141 (16), 140 (13), 139 (16), 57 (64).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.78; H, 7.68.

8,9-Dihydro-9,9-dimethyl-7-oxocyclohepta[*b*]naphthalene (29). A mixture containing 2.7 g (11.3 mmol) of **26**, 2.0 g (11.3 mmol) of freshly recrystallized *N*-bromosuccinimide, and 0.1 g of azobisisobutyronitrile in 80 mL of carbon tetrachloride was heated at reflux for 2 h, then cooled to room temperature and filtered to remove the succinimide, and the solvent was removed by rotary evaporation. 2,4,6-Collidine (2.7 g, 22.5 mmol, freshly distilled) was added and the mixture was heated at 115–120 °C for 12 h. The cooled reaction mixture was triturated with carbon tetrachloride, the CCl_4 layer was washed with 10% hydrochloric acid, water, and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the oily residue was chromatographed on silica gel. The first fraction gave 210 mg (5.9%) of a yellow oil believed to be 11-bromo-8,9-dihydro-9,9-dimethyl-7-oxocyclohepta[*b*]naphthalene (**43**). The second fraction gave 1.86 g (70%) of **29**, mp 65–66 °C (colorless prisms for hexanes).[33] The last fraction was 0.35 g (13%) of recovered **26**.

For **29**: IR (Nujol) 1661, 1617 cm^{-1}; λ_{max} (cyclohexane) 360 nm (ϵ 990), 304 (sh, 4600), 293 (9190), 284 (10 510), 270 (sh, 25 610), 251 (41 370), 244 (sh, 32 170), 225 (20 680); NMR ($CDCl_3$) δ 1.20 (s, 6 H, *gem*-dimethyl), 2.93 (s, 2 H, methylene), 5.87 (d, 1 H, J = 11.5 Hz, C(10) vinyl), 6.48 (d, 1 H, J = 11.5 Hz, C(11) vinyl), 7.25–8.08 (m, 5 H, arom), 8.43 (s, 1 H, C(6) arom); mass spectrum, *m/e* (rel intensity) 236 (88), 221 (100), 207 (14), 194 (38), 193 (43), 179 (22), 178 (52), 165 (25), 152 (21).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.44; H, 6.95.

For **43**: NMR ($CDCl_3$) δ 1.20 (s, 6 H, *gem*-dimethyl), 2.97 (s, 2 H, methylene), 6.77 (s, 1 H, vinyl), 7.37–8.13 (m, 4 H, arom), 8.30 (s, 1 H, C(1) arom), 8.53 (s, 1 H, C(6) arom).

8,9-Dihydro-9,9-dimethyl-7-oxocyclohepta[*a*]naphthalene (30). A mixture containing 0.71 g (3 mmol) of **27**, 0.53 g (3 mmol) of freshly recrystallized *N*-bromosuccinimide, and 0.02 g of azobisisobutyronitrile in 20 mL of carbon tetrachloride was heated at reflux for 2 h, then cooled to room temperature and filtered to remove the succinimide, and the solvent was removed by rotary evaporation. 2,4,6-Collidine (0.7 g, 6 mmol, freshly distilled) was added and the mixture was heated at 115–120 °C for 12 h. The cooled reaction mixture was triturated with carbon tetrachloride, the CCl_4 layer was washed with 10% hydrochloric acid and water, and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the oily residue was chromatographed on silica gel. The first fraction gave 80 mg (8.5%) of a yellow oil believed to be 11-bromo-8,9-dihydro-9,9-dimethyl-7-oxocyclohepta[*a*]naphthalene (**44**). The second fraction was the desired **30** (515 mg, 73%) isolated as a pale yellow oil.[34] This product was further purified by gas–liquid chromatography, 5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 210 °C. The last fraction was recovered **27** (60 mg, 8%).

For **30**: IR (neat) $\nu_{C=O}$ 1675 cm^{-1}; λ_{max} (cyclohexane) 348 nm (ϵ 5190, sh), 327 (7320), 321 (7320), 270 (34 220), 259 (38 230), 252 (37 340), 243 (sh, 33 040), 228 (37 340); NMR ($CDCl_3$) δ 1.20 (s, 6 H, *gem*-dimethyl), 2.98 (s, 2 H, methylene), 5.77 (d, 1 H, J = 12 Hz, C(10) vinyl), 6.32 (d, 1 H, J = 12 Hz, C(11) vinyl), 7.13–7.93 (m, 5 H, arom), 8.18–8.42 (m, 1 H, C(6) arom); mass spectrum, *m/e* (rel intensity) 236 (100), 221 (68), 207 (18), 194 (64), 179 (52), 165 (29), 152 (36).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.46; H, 6.91.

For **44**: NMR ($CDCl_3$) δ 1.15 (s, 6 H, *gem*-dimethyl), 3.07 (s, 2 H, methylene), 6.62 (s, 1 H, vinyl), 7.2–8.1 (m, 6 H, arom).

3,3-Dimethyl-5-(1′-naphthyl)pentanoic acid (25). To a solution of potassium hydroxide (600 mg, 11 mmol) in 2.5 mL of ethylene glycol was added a solution of **23** (540 mg, 2 mmol) in 1.5 mL of the same solvent. The solution was cooled to room temperature and hydrazine hydrate (0.5 mL, 10 mmol) was slowly added. The solution was stirred and slowly brought to 200 °C, all volatile components boiling below 200 °C being removed by distillation. The mixture was refluxed for 10 h, cooled to room temperature, and poured into ice water containing 1.6 mL of concentrated hydrochloric acid, affording **25** as an off-white solid which was recrystallized from hexanes to give 0.35 g (68.6%) of pure **25**, mp 82–83 °C (colorless needles): IR (Nujol) $\nu_{C=O}$ 1700 cm^{-1}; λ_{max}^{MeOH} 292 nm (ϵ 5360, sh), 282 (7660), 272 (6380), 261 (sh, 3830); NMR ($CDCl_3$) δ 1.23 (s, 6 H, *gem*-dimethyl), 1.58–1.92 (m, 2 H, C(4) methylene), 2.43 (s, 2 H, C(2) methylene), 2.92–3.30 (m, 2 H, C(5) methylene), 7.25–8.23 (m, 7 H, arom); mass spectrum, *m/e* (rel intensity) 256 (39), 238 (6), 155 (51), 141 (100), 115 (15).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.76; H, 7.89.

7,8,9,10-Tetrahydro-9,9-dimethyl-11-oxocyclohepta[*a*]naphthalene (28). To a freshly prepared solution of 2.8 g of phosphoric anhydride in 2 mL of phosphoric acid was added 210 mg (0.82 mmol) of **25** and the mixture was heated on a steam bath for 2 h, then poured while hot into ice water. The yellow oil which separated was extracted with chloroform, and the chloroform layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give **28** as an oil which was subjected to column chromatography on silica gel, affording 172 mg (88%) of **28** as a colorless oil. The product could be further purified by GLC (5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 220 °C): IR (neat) $\nu_{C=O}$ 1667 cm^{-1}; λ_{max}^{MeOH} 334 nm (ϵ 2380), 297 (7520), 287 (8980), 276 (sh, 6600), 251 (48 700), 247 (43 030);[35] NMR ($CDCl_3$) δ 1.17 (s, 6 H, *gem*-dimethyl), 1.67–1.93 (m, 2 H, C(8) methylene), 2.70 (s, 2 H, C(10) methylene), 3.32–3.60 (m, 2 H, C(7) methylene), 7.38–8.00 (m, 5 H, arom), 8.10–8.37 (m, 1 H, C(1) arom); mass spectrum, *m/e* (rel intensity) 238 (79), 223 (7), 210 (5), 195 (29), 182 (22), 181 (34), 169 (100), 154 (31), 153 (39), 152 (26), 141 (20), 140 (16), 139 (18).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.69; H, 7.72.

9,10-Dihydro-9,9-dimethyl-11-oxocyclohepta[*a*]naphthalene (31). A mixture containing 152 mg (0.63 mmol) of **28**, 115 mg (0.65 mmol) of freshly recrystallized *N*-bromosuccinimide, and 10 mg of azobisisobutyronitrile in 5 mL of carbon tetrachloride was heated at reflux for 5 h until the NBS was consumed, then cooled to room temperature and filtered to remove the succinimide. The solvent was removed by rotary evaporation. 2,4,6-Collidine (150 mg, 1.3 mmol, freshly distilled) was added to the residue and the mixture was heated at 115–120 °C for 10 h. The cooled reaction mixture was triturated with carbon tetrachloride, the CCl_4 layer was washed with 10% hydrochloric acid and water, and dried ($MgSO_4$). The solvent was removed by evaporation and the product was isolated by column chromatography on silica gel to give 110 mg (73%) of **31** as a pale yellow oil. The product could be further purified by GLC (5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 220 °C): IR (neat) $\nu_{C=O}$ 1667 cm^{-1}; λ_{max} (cyclohexane) 350 nm (ϵ 5020), 317 (6790), 305 (6790), 293 (sh, 4720), 266 (sh, 27 730), 252 (42 480), 247 (sh, 41 300), 238 (sh, 25 960); NMR ($CDCl_3$) δ 1.20 (s, 6 H, *gem*-dimethyl), 3.00 (s, 2 H, methylene), 6.13 (d, 1 H, J = 12 Hz, C(8) vinyl), 7.20 (d, 1 H, J = 12 Hz, C(7) vinyl), 7.38–8.05 (m, 5 H, arom), 8.22–8.50 (m, 1 H, C(1) arom); mass spectrum, *m/e* (rel intensity) 236 (100), 221 (81), 207 (18), 195 (19), 194 (76), 193 (50), 179 (23), 178 (46), 165 (33), 152 (25).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.51; H, 6.81.

Irradiation of 29 in Cyclohexane. A solution (0.05 M) containing 475 mg (2 mmol) of **29** in 40 mL of cyclohexane was irradiated (Pyrex) for 4 h. At this time, a crystalline product which had deposited was filtered and recrystallized from acetone to give 108 mg (22.5%) of the dimer **35**, colorless needles, mp >300 °C. The solvent was evaporated from the filtrate, and the residue was chromatographed on silica gel to give three additional dimers. Fraction 1 gave 31 mg (6.5%) of **34**, colorless needles from acetone, mp >300 °C. Fraction 2 gave 168 mg (35%) of **32**, colorless prisms from acetone, mp 259–259.5 °C dec. Fraction 3 gave 72 mg (15.0%) of **33**, colorless needles from acetone, mp 278–279 °C dec.

For **35**: IR (Nujol) $\nu_{C=O}$ 1682, 1660 cm^{-1}; λ_{max}^{MeOH} 350 nm (ϵ 3310), 291 (8510), 256 (40 170), 217 (47 260); NMR ($CDCl_3$) δ 1.03 (s, 3 H, methyl), 1.37 (s, 3 H, methyl), 1.47 (s, 3 H, methyl), 1.55 (s, 3 H, methyl), 1.8–3.5 (m, 8 H), 4.0 (br d, 1 H, J = 9 Hz), 5.15 (br s, 1 H), 6.13 (br d, 1 H, J = 9 Hz), 6.8–8.1 (m, 9 H, arom); mass spectrum, *m/e* (rel intensity) 473 (39), 472 (100), 416 (19), 388 (32), 332 (41), 331 (40), 304 (47), 303 (71), 302 (45), 289 (16), 276 (11), 265 (10), 236 (7), 151 (26).

Anal. Calcd for $(C_{17}H_{16}O)_2$: C, 86.40; H, 6.83. Found: C, 86.52; H, 6.90.

For **34**: IR (Nujol) 1654, 1618 cm^{-1}; λ_{max}^{MeOH} 347 nm (ϵ 3440), 286 (14 180), 248 (77 760), 214 (54 130); NMR ($CDCl_3$) δ 0.88 (s, 6 H, methyls), 1.05 (s, 6 H, methyls), 2.38 (d, 2 H, J = 8 Hz), 2.78 (d, 2 H, J = 20 Hz), 3.42 (d, 2 H, J = 20 Hz), 3.87 (d, 2 H, J = 8 Hz), 7.25–8.07 (m, 10 H, arom), 8.35 (s, 2 H, arom); mass spectrum, *m/e* (rel intensity) 472 (0.5), 237 (20), 236 (100), 221 (42), 194 (17), 193 (16), 178 (16).

Anal. Calcd for $(C_{17}H_{16}O)_2$: C, 86.40; H, 6.83. Found: C, 86.47; H, 6.80.

For **32**: IR (Nujol) 1668, 1654, 1619 cm^{-1}; λ_{max}^{MeOH} 342 nm (ϵ 4250), 284 (17 490), 245 (95 470), 214 (65 540); NMR ($CDCl_3$) δ 0.87 (s, 3 H, methyl), 1.23 (s, 3 H, methyl), 1.35 (s, 3 H, methyl), 1.47 (s, 3 H, methyl), 2.4–4.1 (m, 8 H), 7.25–8.35 (m, 12 H, arom); mass spectrum, *m/e* (rel intensity) 472 (6), 237 (20), 236 (100), 221 (43), 194 (19), 193 (15), 180 (14), 178 (15), 165 (11), 151 (9).

Anal. Calcd for $(C_{17}H_{16}O)_2$: C, 86.40; H, 6.83. Found: C, 86.37; H, 6.79.

For **33**: IR (Nujol) 1660, 1618 cm^{-1}; λ_{max}^{MeOH} 344 nm (ϵ 2840), 286 (12 290), 245 (62 860), 213 (58 130); NMR ($CDCl_3$) δ 0.60 (s, 3 H, methyl), 1.05 (s, 3 H, methyl), 1.23 (s, 3 H, methyl), 1.32 (s, 3 H, methyl), 2.3–3.2 (m, 6 H), 3.8–4.7 (m, 2 H), 7.0–8.4 (m, 12 H, arom); mass spectrum, *m/e* (rel intensity) 472 (5), 237 (20), 236 (100), 221 (38), 195 (17), 194 (13), 180 (15), 178 (11), 151 (10).

Anal. Calcd for $(C_{17}H_{16}O)_2$: C, 86.40; H, 6.83. Found: C, 86.48; H, 6.72.

Irradiation of 29 in Methanol. A solution containing 80 mg (0.34 mmol) of **29** in 7 mL of methanol was irradiated for 3 h. Concentration under reduced pressure gave an oily residue which was chromatographed on silica gel to give as successive fractions 13 mg (16%) of **32**, 23 mg (29%) of **33**, and 25 mg (33%) of **35**. None of dimer **34** was isolated, nor could its presence be detected in the crude reaction mixture (NMR).

Irradiation of 30 and 31 in Cyclohexane. Irradiation of 0.05 M solutions of either **30** or **31** in cyclohexane under identical conditions as used in the irradiation of **29** gave only recovered starting material (>95%).

Irradiation of 29 in Furan. A solution (0.049 M) containing 800 mg (3.4 mmol) of **29** in 70 mL of furan was irradiated (Pyrex) for 4 h. The solvent was evaporated and the residue was chromatographed on silica gel to give as the first fraction 605 mg (59%) of adduct **36**, mp 129–130 °C (colorless prisms from hexanes), and as the second fraction 217 mg (21%) of adduct **37**, mp 171–172 °C (colorless needles from hexanes).

For **36**: IR (Nujol) $\nu_{C=O}$ 1669 cm^{-1}; λ_{max}^{MeOH} 341 nm (ϵ 2690), 296 (sh, 8290), 285 (10 530), 273 (8060), 251 (41 660), 243 (sh, 39 870); NMR ($CDCl_3$) δ 1.10 (s, 3 H, methyl), 1.20 (s, 3 H, methyl), 1.30 (d, 1 H, J = 6 Hz, H(7)), 2.43 (d, 1 H, J = 11 Hz, methylene), 2.87 (d, 1 H, J = 11 Hz, methylene), 3.50 (dd, 1 H, J = 4, 6 Hz, H(1)), 4.67 (br s, 1 H, H(8)), 5.52 (d, 1 H, J = 4 Hz, H(11)), 6.28 (m, 2 H, H(9), H(10)), 7.15–7.87 (m, 5 H, arom), 8.15 (s, 1 H, arom); mass spectrum, *m/e* (rel intensity) 304 (2), 236 (100), 221 (73), 194 (28), 193 (24), 178 (30), 165 (26), 152 (15).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.79; H, 6.62.

For **37**: IR (Nujol) $\nu_{C=O}$ 1668 cm^{-1}; λ_{max}^{MeOH} 337 nm (ϵ 2450), 296 (sh, 7360), 285 (9590), 275 (8030), 250 (40 140), 244 (sh, 38 360); NMR ($CDCl_3$) δ 0.82 (s, 3 H, methyl), 1.22 (s, 3 H, methyl), 2.17 (dd, 1 H, J = 4, 6 Hz, H(7)), 2.37 (d, 1 H, J = 11 Hz, methylene), 2.70 (d, 1 H, J = 11 Hz, methylene), 2.85 (d, 1 H, J = 6 Hz, H(1)), 4.87 (dd, 1 H, J = 1.5, 4 Hz, H(8)), 5.53 (d, 1 H, J = 2 Hz, H(11)), 6.27 (dd, 1 H, J = 1.5, 6 Hz, H(9)), 6.52 (dd, 1 H, J = 2, 6 Hz, H(10)), 7.23–7.90 (m, 5 H, arom), 8.17 (s, 1 H, arom); mass spectrum, *m/e* (rel intensity) 304 (1.5), 236 (100), 221 (71), 194 (28), 193 (22), 191 (17), 178 (29), 165 (27), 152 (14).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; C, 6.62. Found: C, 82.79; H,

6.62.

Irradiation of 30 in Furan. A solution (0.042 M) containing 120 mg (0.508 mmol) of **30** in 12 mL of furan was irradiated (Pyrex) for 4 h. The solvent was evaporated and the residue was chromatographed on silica gel to give as the first fraction 91 mg (59%) of adduct **38**, mp 167–168 °C (colorless prisms from hexanes) and as the second fraction 30 mg (19%) of adduct **39**, mp 179–180 °C (colorless needles from hexanes).

For **38**: IR ($CHCl_3$) $\nu_{C=O}$ 1678 cm^{-1}; λ_{max}^{MeOH} 305 nm (ϵ 7610), 242 (25 870), 223 (41 400); NMR ($CDCl_3$) δ 1.12 (s, 3 H, methyl), 1.23 (s, 3 H, methyl), 1.43 (d, 1 H, J = 6 Hz, H(7)), 2.50 (d, 1 H, J = 11 Hz, methylene), 2.88 (d, 1 H, J = 11 Hz, methylene), 3.48 (dd, 1 H, J = 4, 6 Hz, H(1)), 4.68 (d, 1 H, J = 1.5 Hz, H(8)), 5.47 (dd, 1 H, J = 4 Hz, H(11)), 6.22 (dd, 1 H, J = 1, 5 Hz, H(10)), 6.37 (dd, 1 H, J = 1.5, 5 Hz, H(9)), 6.98–7.83 (m, 5 H, arom), 8.10–8.35 (m, 1 H, arom); mass spectrum, *m/e* (rel intensity) 304 (2), 236 (100), 221 (44).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.93; H, 6.56.

For **39**: IR ($CHCl_3$) $\nu_{C=O}$ 1667 cm^{-1}; λ_{max}^{MeOH} 294 nm (ϵ 4570), 240 (sh, 14 610), 224 (40 490); NMR ($CDCl_3$) δ 0.82 (s, 3 H, methyl), 1.17 (s, 3 H, methyl), 2.33 (dd, 1 H, J = 4, 7 Hz, H(7)), 2.47 (d, 1 H, J = 11 Hz, methylene), 2.72 (d, 1 H, J = 11 Hz, methylene), 2.80 (d, 1 H, J = 7 Hz, H(1)), 4.90 (dd, 1 H, J = 1.5, 4 Hz, H(8)), 5.40 (d, 1 H, J = 2 Hz, H(11)), 6.23 (dd, 1 H, J = 1.5, 5.5 Hz, H(9)), 6.47 (dd, 1 H, J = 2, 5.5 Hz, H(10)), 7.07–7.88 (m, 6 H, arom); mass spectrum, *m/e* (rel intensity) 204 (7), 236 (100), 221 (40).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.90; H, 6.59.

Irradiation of 31 in Furan. A solution (0.03 M) containing 36 mg (0.152 mmol) of **31** in 5 mL of furan was irradiated (Pyrex) for 4 h. The solvent was evaporated and the residue was chromatographed on silica gel to give as the first fraction 19 mg (41%) of adduct **40**, mp 163–164 °C (colorless prisms from hexanes) and as the second fraction 13 mg (28%) of adduct **41**, mp 186–187 °C (colorless prisms from hexanes).

For **40**: IR ($CHCl_3$) $\nu_{C=O}$ 1666 cm^{-1}; λ_{max}^{MeOH} 332 nm (ϵ 3040), 299 (8220), 288 (9130), 251 (48 100); NMR ($CDCl_3$) δ 1.17 (s, 3 H, methyl), 1.23 (s, 3 H, methyl), 1.47 (d, 1 H, J = 5 Hz, H(7)), 2.47 (d, 1 H, J = 11 Hz, methylene), 2.92 (d, 1 H, J = 11 Hz, methylene), 3.83 (t, 1 H, J = 5 Hz, H(1)), 4.70 (d, 1 H, J = 2 Hz, H(8)), 5.83 (dd, 1 H, J = 1.5, 6 Hz, H(10)), 6.12 (dd, 1 H, J = 1.5, 5 Hz, H(11)), 6.18 (dd, 1 H, J = 2, 6 Hz, H(9)), 7.33–7.92 (m, 5 H, arom), 8.10–8.33 (m, 1 H, arom); mass spectrum, *m/e* (rel intensity) 304 (1), 236 (100), 221 (54).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.81; H, 6.69.

For **41**: IR ($CHCl_3$) $\nu_{C=O}$ 1671 cm^{-1}; λ_{max}^{MeOH} 344 nm (ϵ 2440, sh), 301 (5780), 291 (6090), 249 (36 830); NMR ($CDCl_3$) δ 0.90 (s, 3 H, methyl), 1.37 (s, 3 H, methyl), 2.28 (d, 1 H, J = 10 Hz, methylene), 2.52 (dd, 1 H, J = 3.5, 7 Hz, H(7)), 2.67 (d, 1 H, J = 10 Hz, methylene), 3.33 (d, 1 H, J = 7 Hz, H(1)), 4.85 (dd, 1 H, J = 1.5, 3.5 Hz, H(8)), 5.58 (d, 1 H, J = 2 Hz, H(11)), 6.28 (dd, 1 H, J = 1.5, 6 Hz, H(9)), 6.87 (dd, 1 H, J = 2, 6 Hz, H(10)), 7.20–8.03 (m, 6 H, arom); mass spectrum, *m/e* (rel intensity) 304 (2), 236 (100), 221 (56).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.77; H, 6.55.

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References and Notes

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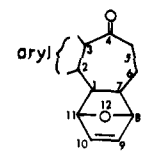
(8) H. Hart, T. Miyashi, D. N. Buchanan, and S. Sasson, *J. Am. Chem. Soc.*, **96**, 4857 (1974).
(9) The numbering system for all the furan adducts described in this paper is as follows. The name for **7** and **8**, without designating the stereochemistry of the ring juncture, is 6,6-dimethyl-2,3-benzo-12-oxatricyclo-



[5.4.0.$1^{8,11}$]dodecan-4-one. We further designate these adducts as H(1) (exo) H(7) (endo) for **7** and H(1) (endo) H(7) (exo) for **8**, since it is the chemical shifts and coupling constants of these protons which largely permit structural assignments. Other substituents (for example, the C(6) methyl groups) are designated as exo or endo depending on their relationship to the oxygen bridge.
(10) F. A. L. Anet, *Tetrahedron Lett.*, 1219 (1962).
(11) R. P. Fraser, *Can. J. Chem.*, **40**, 78 (1962).
(12) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).
(13) P. Ramart and M. J. Hoch, *Bull. Soc. Chim. Fr.*, 848 (1938).
(14) This was also true for the minor products.
(15) We are indebted to Dr. Donald Ward and Dr. Kwo-Tsair Wei for determining the crystal structure. Details will be published elsewhere.
(16) For example, in **13** $J_{1,11}$ = 4 and $J_{7,8}$ = 0 Hz, whereas in **14**, $J_{1,11}$ = 0 and $J_{7,8}$ >0 Hz, establishing endo geometry for H(7) in **13** and H(1) in **14**. Also, H(1) was at lower field in **13** than in **14**.
(17) Although **15** was nearly pure (NMR) directly from the hexane extraction which separated it from **12**, it always contained a small amount of impurities (carbonyl in IR). The amount of these impurities could be reduced, but not completely eliminated by chromatography on Florisil (see Experimental Section).
(18) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).
(19) The benzylic protons of **19** appeared in the NMR spectrum as a clean doublet, J = 8 Hz, requiring a symmetric structure in which these protons are equivalent.
(20) The benzylic proton in **18** was a singlet (δ 4.25) analogous to that proton in **15**, supporting the stereochemistry shown in the structure.
(21) In particular, $J_{1,11}$ = 4 and $J_{7,8}$ = 0 in **20** as expected for H(1) (exo), H(7) (endo), and in **21**, $J_{1,11}$ = 0 and $J_{7,8}$ > 0 Hz as expected for the converse stereochemistry. Also, H(1) appeared at appreciably lower field in **20** than in **21**, consistent with exo stereochemistry in the former.
(22) The UV spectrum of **22** resembled that of 2-acetonaphthone [λ_{max}^{EtOH} 322 nm (ϵ 1730) 292 (sh 3600), 280 (9330), 247 (62 670), 237 (52 670)] and that of **23** resembled the spectrum of 1-acetonaphthone [291 nm (ϵ 5660), 241 (25 330)]; see R. Huisgen and U. Rietz, *Chem. Ber.*, **90**, 2768 (1957).
(23) Ketone **26** absorbed at longer wavelengths (347 nm) than did ketone **27** (299 nm); see also ref 22.
(24) Ketone **26** had a sharp singlet at δ 8.40 for the aromatic proton adjacent to the carbonyl group; **29**, on the other hand, had doublets at δ 7.25 and 7.88 (J = 8.5 Hz) for the two aromatic protons adjacent to the fused seven-membered ring.
(25) We are indebted to Dr. Carol Blefeld for the structure of **32** and to Dr. Donald Ward for the structures of **33–35**; details will be published elsewhere.
(26) If the reaction had diradical character, initial C(5)–C(5) bonding would result in two benzylic radicals, whereas initial C(5)–C(4) bonding would leave an isolated secondary radical in the 2π component.
(27) For a brief discussion and leading references, see J. A. Barltrop and J. D. Coyle, "Excited States in Organic Chemistry", Wiley, New York, N.Y., 1975, pp 212–215.
(28) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y. 1970, p 75; (b) Y. Kayama, M. Oda, and Y. Kitahara, *Chem. Lett.*, 345 (1974). (c) The reaction of *trans*-2-cycloheptenone with itself is several orders of magnitude faster than its reaction with the cis isomer (private communication from R. Bonneau and J. Joussot-Dubien).
(29) The stereochemistry of methanol addition to other *trans*-cycloheptenones (**2**[4,5] and **3**[6]) has not been investigated. We have evidence that 1,2 additions of this type are also stereospecific and we are actively pursuing this question (E.D. and H.H., unpublished results).
(30) NMR spectra were measured against Me_4Si as an internal standard on a Varian T-60 or HA-100 spectrometer. IR spectra were calibrated against a polystyrene film, and were recorded on a Unicam SP200 or a Perkin-Elmer 237 grating spectrometer. UV spectra were obtained on a Unicam SP-800 spectrometer. Mass spectra were obtained at 70 eV with a Hitachi-Perkin-Elmer RMU-6 instrument operated by Mrs. Ralph Guile, to whom we are indebted. Melting points are uncorrected. Unless otherwise stated, column chromatography was performed using EM reagent silica gel 60, >230 mesh, with methylene chloride as the eluent. All irradiations were carried out with a Hanovia Type L 450-W lamp, under N_2 atmosphere. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Clark Microanalytical Laboratory, Urbana, Ill.
(31) The last number in parentheses is the relative shift of the signal, using $Eu(fod)_3$ shift reagent.
(32) For identification of the various J values, see Table I.
(33) Sometimes compound **29** was contaminated with <5% of unreacted **26**, which was removed by repeated silica gel chromatography. Comparison of the C(8) methylene peaks (δ 2.93 in **29** and 2.70 in **26**) provided the best analytical method.
(34) Sometimes compound **30** was contaminated with <5% of unreacted **27**, which was removed by repeated silica gel chromatography. Comparison of the C(8) methylene peaks (δ 2.98 in **30** and 2.68 in **27**) provided the best analytical method.
(35) The UV spectrum of **28** resembled that of 7,8,9,10-tetrahydro-11-oxocyclohepta(*a*)naphthalene [λ_{max}^{EtOH} 333 nm (ϵ 2600), 302 (sh, 6100), 292 (8100), 249 (36 400)]; see R. Huisgen and U. Rietz, *Tetrahedron*, **2**, 271 (1958).