246.140369 (calcd for $C_{19}H_{18}$, 246.14084); (**33**), 246.14105; (**34**), 246.13989.

Photochemical Stability of the Cyclopropanes. In a typical experiment, **8** (along with small amounts of isomers **9**, **10**, and **11**) was dissolved in benzene-d_6 and irradiated with two G.E. sun lamps for 12 hr. Nmr analysis revealed no change in the isomer distribution or absolute amount of **8**. Addition of benzophenone or DPDM was without effect as was duration of irradiation.

Methyleneketenes by Irradiation of α,β-Unsaturated Ketones

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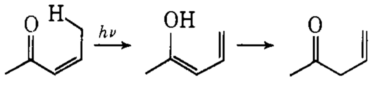
Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received February 15, 1973*

Abstract: Irradiation of 3-methylenedibenzobicyclo[2.2.2]octadien-2-one (**17**, $R_1 = R_2 = H$) in methanol gave mainly (>93%) 2-carbomethoxydibenzobicyclo[2.2.2]octa-5,7-diene (**18**); in ether containing diethylamine the product was the corresponding amide. A mechanism involving α′ cleavage, electron delocalization to the α,β-double bond, and rebonding between the α′- and β-carbon atoms to form ketene **19** is supported by experiments with methyl labeling at the bridgehead positions. Thus **21** gave ester **22** and **23** gave ester **24**. A small amount (0.6%) of dianthracene was isolated from the irradiation of **17**, suggesting that some small amount of α,β′-bond cleavage to methyleneketene occurred. This latter path became considerably more important on β-phenyl substitution. Irradiation of 3-benzylidenedibenzobicyclo[2.2.2]octadien-2-one (**17**, $R_1 = H$, $R_2 = C_6H_5$) in methanol gave dianthracene and methyl *cis*- and *trans*-cinnamates in 42% yield; the cinnamates presumably arise from trapping of benzylideneketene by methanol. In addition, a 58% yield of *cis*- and *trans*-2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-dienes (**25c** and **25t**) was obtained through intramolecular rearrangement. Thus, α,β-unsaturated ketones of the type **17** undergo α′ cleavage in preference to other possible reaction paths. This may be followed by rearrangement to a bicyclic ketene (**19**) or fragmentation to a methyleneketene (**26**) and anthracene. These paths compete with the more common cis–trans isomerism of acyclic enones, probably because of stabilization of the α′ radical by aryl rings.

A diverse number of inter- and intramolecular photochemical transformations are undergone by α,β-unsaturated ketones. Although the excitation energy always involves the same chromophore, the particular reaction path may depend upon the overall molecular structure, the solvent, the presence of another reactant, and the multiplicity of the excited state. Six distinct reaction types have been identified: (a) hydrogen abstraction, (b) dimerization, (c) oxetane formation, (d) photoisomerization, (e) cis–trans isomerization, and (f) α cleavage.[1]

Hydrogen abstraction may occur intramolecularly by the oxygen from a γ position to give a nonconjugated enone[2] (1 → 2) or from a γ′ position to give a cyclobutyl ketone (3 → 4).[3] Hydrogen abstractions from the β position (5 → 6)[4] or by the β-carbon atom (7 → 8)[5] are also known. Intermolecular hydrogen abstraction may be observed, particularly when the molecular geometry is detrimental to the intramolecular reaction; the net result is either reduction of the carbon–carbon double bond or addition of hydrogen and a radical to the double bond.[6]



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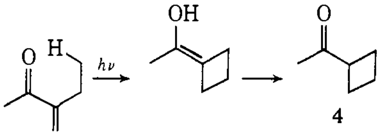

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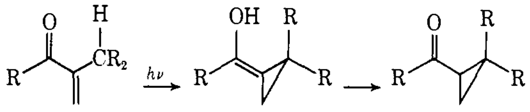

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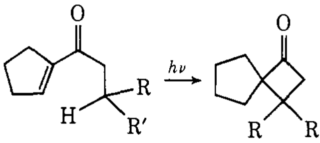

7 8

When the carbon–carbon double bond of an enone is part of a five- or six-membered ring, and no γ hydrogens are available, the most frequently observed photochemical reaction is the formation of a cyclobutane dimer.[7] This cycloaddition may also occur with added olefins[8] or with a suitably located intramolecular double bond.[9] Cycloaddition may also occur at the carbon–oxygen double bond, resulting in an oxetane. The re-

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[1] For recent reviews, see Vol. I–III of the Chemical Society Specialist Reports on Photochemistry.

[2] K. J. Crowley, R. A. Schneider, and J. Meinwald, *J. Chem. Soc. C*, 571 (1966).

[3] W. L. Schreiber and W. C. Agosta, *J. Amer. Chem. Soc.*, **93**, 6292 (1971).

[4] R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 729 (1972).

[5] A. B. Smith, III, A. M. Foster, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 5100 (1972); S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *ibid.*, **94**, 7797 (1972).

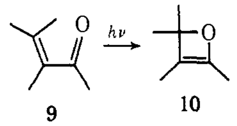
[6] P. Bladon and I. A. Williams, *J. Chem. Soc. C*, 2032 (1967).

[7] For a review, see D. J. Trecker, *Org. Photochem.*, 2, 71 (1969).

[8] P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2454 (1962); P. E. deMayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); P. E. Eaton, *Tetrahedron Lett.*, 3695 (1964); E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[9] G. Büchi and I. M. Goldman, *ibid.*, **79**, 4741 (1957).

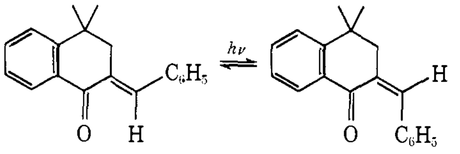
action may be inter-[10] or intramolecular (**9** → **10**).[11]



9 **10**

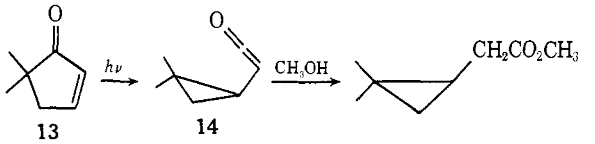
In the case of 4,4-disubstituted cyclohexenones photoisomerization to a bicyclo[3.1.0]cyclohexan-2-one (so-called "lumi-product") may compete with or entirely replace these cycloaddition reactions.[12]

Enones in which the carbon–carbon double bond is not part of an ordinary sized ring may undergo cis–trans isomerization about the double bond.[13] This reaction may dominate the observed photochemistry when alternative reaction paths are either unavailable or slow, as in the conversion **11** → **12**.

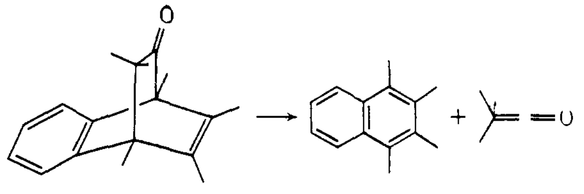


11 **12**

Finally, α,β-unsaturated ketones with radical-stabilizing groups at the α' position may undergo a Norrish type I cleavage. The diradical thus formed may valence isomerize to a ketene (**13** → **14**)[14] or dispose of its energy in some other way.[16]

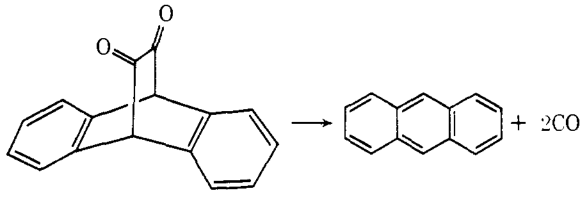


13 **14**



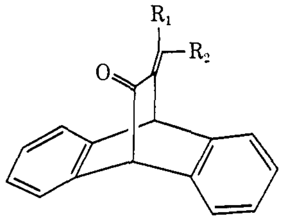
15

The present work[17] was undertaken with the idea of using suitably constituted α,β-unsaturated ketones as a means of generating methyleneketenes photochemically. The retro-Diels–Alder reaction of ethanoanthracenes and related bridged aromatics has been used to synthesize numerous otherwise difficultly accessible molecules.[18] The ethano bridge can be eliminated thermally or photochemically, but when the bridge contains a carbonyl group so that the eliminated molecule is a ketene, the photochemical path is much more facile. Thus **15** is converted to 1,2,3,4-tetramethylnaphthalene and dimethyl ketene only at 450–550° thermally, but very efficiently on irradiation.[19] Similarly, α-diketones such as **16** are thermally stable (>300°) but readily eliminate carbon monoxide photochemically.[20] In this case, the question of whether the ethano bridge is eliminated intact, as oxoketene O=C=C=O, or whether the process is stepwise has not been resolved. The mass spectrum of **16** indicates that a $C_2O_2^+$ fragment can be formed, but all attempts to trap the neutral molecule have failed, and theoretical arguments which favor the stepwise elimination of two carbon monoxide molecules have been advanced.[21]



16

We studied α-methylene ketones of the type **17** with the hope that they might fragment photochemically to anthracene and methyleneketenes.[22] If **17** is viewed as an α,β-unsaturated ketone, then α' cleavage might be expected to be particularly facile since the α' fragment would be stabilized by two aromatic rings. It was not at all clear, however, that the necessary cleavage of the α,β' bond would follow. A likely possibility was that **17** would consume radiation energy by isomerizing about the carbon–carbon double bond. If R_1 were to contain a γ hydrogen, yet another reaction path (intramolecular hydrogen abstraction) would be available. The two remaining common photochemical reactions of α,β-unsaturated ketones (dimerization or oxetane formation) seemed the least likely of the possibilities.



17

Results and Discussion

Irradiation of **17** ($R_1 = R_2 = H$) was carried out in methanol with the thought that if methyleneketene were

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[10] P. J. Nelson, D. Ostreem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, **34**, 811 (1969); N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 96 (1972).

[11] L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, **91**, 7204 (1969).

[12] For a review, see P. J. Kropp, *Org. Photochem.*, **1**, 67 (1967).

[13] For a review, see Chemical Society Specialist Report on Photochemistry, Vol. 3, 1972, pp 430–437.

[14] W. C. Agosta, A. B. Smith, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Lett.*, 4517 (1969). In a sense, this constitutes the reverse of a photochemical vinylcyclopropane–cyclopentene isomerization.[15]

[15] For other examples and leading references, see P. H. Mazzocchi and R. C. Ladenson, *J. Chem. Soc. D*, 469 (1970).

[16] Though 6,7-benzobicyclo[3.2.2]nona-3,6,9-trien-2-one is not a simple enone, its photoisomerization is similar to that of **13**, but it may also undergo a 1,3-acyl migration: J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967); O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *ibid.*, **91**, 6856 (1969); A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969).

[17] For a preliminary account of this work, see D. L. Dean and H. Hart, *ibid.*, **94**, 687 (1972).

[18] For reviews see H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966).

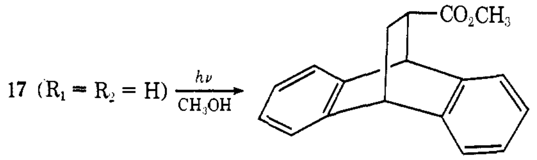
[19] R. K. Murray, Jr., and H. Hart, *Tetrahedron Lett.*, 4995 (1968); A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, **89**, 4554 (1967).

[20] J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Lett.*, 125 (1969).

[21] R. C. Haddon, *ibid.*, 3897 (1972).

[22] Early attempts to synthesize methyleneketenes by more conventional routes were largely unsuccessful [see H. Staudinger, "Die Ketene," Verlag von Ferdin and Enke, Stuttgart, 1912] and the subject has not been further pursued; see D. Borrmann in "Methoden der Organischen Chemie," Vol. VII/4, Georg Thieme Verlag, Stuttgart, 1968.

produced, it would be trapped as methyl acrylate. Starting material was consumed efficiently, but the major product was 2-carbomethoxydibenzobicyclo-[2.2.2]octadiene (**18**), isolated in over 93% yield. The

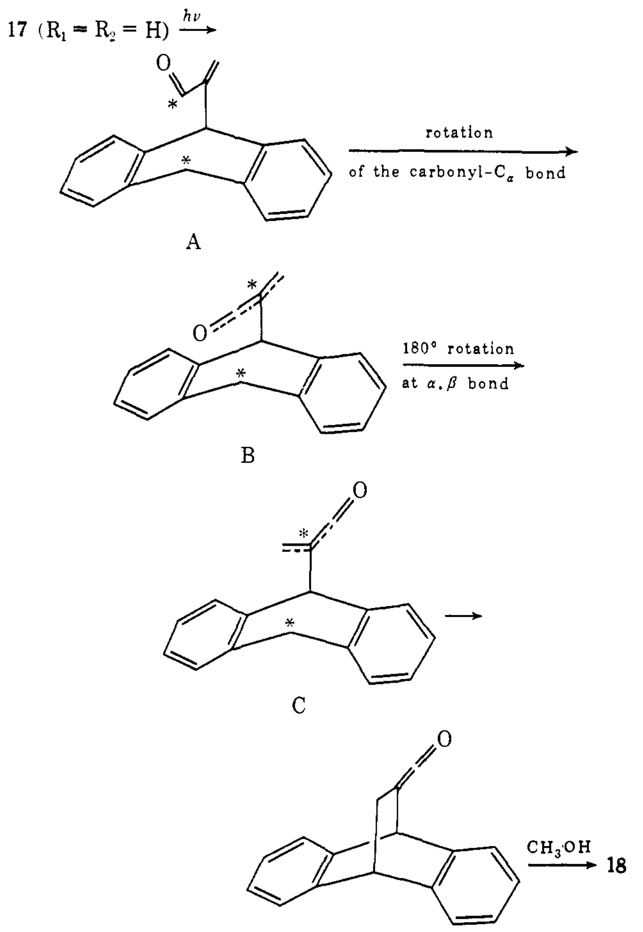


18

ester was identified by comparison (melting point, ir, nmr) with an authentic sample.[23] Also produced during the photolysis was a 0.6% yield of anthracene dimer, identified by its insolubility in the reaction medium, its melting point, and its ir spectrum. Presumably a small amount of the desired ethano bridge expulsion of methyleneketene occurred, though we did not isolate any products from the bridge fragment.

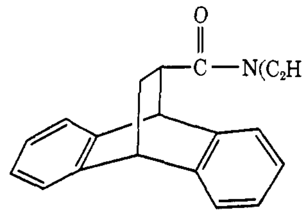
The formation of **18** from **17** ($R_1 = R_2 = H$) can be rationalized by a Norrish type I cleavage, structural reorganization to permit electron delocalization to the methylene group, 180° rotation about the α,β' C–C bond, and bond formation between the α'- and β-carbon atoms (Scheme I). The product is a ketene,

Scheme I



19

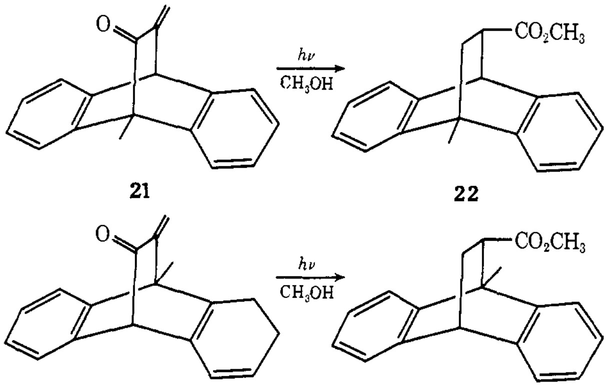
and the reaction is analogous to the recently observed conversion of **13** to **14**. Irradiation of **17** ($R_1 = R_2 = H$) in ether containing diethylamine gave the amide **20**,



20

supporting the suggestion that the actual photoproduct is the ketene **19**.

One can envision other mechanisms by which **17** could be converted to **18**. For example, one might eliminate methyleneketene, which could react with the solvent, and the resulting methyl methacrylate might then add to anthracene to give **18**. To test the 180° "turn-around" mechanism shown in Scheme I, we labeled the bridgehead positions with methyl groups. Irradiation of **21** in methanol gave a single ester **22** (56%) together with some 9-methylanthracene (2%) and some polymeric material. Analogous irradiation of **23** gave more polymer and 9-methylanthracene (4%) but only a single ester **24** (32%). These results confirm the



21 **22**

23 **24**

intramolecular nature of the photoisomerization. It is probable that the reaction is not as clean with the methyl ketones **21** and **23** as it is with **17** ($R_1 = R_2 = H$) because of hydrogen abstraction from the methyl groups.

Scheme I, which accounts for the major reaction product from **17** ($R_1 = R_2 = H$), can also rationalize the small amount of anthracene dimer which is formed, if it is assumed that one or more of the intermediates (*i.e.*, A–C) can, in competition with rebonding, dissociate to anthracene and methyleneketene. The substituents at R_1 and R_2 could affect the relative importance of these two processes, particularly if the intermediates which partition between the two paths are the rotamers B and C. To test this idea, several arylidene ketones **17** ($R_1 = H$, $R_2 =$ aryl) were synthesized and irradiated.

As a 10^{-3} *M* solution of **17** ($R_1 = H$, $R_2 = C_6H_5$) in methanol was irradiated through Pyrex, anthracene dimer precipitated from the solution in 37–42% yield. An equivalent amount of an equimolar mixture of methyl *cis*- and *trans*-cinnamates was isolated from the filtrate. The remaining product was a 68:32 mixture of *trans*- and *cis*-2-carbomethoxy-3-phenyldibenzobicyclo-[2.2.2]octadienes (**25t** and **25c**), in 58–63% yield. As with **17** ($R_1 = R_2 = H$), the reaction was clean and gave no polymeric products. The structures of **25** were established by independent synthesis. The 1:1 ratio of

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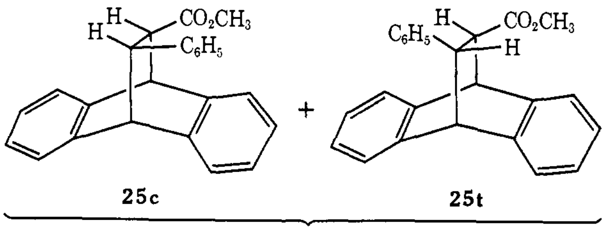
(23) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953); R. K. Hill and G. R. Newkome, *ibid.*, **34**, 740 (1969).

$$17\ (R_1 = H,\ R_2 = C_6H_5) \xrightarrow[CH_3OH]{h\nu}$$

$$\underbrace{\text{dianthracene} + \textit{cis}\text{-and } \textit{trans}\text{-}C_6H_5CH{=}CHCO_2CH_3 +}_{42\%}$$



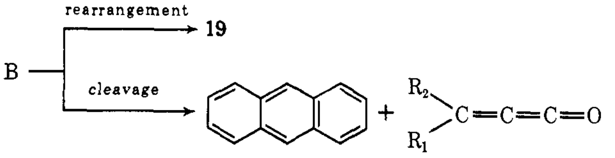
25c **25t**

58%

methyl *cis*- and *trans*-cinnamates is consistent with what would be expected from a reaction of benzylideneketene with methanol,[24] but could also be a consequence of further photoisomerization of these esters.[25] The ratio of **25t**:**25c**, however, is probably a consequence of kinetic control, since alkaline equilibration of these esters gives almost entirely the trans isomer.

The simplest explanation for the increased amount of cleavage to a methyleneketene when R_2 (in **17**) is changed from H to C_6H_5 is that a single intermediate such as B (or its rotamer C) partitions between two reaction paths. The competing paths are shown in Scheme II. The transition state leading to **26** will be lower in energy when $R_2 = C_6H_5$ than when $R_2 = H$ because of incipient conjugation of the phenyl group with a C-2–C-3 double bond in **26**. On the other hand, the transition state leading to the bicyclic ketene (**19** and its phenyl analog) should be relatively little affected by phenyl substitution.[26] Consequently, cleavage becomes more important as R_2 is better able to stabilize the methyleneketene.

Scheme II



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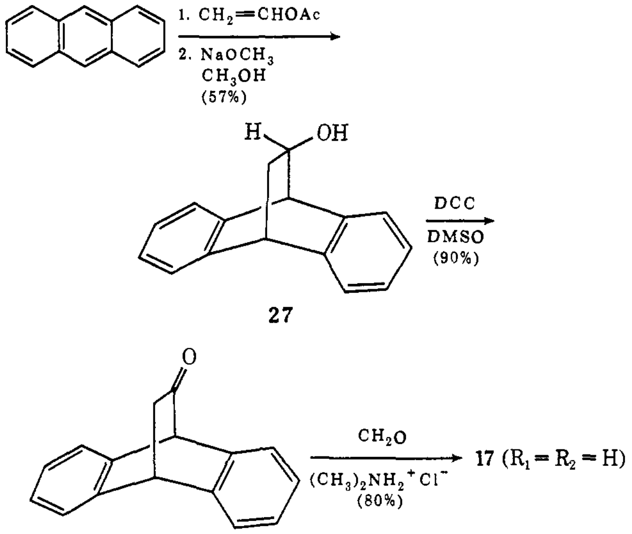
Substitution of a *p*-CH_3, *p*-OCH_3, or *p*-Cl in the phenyl ring of **17** (R_1 = H, R_2 = Ar) was essentially without effect on the ratio of cleavage to rearrangement. This result is not surprising since the substitutions constitute only a minor structural perturbation.[27]

The irradiation of **17** (R_1 = H, R_2 = C_6H_5) showed a significant wavelength dependence. The partition between cleavage and rearrangement was 42:58 for irradiation with a 450-W Hanovia lamp through a Pyrex filter. When the irradiation was carried out in a Rayonet apparatus with 350-nm lamps, the ratio was only 18:82, but with 300-nm lamps this increased to 32:68. The uv spectrum of **17** (R_1 = H, R_2 = C_6H_5) has weak n–π* bands at 380, 363, and 343 nm and a very intense, presumably π–π* band at 298 nm. It seems possible that the n–π* and π–π* triplet states are of similar energy, and that cleavage occurs primarily from a π–π* and rearrangement from an n–π* state. Further work is needed before a definitive explanation can be offered, but these initial experiments suggest another way in which one may control the reaction.

In summary, α,β-unsaturated ketones of the type **17** undergo α′ cleavage in preference to other reaction paths. This may be followed by rearrangement to a bicyclic ketene (**19**) or cleavage to a methyleneketene (**26**) and anthracene. The rearrangement is similar to that observed previously for 5,5-dimethyl-2-cyclopentenone[14] whereas the α,β′ cleavage is novel for enones and presumably arises because of the driving force to form an aromatic system (anthracene). One might predict that cleavage will become more important as the aromatic hydrocarbon thus produced becomes more stable.[28] The latter path also gains significance when R_1 and/or R_2 can conjugate with the C-2–C-3 double bond of the methyleneketene. These paths can compete with the usual cis–trans isomerization of acyclic enones because the α′ radical is stabilized by the adjacent aromatic rings.

Synthetic Methods and Structure Proofs. Enone **17** ($R_1 = R_2 = H$) was first reported by Snyder and Clement,[29] prepared in ten steps and overall 10% yield from anthracene. We found that **17** ($R_1 = R_2 = H$) can be prepared in about 50% yield directly from the α-diketone **16** by a Wittig reaction. However, the best preparation involves four steps from anthracene, with an overall yield of 40% as shown. The nmr spectrum of **17** ($R_1 = R_2 = H$) had four one-proton singlets for the bridgehead and vinyl protons; their unique assignment (Experimental Section) was made using Eu-shift reagent and a comparison of chemical shifts with those for **21**.



28

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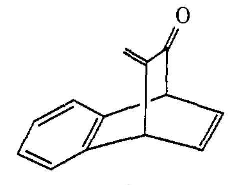
[24] J. S. Walia and L. C. Vishwakarma, *J. Chem. Soc. D*, 396 (1969).

[25] D. R. Arnold, L. B. Gillis, and E. B. Whipple, *ibid.*, 918 (1969).

[26] When R_2 is large compared to hydrogen, a ponderal or steric effect may slow down the 180° rotation needed for bicyclic ketene formation.

[27] P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

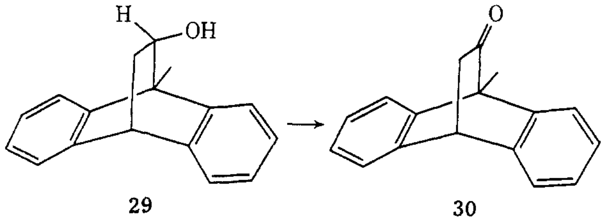
[28] Preliminary results with



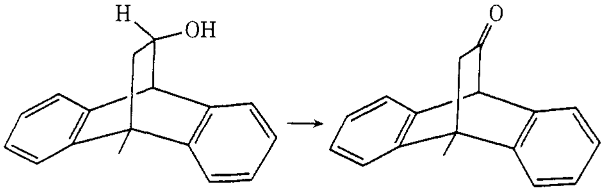
indicate that the predominant path is cleavage to naphthalene (unpublished results of the authors and S-M. Chen).

[29] E. I. Snyder and R. A. Clement, *J. Amer. Chem. Soc.*, **82**, 1424 (1960).

The bridgehead methyl enones **21** and **23** were synthesized by a route similar to that for **17** ($R_1 = R_2 = H$), but starting with 9-methylanthracene. The vinyl acetate adducts were converted directly to the alcohols **29** and **31** (1 : 3 ratio) which were readily separated by chromatography on silica gel. Each alcohol was oxidized to the corresponding ketone whose structure was unambiguous from its nmr spectrum. In **30**, the bridgehead proton and methylene protons appeared as a triplet (δ 4.53) and doublet (δ 2.38), respectively (J = 2.0 Hz), whereas in **32** these protons appeared as sharp singlets (at δ 4.83 and 2.18, respectively). The Mannich reaction on **30** and **32** afforded **21** and **23**, respectively.



29 **30**

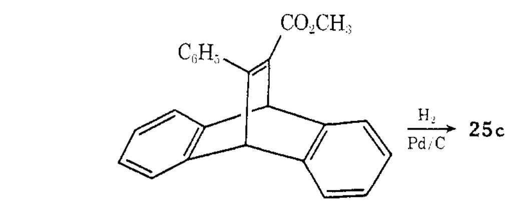


31 **32**

The photolysis products **22** and **24** were synthesized independently by the reaction of 9-methylanthracene with methyl acrylate. The two esters were readily distinguished by their nmr spectra; in particular, the bridgehead proton was a doublet (δ 4.67, J = 2.0 Hz) in **22** and a triplet (δ 4.30, J = 2.0 Hz) in **24**.

The benzylidene ketone **17** ($R_1 = H$, $R_2 = C_6H_5$) was synthesized from **28** which was converted to its α-lithio derivative and then treated with benzaldehyde. Only a single isomer was obtained; there was no evidence for the presence of any **17** ($R_1 = C_6H_5$, $R_2 = H$). The structure was easily assigned using Eu-shift data. Two singlets at δ 5.03 and 7.38 were shifted markedly to lower field by the shift reagent, whereas the singlet at δ 5.70 was much less affected. This is just what one would expect if the vinyl proton (δ 7.38) is cis to the carbonyl group; were it trans to the carbonyl group then only the bridgehead proton adjacent to the carbonyl group would be strongly affected by the shift reagent.

The photolysis product **25t** was readily synthesized from the known[30] trans acid. The cis ester **25c** was prepared from anthracene by catalytic reduction of the adduct **33**. Esters **25c** and **25t** were readily distinguished by their nmr spectra. In particular, the methoxyl singlet in **25c** was appreciably shielded by the adjacent phenyl group (δ 2.98 *vs.* 3.60). The coupling constant between the two ethano bridge protons was large (11.8 Hz) in **25c** and small (6.0 Hz) in **25t**.



33

Experimental Section[31]

Dibenzobicyclo[2.2.2]octadien-2-one (28). (We are indebted to Dr. Robert Pfeiffer for working out this procedure.) Into a mechanically stirred, dry N_2-flushed reaction flask were placed 62.5 g (0.303 mol) of dicyclohexylcarbodiimide, 300 ml of benzene (previously dried over 4A molecular sieve), 296 ml of dimethyl sulfoxide (freshly distilled from CaH_2), 22.5 g (0.101 mol) of dibenzobicyclo[2.2.2]octadien-2-ol (**27**),[23] and 8.2 ml of pyridine (previously dried over KOH). The addition of 4.2 ml of trifluoroacetic acid initiated the formation of a precipitate. After the mixture was stirred for 24 hr at room temperature, 30 g (0.273 mol) of oxalic acid dihydrate was slowly added; this caused extensive foaming. After the mixture had been stirred for 30 min, it was poured into a mixture of water (800 ml) and chloroform (200 ml). The mixture was agitated and the solid was removed with suction filtration. The solid was washed with chloroform. All the chloroform filtrates were combined, washed twice with 1 *N* $NaHCO_3$ and twice with water, and dried ($MgSO_4$). Evaporation of the solvent gave a tan solid which was heated with benzene. The insoluble dicyclohexylurea was removed by suction filtration, and the product was crystallized from the hot benzene, giving 10.7 g of **28**, mp 152–153° (lit.[23] mp 152.5–153°). The mother liquor gave an additional 9.1 g, total yield 89%; nmr ($CDCl_3$) δ 2.37 (2 H, d, J = 3.0 Hz), 4.53 (1 H, t, J = 3.0 Hz, bridgehead proton at C-4), 4.84 (1 H, s, bridgehead proton at C-1), 7.10–7.53 (8 H, m).

3-Methylenedibenzobicyclo[2.2.2]octadien-2-one (17, $R_1 = R_2 = H$). Procedure A. Mannich Reaction on 28. A solution of 0.88 g (4 mmol) of **28**, 0.84 g (28 mmol) of paraformaldehyde, and 2.3 g (28 mmol) of dimethylamine hydrochloride in 10 ml of isoamyl alcohol was refluxed for 24 hr. Shortly after everything dissolved, a dark lower layer and a colorless upper layer formed. When the mixture was cooled, crystals formed in each layer. The upper layer was separated and filtered (suction) to give 0.569 g of **17** ($R_1 = R_2 = H$) and washed with ethanol, mp 222–224° (lit.[29] mp 223.0–223.4°). The lower layer was triturated with ethanol and filtered to give an additional 0.009 g of **17**. Chromatography of the residue (obtained after removal of the amine salts and isoamyl alcohol) on silica gel, using benzene or chloroform as eluents, can increase the total yield of **17** ($R_1 = R_2 = H$) to 80%: ir (KBr) 1708 (conj C=O), 1633 (C=C) cm^{-1}; uv (cyclohexane) 246 nm (ϵ 5470), 280 sh (3480), 284 (4160), 309 sh (149), 322 (274), 335 (460), 348 (564), 367 (503), 384 (192); nmr ($CDCl_3$) δ 4.95 (1 H, s), 5.07 (1 H, s), 5.42 (1 H, s), 5.97 (1 H, s), 7.12–7.52 (8 H, m). The $Eu(fod)_3$[32] shift numbers[33] for the singlets, in order of increasing δ, are 2.6, 1.0, 1.0, and 2.5.

Procedure B. Wittig Reaction on Dibenzobicyclo[2.2.2]octadiene-2,3-dione (16). Into a reaction flask equipped with a magnetic stirrer and flushed with dry N_2 were placed 0.77 g (0.032 mol) of pulverized sodium hydride and 8 ml of dimethyl sulfoxide (freshly distilled from CaH_2). The mixture was heated (oil bath) at 70° for 75 min, then cooled to room temperature, and a solution of 11.4 g (0.032 mol) of methyltriphenylphosphonium bromide in 30 ml of dry dimethyl sulfoxide was added *via* a syringe. The yellow-green ylide solution was added dropwise (N_2 atmosphere, magnetic stirring) to the orange solution of 3.74 g (0.016 mol) of **16**[34] in 30 ml of dimethyl sulfoxide over a period of 50 min. The mixture became deep red, and darkened as the reaction proceeded. After 22 hr, the mixture was poured

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(30) E. deB. Barnett, N. F. Goodway, and E. V. Weekes, *J. Chem. Soc.*, 1102 (1935).

(31) Nmr spectra were determined in $CDCl_3$ with tetramethylsilane as an internal reference, unless otherwise stated, and are reported in δ; ir spectra of solids were determined in KBr pellets, those of oils were obtained from neat smears between NaCl plates; uv spectra were determined in cyclohexane unless otherwise stated; mass spectra were determined at 70 eV on a Hitachi Perkin-Elmer RMU-6 spectrometer; analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(32) Europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione).

(33) The extent to which each nmr signal is shifted relative to the least shifted signal.

(34) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 528 (1957).

into 175 ml of water and extracted (three times) with benzene. The dark benzene solution was evaporated to give an oil which solidified on standing to a gray-green solid. This was triturated with 15 ml of ethanol and filtered to give 1.82 g (50%) of **17** ($R_1 = R_2 =$ H), mp 221–224°, identical with the product obtained by procedure A. The use of less (1.5 equiv) or more (2.5 equiv) of the ylide decreased the yield of **17**.

General Photolysis Procedures. Unless otherwise stated, irradiations were carried out with a 450-W Hanovia Type L medium-pressure mercury lamp. In a few instances, a Rayonet reactor was used instead. The solutions were not degassed, as control experiments showed that this appeared to have no effect on the reactions. Large volumes were irradiated at 12–17° (tap water coolant) in an open well through an appropriate filter and the immersion well. Smaller volumes were placed in capped Pyrex test tubes hung in a water bath (15–20°) outside the immersion well. Reactions were monitored by uv; products in general absorbed at shorter wavelengths and/or with lower extinction coefficients than the reactant. Control experiments eliminated the possibility of dark reactions.

Irradiation of 3-Methylenedibenzobicyclo[2.2.2]octadien-2-one (17, $R_1 = R_2 =$ H) in Methanol. A solution of 0.464 g of **17** ($R_1 = R_2 =$ H) in 400 ml of methanol (5.0×10^{-3} *M*) was irradiated through Pyrex for 2 hr. The original maximum at 286 nm had essentially vanished, new maxima appeared at 264 and 271 nm, and a small amount of a white solid had precipitated from solution. Suction filtration gave 2.1 mg (0.6%) of dianthracene, ir identical with that of an authentic sample. Evaporation of the solvent gave 0.494 g (93.6%) of 2-carbomethoxydibenzobicyclo[2.2.2]octa-5,7-diene (**18**) as an off-white solid. An nmr spectrum showed no significant impurities. Recrystallization from methanol gave **18** as pure white crystals, mp 117–118° (lit.[23] mp 117–118°), identical with an authentic sample prepared from anthracene and methyl acrylate: uv (cyclohexane) 249 nm sh (ϵ 489), 258 sh (728), 264 (1140), 271 (1420); ir (KBr) 1721 cm^{-1}; nmr ($CDCl_3$) δ 1.90–2.23 (2 H, m, methylene), 2.70–3.04 (1 H, m, C-2 proton), 3.58 (3 H, s, methoxyl), 4.33 (1 H, t, J = 5.0 Hz, C-4 proton), 4.69 (1 H, d, J = 5.0 Hz, C-1 proton), 7.00–7.46 (8 H, m, aryl).

Irradiation of 3-Methylenedibenzobicyclo[2.2.2]octadien-2-one (17, $R_1 = R_2 =$ H) in Ether Containing Diethylamine. The enone **17** (0.116 g, 0.5 mmol) was dissolved in a solution containing 48 ml of diethyl ether and 2 ml of diethylamine. Two milliliters was removed, one for an initial uv spectrum, the other to monitor any dark reaction. The remainder was irradiated (Pyrex) for 100 min, at which time starting material was consumed (no maximum at 286 nm); new maxima had appeared at 266, 273, and 307 nm. The latter was due to a product of a dark reaction; the control showed that about 4% of the starting material was consumed during this time in the formation of the dark product.

Evaporation of the solvent left a residue of 0.152 g which was chromatographed (silica gel, 19 × 2 cm column). With CCl_4, only a minor product (16 mg; discarded) was eluted. A change to 9:1 $CHCl_3/CCl_4$ gave 0.135 g (92%) of 2-diethylcarbamidodibenzobicyclo[2.2.2]octadiene (**20**) as a light yellow oil: ir (neat) 1643 cm^{-1}; nmr ($CDCl_3$) δ 1.02 (3 H, t, J = 7.0 Hz, methyl), 1.07 (3 H, t, J = 7.0 Hz, methyl), 2.00 (2 H, d of d, J = 8.0 and 2.7 Hz, C-3 protons), 2.74–3.83 (5 H, m, methylenes of ethyl groups and C-2 proton), 4.39 (1 H, t, J = 2.7 Hz, C-4 proton), 4.41 (1 H, d, J = 2.0 Hz, C-1 proton), 7.01–7.46 (8 H, m, aryl). The identical product was obtained by treating dibenzobicyclo[2.2.2]octadiene-2-carboxylic acid[35] first with thionyl chloride, then with diethylamine in benzene.

1- and 4-Methyldibenzobicyclo[2.2.2]octa-5,7-dien-2-ols (29 and 31). A degassed solution of 9-methylanthracene (0.500 g, 2.60 mmol) and vinyl acetate (6.71 g, 78.0 mmol) in 5 ml of xylene was sealed in a thick-walled glass tube and heated at 250–270° for 15 hr. The tube was cooled in a Dry Ice bath and opened, and the yellow solution was concentrated to an oil under reduced pressure. The oil was dissolved in $CHCl_3$ and chromatographed (silica gel) to give 0.528 g (73%) of a white solid, mp 82–85°, which was a mixture of acetates: ir (KBr) 3050, 2950, 1720, 1375, 1240 cm^{-1}.

The mixture of esters was dissolved in 25 ml of freshly distilled tetrahydrofuran and slowly added to a mixture of an equal weight of lithium aluminum hydride in 25 ml of tetrahydrofuran, under N_2. The mixture was refluxed for 10 hr; excess hydride was destroyed by adding ethyl acetate to the cooled mixture. After hydrolysis by dropwise addition of 50 ml of 10% hydrochloric acid, the mixture was diluted with water (100 ml) and extracted with ether (4 × 50 ml). The combined ether extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), and concentrated *in vacuo* to a colorless oil. This oil was dissolved in a 50:50 chloroform–benzene mixture and chromatographed (silica gel) to give two white solids. Fraction 1 (0.101 g, 23% of the mixture) was 1-methyldibenzobicyclo[2.2.2]octa-5,7-dien-2-ol (**29**): mp 132.5–133.5°; ir (KBr) 3360, 3080, 2980, 1160, 1140, 770 cm^{-1}; nmr ($CDCl_3$) δ 1.22–1.60 (2 H, m, one proton exchangeable with D_2O, OH, and one methylene proton), 1.97 (3 H, s, methyl), 2.20–2.65 (1 H, m, a methylene proton), 3.55–4.00 (1 H, m, C-2 proton), 4.22 (1 H, t, J = 2.0 Hz, C-4 proton), 7.00–7.50 (8 H, m, aryl); mass spectrum (70 eV) *m/e* 218, 192 (base).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.05; H, 6.69.

Fraction 2 (0.347 g, 77% of the mixture) was 4-methyldibenzobicyclo[2.2.2]octa-5,7-dien-2-ol (**31**): mp 136–137°; ir (KBr) 3310, 3070, 2960, 1060, 1042, 768 cm^{-1}; nmr ($CDCl_3$) δ 0.98–1.58 (2 H, m, one proton exchangeable with D_2O, OH, and one methylene proton), 1.82 (3 H, s, methyl), 2.00–2.22 (1 H, m, one methylene proton), 3.90–4.20 (1 H, m, C-2 proton), 4.28 (1 H, d, J = 4 Hz, C-1 proton), 6.98–7.40 (8 H, m, aryl); mass spectrum (70 eV) *m/e* 218, 192 (base).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.49; H, 6.89.

1- and 4-Methyldibenzobicyclo[2.2.2]octadien-2-ones (30 and 32). The alcohols **29** and **31** were oxidized with chromic acid in acetone.[36] From 0.150 g (0.635 mmol) of **29** there was obtained 0.122 g (82%) of 1-methyldibenzobicyclo[2.2.2]octadien-2-one (**30**): mp (ethanol) 148–149°; ir (KBr) 3050, 3000, 2950, 1718, 1390, 1150, 760 cm^{-1}; nmr ($CDCl_3$) δ 1.98 (3 H, s, methyl), 2.38 (2 H, d, J = 2.0 Hz, methylene), 4.53 (1 H, t, J = 2.0 Hz, C-4 proton), 7.08–7.50 (8 H, m, aryl).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.98; H, 6.09.

From 0.640 g (2.72 mmol) of **31** there was obtained 0.524 g (82%) of 4-methyldibenzobicyclo[2.2.2]octadien-2-one (**32**): mp (ethanol) 114–116°; ir (KBr) 3080, 3000, 2950, 1727, 1359, 800, 768 cm^{-1}; nmr ($CDCl_3$) δ 1.97 (3 H, s, methyl), 2.18 (2 H, s, methylene), 4.83 (1 H, s, bridgehead), 7.05–7.50 (8 H, m, aryl).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.26; H, 6.08.

1-Methyl-3-methylenedibenzobicyclo[2.2.2]octadien-2-one (21). A mixture of 1-methyldibenzobicyclo[2.2.2]octadien-2-one (0.100 g, 0.42 mmol), paraformaldehyde (0.88 g, 2.94 mmol), and dimethylamine hydrochloride (0.241 g, 2.94 mmol) in 1 ml of isoamyl alcohol was heated at 150–160° for 17 hr. Cooling and removal of the solvent under reduced pressure left a dark solid which was triturated with ether (4 × 10 ml). Evaporation of the ether left a yellow oil which was dissolved in petroleum ether (5 ml, bp 65–110°) and passed through a column of 100 mg of silica gel. The eluent was evaporated to dryness and the resulting solid was recrystallized from petroleum ether (65–110°) affording 27 mg (26%) of **21**: mp 160–162°; ir (KBr) 1698, 1635 cm^{-1}; uv (MeOH) 284 nm (ϵ 2360), 341.5 (440); nmr ($CDCl_3$) δ 2.05 (3 H, s, methyl), 5.10 (1 H, s, bridgehead), 5.40 (1 H, d, J = 0.5 Hz, vinyl trans to carbonyl), 5.95 (1 H, d, J = 0.5 Hz, vinyl cis to carbonyl), 7.10–7.60 (8 H, m, aryl). The relative $Eu(fod)_3$[32] shifts[33] of the first four signals were 2.37 1.33, 1.00, and 3.67. Mass spectrum (70 eV) *m/e* 246, 192 (base).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.67; H, 5.94.

4-Methyl-3-methylenedibenzobicyclo[2.2.2]octadien-2-one (23). The procedure was as described for the preparation of **21**. From 0.500 g (2.15 mmol) of 4-methyldibenzobicyclo[2.2.2]octadien-2-one, 0.455 g (15.05 mmol) of paraformaldehyde, and 1.205 g (15.05 mmol) of dimethylamine hydrochloride in 5 ml of isoamyl alcohol there was obtained 0.338 g (64%) of **23** as a white solid: mp 199–201°; ir (KBr) 1714, 1629 cm^{-1}; uv (MeOH) 286 nm (ϵ 3370), 340 (713); nmr ($CDCl_3$) δ 2.18 (3 H, s, methyl), 4.98 (1 H, s, vinyl cis to carbonyl), 5.35 (1 H, s, vinyl trans to carbonyl), 6.00 (1 H, s, bridgehead), 7.10–7.55 (8 H, m, aryl). The relative $Eu(fod)_3$[32] shifts[33] of the first four signals were 1.00, 4.10, 1.82, and 3.87. Mass spectrum (70 eV) *m/e* 246, 192 (base).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.76; H, 5.65.

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(35) H. Scheibler and U. Scheibler, *Chem. Ber.*, 87, 379 (1954).

(36) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, 21, 1547 (1956).

Irradiation of 1-Methyl-3-methylenedibenzobicyclo[2.2.2]octadien-2-one (21). A solution of **21** (50 mg) in 50 ml of absolute methanol was irradiated for 4 hr in a Rayonet reactor equipped with 350-nm lamps. The solution, which then contained a very small amount of suspended solid, was filtered and evaporated to leave an oily white solid. This was dissolved in a minimum volume of chloroform and chromatographed on a thick-layer silica gel plate with chloroform as eluent. Two bands were collected: (1) 9-methylanthracene (1 mg, 2%) identified by uv, and (2) 2-carbomethoxy-4-methyldibenzobicyclo[2.2.2]octa-5,7-diene (**22**), a colorless oil (28 mg, 56%); ir (neat) 3050, 2980, 1730, 1215, 770 cm^{-1}; nmr ($CDCl_3$) δ 1.70–2.20 (2 H, m, methylene), 1.95 (3 H, s, methyl), 2.75–3.12 (1 H, m, C-2 proton), 3.58 (3 H, s, methoxyl), 4.68 (1 H, d, J = 2.0 Hz, bridgehead), 7.00–7.42 (8 H, m, aryl). The oil crystallized on long standing, mp 68°, from petroleum ether (30–60°).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.00; H, 6.46.

Irradiation of 4-Methyl-3-methylenedibenzobicyclo[2.2.2]octadien-2-one (23). A solution of **23** (50 mg) in 50 ml of absolute methanol was irradiated for 1 hr through Pyrex with the 450-W Hanovia lamp. Work-up as described for **21** gave three fractions: (1) 9-methylanthracene (2 mg, 4%), (2) 2-carbomethoxy-1-methyldibenzobicyclo[2.2.2]octa-5,7-diene (**24**), a yellow oil (16 mg, 32%) [ir (neat) 1730, 1175 cm^{-1}; nmr ($CDCl_3$) δ 1.90–2.20 (2 H, m, methylene), 1.95 (3 H, s, methyl), 2.25–2.75 (1 H, m, C-2 proton), 3.55 (3 H, s, methoxyl), 4.38 (1 H, t, J = 2.0 Hz, bridgehead), 7.02–7.50 (8 H, m, aryl)], and (3) a golden, polar, noncrystalline solid (14 mg, 28%) which appeared to be polymeric.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.02; H, 6.42.

Irradiation of **23** for 3.75 hr in a Rayonet reactor with 350-nm lamps gave a similar mixture of products.

2-Carbomethoxy-1- and -4-methyldibenzobicyclo[2.2.2]octa-5,7-dienes (22 and 24). A degassed solution of 9-methylanthracene (0.50 g, 2.60 mmol) and methyl methacrylate (0.860 g, 10 mmol) in 3 ml of xylene was heated in a thick-walled sealed tube at 260° for 17 hr. The tube was cooled in a Dry Ice bath and opened, and the yellow solution was concentrated under reduced pressure. The residual oil was dissolved in chloroform and chromatographed on silica gel. The ester fractions (ir) were collected and rechromatographed using 50:50 heptane–benzene as eluent to give two fractions. These were **22** and **24**, with identical ir and nmr spectra with the photolysis products of **21** and **23**, respectively.

3-Lithiodibenzobicyclo[2.2.2]octadien-2-one. *n*-Butyllithium in hexane (1.6 *N*, 8.25 ml, 13.2 mmol) was added to 15 ml of tetrahydrofuran (previously dried over 4A molecular sieve) in a flask equipped with a magnetic stirrer, flushed with dry N_2, and cooled in an ice bath. The addition of 2.85 ml (13.2 mmol) of hexamethyldisilazane (Dow Corning Z-6079 silane) discharged the yellow color. The dropwise addition of a tetrahydrofuran solution of dibenzobicyclo[2.2.2]octadien-2-one (2.64 g, 12 mmol) resulted in a white precipitate of the lithio salt.

3-Benzylidenedibenzobicyclo[2.2.2]octadien-2-one (17, R_1 = H, R_2 = C_6H_5). To a suspension of the lithio salt prepared as described above was added a solution of benzaldehyde (1.27 g, 12 mmol) in tetrahydrofuran (5 ml). There was no immediate change. The mixture was heated to reflux; after 1 hr the lithio salt had dissolved (reacted) and the solution was orange. The cooled solution was diluted with ether, washed with 25% hydrochloric acid (4×) and water, and dried ($MgSO_4$). Evaporation to dryness gave 1.65 g (45%) of crude 3-benzylidenedibenzobicyclo[2.2.2]octadien-2-one, mp 214–215°. Recrystallization from ethanol gave pure **17** (R_1 = H, R_2 = C_6H_5): mp 216.5–217.5°; ir (KBr) 1701, 1625 cm^{-1}; uv (cyclohexane) 271 nm (ϵ 13,400), 298 (16,000), 343 sh (660), 363 sh (499), 380 sh (211); nmr ($CDCl_3$) δ 5.03 (1 H, s, C-1 proton), 5.70 (1 H, s, C-4 proton), 7.00–7.53 (14, m, aryl and vinyl). Eu(fod)$_3$ shift numbers[33] for the two singlets were 2.8 and 1.0, respectively; that for the vinyl proton which was buried in the low field multiplet was 2.8. Mass spectrum (70 eV) *m/e* (rel intensity) 308 (1), 178 (100).

Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.64; H, 5.26.

3-(*p*-Tolylidene)dibenzobicyclo[2.2.2]octadien-2-one (34). The procedure was the same as that for **17** (R_1 = H, R_2 = C_6H_5) except that the mixture became yellow on addition of the *p*-tolualdehyde, and reaction was complete after only 30 min reflux. Work-up as above gave 3.9 g of crude product which, on recrystallization from ethanol, gave 1.75 g (45%) of pure **34**, mp 203.5–204°. An nmr spectrum of the mother liquors from the crystallization showed that they did not contain additional **34**: ir (KBr) 1698, 1624 cm^{-1}; uv (cyclohexane) 273 nm (ϵ 13,200), 303 (19,600), 344 sh (769), 361 sh (515), 382 sh (185); nmr ($CDCl_3$) δ 2.40 (3 H, s, methyl), 5.00 (1 H, s, C-1 proton), 5.69 (1 H, s, C-4 proton), 7.10–7.53 (13 H, m, aryl and vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 322 (2), 178 (100).

Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.53; H, 5.59.

3-(*p*-Anisylidene)dibenzobicyclo[2.2.2]octadien-2-one (35). The procedure, using *p*-anisaldehyde, was analogous to that for **34**. The product on evaporation of the ether was an oil which would not crystallize. The oil was chromatographed on a 2-cm silica gel column (70 g, >200 mesh) with benzene as eluent. The first material was discarded but the second band was yellow and gave 2.00 g (49%) of the desired **35**: mp 161.8–162.3° (ethanol); ir (KBr) 1699, 1628 cm^{-1}; uv (cyclohexane) 279 nm, sh (ϵ 10,200), 315 (23,000), 364 sh (702), 382 sh (236); nmr ($CDCl_3$) δ 3.88 (3 H, s, methoxyl), 5.00 (1 H, s, C-1 proton), 5.72 (1 H, s, C-4 proton), 7.10–7.58 (13 H, m, aryl and vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 338 (4), 176 (100).

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.05; H, 5.33.

3-(*p*-Chlorobenzylidene)dibenzobicyclo[2.2.2]octadien-2-one (36). The procedure using *p*-chlorobenzaldehyde was analogous to that for **34**. The product on evaporation of the ether was a yellow oil which, after 3 days, contained some crystals. The oil was diluted with chloroform and 60 mg of colorless crystals (mp 237–239°, subl.) were collected; they showed an ir band at 1680 cm^{-1} but none at 1630 cm^{-1}, and were not examined further. Evaporation of the chloroform gave a viscous oil which, when treated with 95% ethanol, gave a precipitate (1.1 g) whose nmr spectrum showed that some of the desired product was present. The solid was taken up in benzene and chromatographed on a 2-cm silica gel column (25 g, >200 mesh) with benzene as eluent. The first fraction showed no carbonyl absorption and was discarded. The second fraction was yellow and gave 0.227 g (7%) of **36**: mp 191.5–192.5° (ethanol); ir (KBr) 1701, 1628 cm^{-1}; uv (cyclohexane) 273 nm (ϵ 14,000), 302 (16,900), 341 sh (839), 362 sh (524), 384 sh (205); nmr ($CDCl_3$) δ 5.03 (1 H, s, C-1 proton), 5.60 (1 H, s, C-4 proton), 7.10–7.54 (13 H, m, aryl and vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 344 (0.23), 342 (0.68), 178 (100).

Anal. Calcd for $C_{23}H_{15}ClO$: C, 80.58; H, 4.41. Found: C, 80.47; H, 4.51.

***trans*-2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-diene (25t).** After the initial reaction had subsided, a mixture of 0.100 g (4.24 mmol) of *trans*-3-phenyldibenzobicyclo[2.2.2]octadiene-2-carboxylic acid[30] and 2 ml of thionyl chloride was heated until the acid dissolved. Excess thionyl chloride was removed by rotary evaporation and the residue was dissolved in benzene (2 ml) and treated with methanol (0.35 ml). Removal of the solvent and recrystallization from methanol gave a nearly quantitative yield of **25t**: mp 116–116.5°; ir (KBr) 1727 cm^{-1}; uv (cyclohexane) 259 nm sh (ϵ 759), 258 (953), 265 (1250), 272 (1330); nmr ($CDCl_3$) δ 2.98 (1 H, d of d, J = 6.0 and 2.4 Hz, C-2 proton), 3.58 (3 H, s, methoxyl), 3.61 (1 H, d of d, J = 6.0 and 2.4 Hz, C-3 proton), 4.20 (1 H, d, J = 2.4 Hz, C-4 proton), 4.77 (1 H, d, J = 2.4 Hz, C-1 proton), 6.52–6.70 (2 H, m, aryl), 6.94–7.55 (11 H, m, aryl) with Eu(fod)$_3$[32] shift numbers[33] for the first five peaks of 3.6, 2.5, 3.2, 1.0, and 3.1, respectively.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.65; H, 6.04.

2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octatriene (33). A solution of methyl phenylpropynoate (3.5 g, 21.9 mmol) and anthracene (7.8 g, 43.8 mmol) in 8 ml of *o*-dichlorobenzene was refluxed for 4 hr. After removal of the solvent by steam distillation, the solid was collected and extracted with methanol. Undissolved excess anthracene was removed by filtration, and the methanol was concentrated to give 2.95 g (40%) of **33**: mp 153.5–154.5° (methanol); ir (KBr) 1688 cm^{-1}; nmr ($CDCl_3$) δ 3.57 (3 H, s, methoxyl), 5.30 (1 H, s, C-1 proton), 5.78 (1 H, s, C-4 proton), 6.92–7.55 (13 H, m, aryl).

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.25; H, 5.29.

***cis*-2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-diene (25c).** A solution of the triene **33** (0.60 g, 1.77 mmol) in 60 ml of ethanol containing 40 mg of 5% Pd/C was stirred at room temperature and at approximately 1 atm of H_2 in a Brown[2] hydrogenation apparatus[37] for 3 days. The catalyst was removed (filtration) and

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(37) H. C. Brown, K. Sivasankaran, and C. A. Brown, *J. Org. Chem.*, 28, 214 (1963).

the solvent evaporated to give a quantitative yield of **25c:** mp 104–105° (methanol); ir (KBr) 1726 cm^{-1}; uv (cyclohexane) 252 nm sh (ϵ 743), 258 (989), 265 (1310), 272 (1360); nmr ($CDCl_3$) δ 2.98 (3 H, s, methoxyl), 3.28 (1 H, d of d, J = 11.8 and 1.8 Hz, C-2 proton), 3.71 (1 H, d of d, J = 11.8 and 2.4 Hz, C-3 proton), 4.25 (1 H, d, J = 2.4 Hz, C-4 proton), 4.64 (1 H, d, J = 1.8 Hz, C-1 proton), 6.18–6.48 (2 H, m, aryl), 6.82–7.42 (10 H, m, aryl), 7.52 (1 H, m, aryl), with $Eu(fod)_3$[32] shift numbers[33] for the first five peaks of 1.9, 2.1, 1.4, 1.0, and 2.1, respectively.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.84; H, 5.91.

Equilibration of *cis*- and *trans*-2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-dienes. A solution of 34 mg of **25c** and 2 mg of sodium methoxide in 3 ml of methanol was refluxed for 6 hr. Evaporation of the solvent gave 34 mg of residue whose nmr spectrum in $CDCl_3$ was indistinguishable from that of the trans isomer. Similar treatment of the trans isomer gave pure trans product (nmr).

Irradiation of 3-Benzylidenedibenzobicyclo[2.2.2]octadien-2-one (17, R_1 = H, R_2 = C_6H_5). A solution of **17** (100 mg) in 150 ml of methanol was irradiated (Pyrex, Hanovia 450 W) for 1 hr. The solution contained a precipitate (24 mg, 42%) whose ir spectrum was identical with that of dianthracene.[38] An nmr spectrum ($CDCl_3$) of the filtrate showed two sharp, nearly equal, singlets at δ 3.68 and 3.80 due to the methoxyl protons of methyl *cis*- and *trans*-cinnamates, respectively.[27] With the exclusion of the cinnamate peaks, all the remaining peaks could be ascribed to *cis*- and *trans*-2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-dienes (**25c** and **25t**), present in a ratio of 32:68. No other products were present.

When **17** (100 mg in 190 ml of methanol) was irradiated at 350 nm in a Rayonet apparatus until the uv maximum at 252 nm due to anthracene showed its concentration to be less than 10^{-5} *M*, the yield of dianthracene was 10.6 mg (18%). A similar irradiation at 300 nm monitored by the enone peak at 298 nm until all the starting material was consumed, followed by irradiation at 350 nm to dimerize the anthracene, gave 18.8 mg (32%) of dianthracene.

Irradiation of 3-(*p*-X-Benzylidene)dibenzobicyclo[2.2.2]octadien-2-ones (34, 35, and 36). A solution of each enone (100 mg) in methanol (190 ml) was irradiated (Pyrex, Hanovia 450 W) until the uv maximum at 252 nm due to anthracene showed its concentration to be less than 10^{-5} *M*. The insoluble dianthracene was collected. Two runs with **34** gave 20.3 and 23.0 mg (37 and 42%). Runs with **35** and **36** gave 22.3 mg (38%) and 18.9 mg (37%), respectively. Solvent was evaporated from the filtrate and an nmr spectrum of the crude residue in each case showed the presence only of the cinnamates and the ethanoanthracene esters.

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[38] Sadtler standard infrared spectrum No. 20684.

Kinetics and Mechanism of the Thermal Rearrangements of Optically Active α-Hydroxy Ketones. Example of a Cyclic Three-Component Equilibrium[1]

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Abstract: Two optically active α-hydroxy ketones, (*R*)- and (*S*)-3-hydroxy-3-phenyl-2-butanones, were synthesized. The rates of rearrangement for these two compounds and their optically inactive isomer, α-hydroxyisobutyrophenone, were studied at 252, 235, and 214°. The reaction kinetics was analyzed using an IBM 360 Model 67 computer. A mathematical model which uses the concentration *vs.* time profile of any one hydroxy ketone and the equilibrium concentrations of all the three isomers was developed to calculate the rate constants. These values were checked by another mathematical model derived from the reaction kinetics of two-component systems. The kinetic data provide evidence that the three isomeric hydroxy ketones exist in a first-order, three-component cyclic equilibrium under the rearrangement conditions. The activation parameters for the reactions were calculated and the mechanism for the rearrangement is discussed.

Although the stereochemistry of the thermal rearrangements of α-hydroxy ketones has been established both in steroids[3] and in bicyclic ring systems,[1] a kinetic analysis of the rearrangement has not been recorded. We are now reporting the stereospecific synthesis of the two optical isomers (**1** and **2**) of 3-hydroxy-3-phenyl-2-butanone and a detailed kinetic study of the rearrangement involving **1**, **2**, and the optically inactive isomer, α-hydroxyisobutyrophenone (**3**). The rate constants calculated from the kinetic data by two mathematical models (Appendix I and Appendix II) support the stereospecific nature of this rearrangement and provide evidence that the reaction kinetics is dictated by a cyclic three-component system[4] (Scheme I).

Results

(*R*)-3-Hydroxy-3-phenyl-2-butanone (**1**) was prepared by the treatment of 3 equiv of methyllithium with (*R*)-(−)-atrolactic acid[5] (**4**) in refluxing ether for 8

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[1] Hydroxy Ketone Rearrangements. II. For part I, see C. L. Stevens, T. A. Treat, and P. M. Pillai, *J. Org. Chem.*, **37**, 2091 (1972).

[2] Taken in part from the Ph.D. Dissertation of F. E. Glenn, Wayne State University, 1973.

[3] For a review, see N. L. Wendler in "Molecular Rearrangements," Part II, P. deMayo, Ed., Interscience, New York, N. Y., 1964, p 1114.

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