δ 1.17 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.34 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.94 (t, 2, J = 7 Hz, C-6 H), 6.40 (d, 1, J = 9.5 Hz, C-4 H), 7.34 (d, 1, J = 9.5 Hz, C-3 H), and 2.9–3.5 ppm (m, 2, C-5 and C-7 H). The cis isomer showed nmr ($CDCl_3$) δ 1.22 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.42 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.1–1.55 (1, C-6 H), 2.3–2.9 (m, 1, C-6 H), 2.7–3.4 ppm (m, 2, C-5 and C-6 H).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.71; H, 8.03; N, 8.61.

cis- and _trans_-5,7-Dimethyl-6,7-dihydro-5_H_-1-pyrindine (3 and 1).—The mixture of **18** (310 mg, 1.9 mmol) and dichlorophenylphosphine oxide (3 g, 15.4 mmol) was treated as described above. The crude product was filtered through silica gel with chloroform to yield 320 mg (93%) of 5,7-dimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine: nmr ($CDCl_3$) δ 1.00–1.40 (6, C-5 and C-7 CH_3), 1.2–1.5 (0.6, cis C_6 H), 1.78 (t, 0.8, J = 7 Hz, trans C_6 H_2), 2.17–2.77 (m, 0.6, cis C_6 H_2), 2.7–3.5 (m, 2, C_5 and C_7 H), 6.88 (d, 1, J = 8 Hz, C_4 H), 7.25 (d, 2, J = 8 Hz, C_3 H); mass spectrum m/e 181 (molecular ion).

A mixture of the 2-chlorodihydropyrindine (300 mg, 1.66 mmol), NaOAc (136 mg, 1.66 mmol), and 5% Pd/C (125 mg) in HOAc was hydrogenated in a Parr apparatus (30 lb, 65°, 3 hr). The mixture was filtered through Celite, concentrated *in vacuo*, diluted with H_2O (30 ml), neutralized with solid $NaHCO_3$, and extracted with ether. The ether was dried ($MgSO_4$) and evaporated to yield 200 mg (76%) of **1** and **3**: nmr (CCl_4) δ 7.0 (dd, 1, J = 8, 6 Hz, C_3 H), 7.4 (br d, 1, J = 8 Hz, C_4 H), 8.37 ppm (br d, 1, J = 6 Hz, C_2 H), and Table I. The picrate mixture showed mp 113–124°. The picrate mixture could be separated by fractional recrystallization (EtOH) into the enriched trans and pure cis isomers. The picrate of the cis isomer, mp 125–127°, showed nmr ($CDCl_3$) δ 7.79 (dd, 1, J = 6, 8 Hz, C_3 H), 8.13 (d, 1, J = 8 Hz, C_4 H), 8.58 ppm (d, 1, J = 6 Hz, C_2 H), and Table I. The mixture melting point of picrate **3** and picrate A was 102–120°.

The picrate of the trans isomer (*ca.* 67% pure) showed nmr ($CDCl_3$) δ 7.76 (dd, 1, J = 6, 8 Hz, C_3 H), 8.21 (d, 1, J = 8 Hz, C_4 H), 8.65 ppm (d, 1, J = 6 Hz, C_2 H), and Table I.

Anal. Calcd for $C_{16}H_{16}N_4O_7$: C, 51.06; H, 4.29; N, 14.89. Found: C, 51.18; H, 4.38; N, 15.06.

Registry No.—**1**, 36358-24-4; **1** picrate, 36358-25-5; **2**, 36358-26-6; **2** picrate, 36358-27-7; **3**, 36358-28-8; **3** picrate, 36358-29-9; **4**, 36411-21-9; **4** picrate, 36358-30-2; **12**, 36358-31-3; **13**, 36358-54-0; **14**, 36358-55-1; **16**, 36358-56-2; *cis*-**17**, 36358-57-3; *trans*-**17**, 36411-24-2; *cis*-**18**, 36358-58-4; *trans*-**18**, 36358-59-5; 5,7-dimethyl-2-chloro-6,7-dihydro-5*H*-1-pyridine (cis), 36358-60-8; 3,3,5-trimethyl-2-hydroxymethylene cyclopentanone, 36358-61-9; *cis*-3,5-dimethyl-2-hydroxymethylenecyclopentanone, 36434-06-7; *trans*-3,5-dimethyl-2-hydroxymethylenecyclopentanone, 36357-91-2; 5,7,7-trimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine, 36357-92-3; 5,5,7-trimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine, 36357-93-4; 5,7-dimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine (trans), 36357-94-5.

Acknowledgment.—Funds generously provided by the National Science Foundation for the purchase of a 100-MHz nmr spectrometer (GP-6940) and a high-resolution mass spectrograph (GP-8509) are gratefully acknowledged.

Mesoionic Compounds. XX. Cycloaddition Reactions of Pyrylium Betaines[1]

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anhydro-3-Hydroxy-2,4,6-triphenylpyrylium hydroxide underwent 1,3-dipolar cycloaddition reactions with a variety of acetylenic and olefinic dipolarophiles, as well as heterocumulenes, forming 1:1 adducts by reaction at the 2,6 positions. Thermolysis of these adducts either resulted in rearrangement to substituted cyclohexadienones or in dissociation to the initial reactants. The adduct from diphenylacetylene was also converted into cycloheptadiene and cycloheptatriene derivatives.

Reports of 1,3-dipolar cycloaddition reactions[2] utilizing carbonyl ylides were, until quite recently, noticeably absent from the literature. The cycloaddition reactions of tetracyanoethylene oxides to olefins, acetylenes, and aromatic compounds,[3] and the thermal condensations of oxiranes in the presence of dipolarophiles,[4] may be interpreted in terms of an intermediate carbonyl ylide **1**. Recently, *cis*- and *trans*-dicyanostilbene oxides were also shown[5] to undergo cycloadditions at temperatures >100° with a variety of acetylenic and olefinic dipolarophiles and, similarly, *cis*- and *trans*-cyanostilbene oxides also underwent cycloadditions. The reactive intermediates in these reactions were carbonyl ylides formed in a conrotatory, electrocyclic ring opening of the oxirane by fission of the C–C bond.[6] The thermal decomposition of Δ^3-1,3,4-oxadiazolines in the presence of dipolarophiles also appears to involve a carbonyl ylide intermediate.[7]

Our interest in cycloaddition reactions in which mesoionic compounds[8a] are utilized as the source of the 1,3 dipole[8b] led us to study whether a suitable mesoionic-type ring system containing a 1,3 dipole of the

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[1] (a) Support of this work by U. S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) presented in part at the XXIII IUPAC Congress, Boston, Mass., July 1971.

[2] R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).

[3] W. J. Lin, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3651 (1965); W. J. Linn and R. E. Benson, *ibid.*, **87**, 3567 (1965); W. J. Linn, *ibid.*, **87**, 3665 (1965).

[4] (a) E. F. Ullman and J. E. Milks, *ibid.*, **86**, 3814 (1964); E. F. Ullman and W. A. Henderson, Jr., *ibid.*, **88**, 4942 (1966); (b) D. R. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970); D. R. Arnold and Y. C. Chang, *J. Heterocycl. Chem.*, **8**, 1097 (1971); (c) T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970); (d) J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **49**, 3444 (1971); (e) J. J. Pommeret and A. Robert, *Tetrahedron*, **27**, 2977 (1971); A. Robert, J. J. Pommeret and A. Foucaud, *Tetrahedron Lett.*, 231 (1971); J. J. Pommeret and A. Robert, *C. R. Acad. Sci., Ser. C*, **272**, 333 (1971); A. Robert, J. J. Pommeret, and A. Foucaud, *ibid.*, **270**, 1739 (1970).

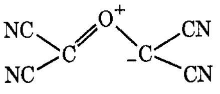
[5] H. Hamberger and R. Huisgen, *Chem. Commun.*, 1190 (1971).

[6] A. Dahman, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.* 1192 (1971).

[7] P. Rajagopalan and B. G. Advani, *Tetrahedron Lett.*, 2689 (1967); R. Hoffman and H. J. Luthardt, *Chem. Ber.*, **101**, 3861 (1968).

[8] (a) W. Baker and W. D. Ollis, *Quart. Rev., Chem. Soc.*, **11**, 15 (1957); for a recent review see M. Ohta and H. Kato in "Nonbenzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, Chapter 4; R. Huisgen in "Aromaticity," Chemical Society Special Publication No. 21, London, 1967, p 51; (b) *e.g.*, K. T. Potts and S. Husain, *J. Org. Chem.*, **36**, 3451 (1971), and references cited therein.

carbonyl ylide type could be devised. In a five-membered ring system *anhydro*-2,5-diphenyl-4-hydroxy-1,3-dioxolium hydroxide (**2**) would contain such a dipole, but this ring system has not yet been synthesized. As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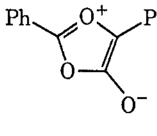
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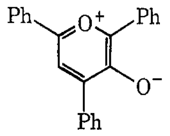
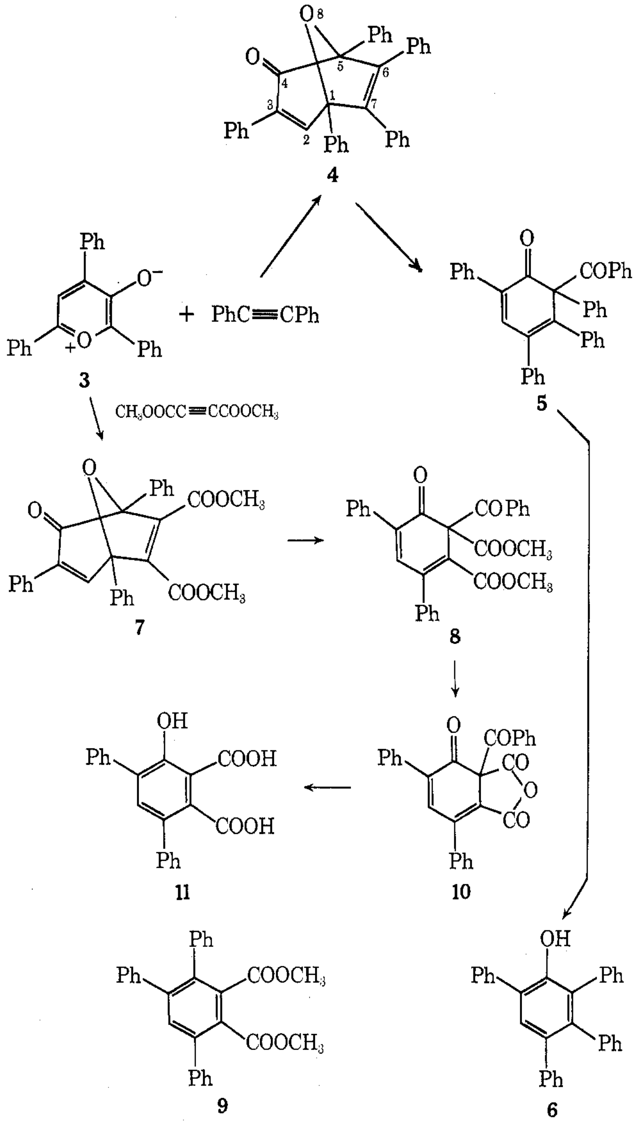

3

the oxygen atom at the 3 position may be considered to contribute two electrons to the 6π position of **2**, its replacement with a vinyl group would be expected to give a product with the desired characteristics of **2**. Such a system is represented by *anhydro*-3-hydroxy-2,4,6-triphenylpyrylium hydroxide (pyrylium betaine) (**3**) and data available in the literature indicate that a study of its cycloaddition reactions would be of great interest.

Other six-membered, heteroaromatic betaines containing 1,3 dipoles of the azomethine ylide type have been shown recently to undergo cycloaddition reactions. With *anhydro*-3-hydroxy-1-methylpyridinium hydroxide, adducts were obtained with olefinic dipolarophiles[9a] but not with acetylenic dipolarophiles[9b] and, with those betaines containing a pyrazine nucleus, 1:1 adducts were obtained with several olefinic and acetylenic dipolarophiles.[9c] The azomethine ylide dipole contained in an isoquinolinium imine has also been shown to react with a variety of olefinic and acetylenic dipolarophiles.[9d]

Studies with pyrylium oxides[10] to date have centered mainly on their photochemical, valence tautomerism characteristics.[4a,11] The benzo[*c*] analog of **3** was found to give 1:1 adducts with dimethyl acetylenedicarboxylate,[4a] norbornadiene,[4a] and several other olefinic dipolarophiles,[4d] and **3** itself reacted with maleic anhydride to give a 1:1 adduct whose structure, assigned on infrared evidence, is consistent with those reported in this communication.[12] The pyrylium betaine **3** was also shown[13] recently to undergo photochemical or thermal addition of oxygen forming ultimately a ring-opened product, 2-benzoyl-2,4-diphenylbut-3-en-4-olide. A pyrylium betaine intermediate was also postulated to explain the structure of the final, nitrogen-free product from 3,4-diazacyclopentadienone *N*,*N*-dioxide and dimethylacetylenedicarboxylate.[14] These indications of the suitability of the pyrylium betaine **3** as a source of a carbonyl ylide intermediate are amply confirmed by the cycloaddition reactions described below. This system is of additional interest in that it could also conceivably act as a 1,5 dipole in addition to a 1,3 dipole, but no products consistent with a 1,5-dipolar intermediate have been isolated.

Condensation of **3** with diphenylacetylene in boiling benzene yielded a 1:1 adduct, 4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**4**); spectral data (Experimental Section) are in accord with this structure and the following transformations provide strong confirmatory evidence. Thermolysis of **4** at 280° (8 mm) resulted in the formation of an isomeric, colorless, crystalline product, $C_{37}H_{26}O_2$, whose spectral characteristics were consistent with those expected for 6-benzoyl-2,4,5,6-tetraphenyl-2,4-cyclohexadienone (**5**). Treatment of **5** with warm potassium hydroxide solution gave 2,3,4,6-tetraphenylphenol (**6**) and benzoic acid.



An analogous 1:1 adduct **7** was formed readily from **3** and dimethyl acetylenedicarboxylate and its spectral characteristics were again consistent with the assigned structure. Moreover, on thermolysis of this adduct, two products were formed, the analogous dimethyl 6-benzoyl-2,4-diphenyl-1-oxo-2,4-cyclohexadiene-5,6-dicarboxylate (**8**) and the related dimethyl 3,4,6-triphenylphthalate (**9**). As anticipated, acid hydrolysis of the ester **8** resulted in formation of the anhydride **10**, which was converted into the phthalic acid **11**.

This mode of addition is a general one with acetylenic dipolarophiles. Dibenzoylacetylene also readily gave the corresponding cycloadduct, 6,7-dibenzoyl-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**12**), but in this case reaction with **3** occurred readily at room temperature, a characteristic of the reaction of dibenzoylacetylene with several other 1,3-dipolar sys-

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[9] (a) A. R. Katritsky and Y. Takeuchi, *J. Amer. Chem. Soc.*, **92**, 4135 (1970); (b) K. T. Potts, A. J. Elliott, and R. Hsia, unpublished results; (c) J. Honzl, M. Sorm, and V. Hanus, *Tetrahedron*, **26**, 2305 (1970); M. Sorm and J. Honzl, *ibid.*, **28**, 603 (1972); R. Huisgen and H. Mader, *Angew. Chem., Int. Ed. Engl.*, **8**, 604 (1969); (d) J. W. Lown and K. Matsumoto, *J. Org. Chem.*, **36**, 1405 (1971).

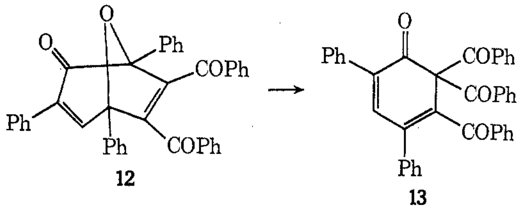
[10] A review on the reaction of pyrylium salts may be found in H. Perst "Oxonium Ions," Verlag Chemie-Academic Press, Weinheim/Bergstr., Germany, 1971.

[11] E. F. Ullman, *J. Amer. Chem. Soc.*, **85**, 3529 (1963); J. M. Dunston and P. Yates, *Tetrahedron Lett.*, 505 (1964).

[12] G. Suld and C. C. Price, *ibid.*, **84**, 2094 (1962).

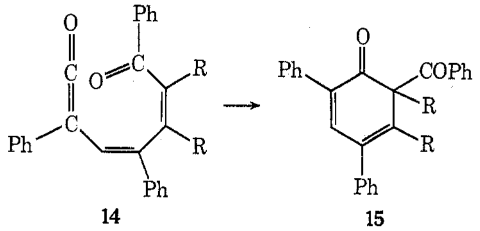
[13] H. H. Wasserman and D. L. Pavia, *Chem. Commun.*, 459 (1970).

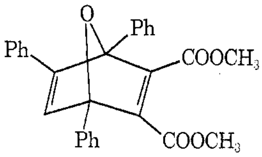
[14] J. P. Freeman and M. J. Hoare, *J. Org. Chem.*, **36**, 19 (1971).



tems. On thermolysis **12** underwent isomerization to **13**, whose spectral characteristics were consistent with the assigned structure and with those of the analogous compounds described above (see Experimental Section).

The thermal isomerization of these acetylenic adducts may be readily explained by assuming an initial cleavage of the 4,5 bond with the formation of an intermediate ketene **14**. This may then undergo cyclization to **15** by addition of the diene system to the ketene carbonyl group. This ketene intermediate also satisfactorily explains the formation of the second product **9**, isolated in the pyrolysis of the cycloadduct **7**. The dimethylphthalate derivative **9** differs from its precursor by an apparent loss of CO_2. Decarbonylation of the ketene **14** with concomitant cyclization to an intermediate bicyclo[2.2.1]heptane system **16** is an unlikely reaction pathway for the formation of **9**, as reactions proceeding with the extrusion of a single atom of oxygen are rare and dehydration processes are usually involved.[15] Such a process is impossible with the substitution pattern of **16**. However, the bond fission leading to the ketene **14** also accounts satisfactorily for the formation of **9**. After fission of the 4,5 bond in **7**, an alternative series of electron shifts would result in the formation of an intermediate **17** which, following attack of the bridge oxygen atom on the carbonyl group, would collapse to **18**. Thermal elimination of CO_2 from systems similar to **18** is well authenticated,[16] and probably involves an intermediate such as **18a**.





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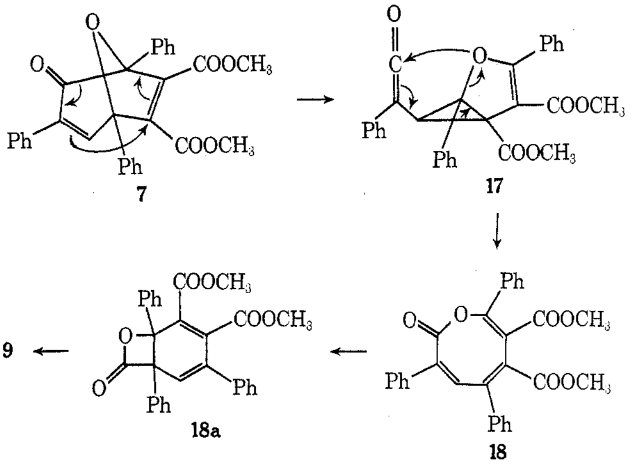
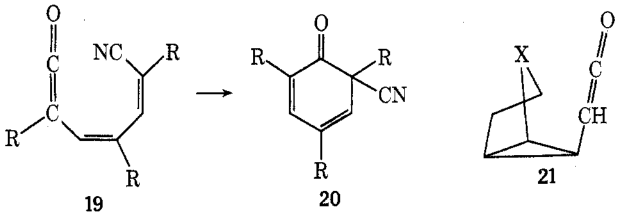
Several analogies may be found for the rationalizations described above. Thermal cyclization of the diene ketene **19** to the cyclohexa-2,4-dienone **20** has been reported[17a] and cyclopropylketene intermediates **21** have been detected in the photolysis of bicyclic dienones.[17b] In addition ketene and heterocumulene intermediates have resulted from the thermal[18a] and photochemical[18b] cleavage of several mesoionic systems.





Other experiments also provided support for the original structure assignments made for the primary 1:1 adducts. Reduction of **4** with H_2/PtO_2 resulted in the absorption of 1 equiv of hydrogen and the formation of 4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]oct-6-ene (**22**). That the 2,3 double bond had been reduced was evident from the nmr spectrum, which was of the ABX type. Also the change of the carbonyl absorption from 1690 to 1720 cm^{-1} indicated removal of the α,β double bond. The dihydro compound was reduced with lithium aluminum hydride to a mixture of epimeric alcohols **23** and an hydrogenolysis product, 1,2,3,4,6-pentaphenylcyclohepta-1,3-diene (**24**). The formation of the latter is not unexpected, as lithium aluminum hydride hydrogenolysis of ether functions has been described.[19] Dehydration of the mixture of epimeric alcohols **23** with *p*-toluenesulfonic acid in hot toluene resulted in complete deoxygenation of the system with the formation of 1,2,3,4,6-pentaphenylcyclohepta-1,3,5-triene (**25**). There was no evidence for the presence of any of the possible norcaradiene valence isomer of **25**, which was also not observed with 1,2,3,4,5,6,7-heptaphenylcyclohepta-1,3,5-triene.[20]

In the above cycloadditions one product only was always isolated from the reaction mixture. The ($4\pi + 2\pi$) cyclization is evidently favored over the alternative ($6\pi + 2\pi$) reaction, which could yield a bicyclo[3.2.1]octane derivative such as **26**. Olefinic dipolarophiles and heterocumulenes also followed a similar reaction pathway, giving products of the type described below.

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(15) B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, London, 1967, Chapter 7. This behavior of oxygen is in marked contrast to that of sulfur, which we have found to be readily extruded from primary cycloadducts containing sulfur bridges of this type.

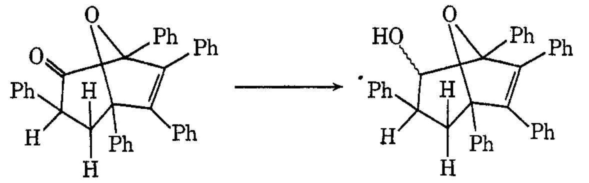
(16) Reference 15, Chapters 3 and 4.

(17) (a) J. D. Hobson, M. M. Al Holly, and J. R. Malpass, *Chem. Commun.*, 764 (1968); (b) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6858 (1969); see also T. Sasaki, S. Eguchi, and M. Ohno, *ibid.*, **92**, 3192 (1970).

(18) (a) H. O. Bayer, R. Huisgen, R. Knorr, and F. C. Schaefer, *Chem. Ber.*, **103**, 2581 (1970); (b) R. M. Moriarty, R. Mukherjee, O. L. Chapman, and D. R. Eckroth, *Tetrahedron Lett.*, 397 (1971).

(19) E. Staude and F. Patat in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967, p 65.

(20) M. A. Battiste, *Chem. Ind.* (*London*), 550 (1961).



22 **23**

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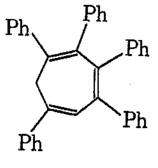

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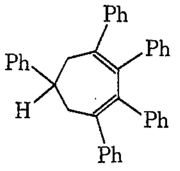

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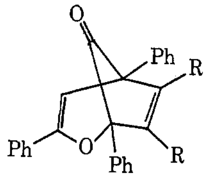

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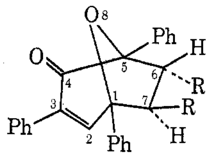

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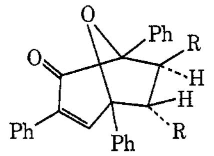

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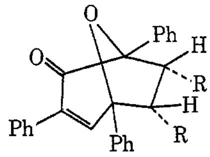

28

Dimethyl maleate, dimethyl fumarate, fumaronitrile, ethyl vinyl ether, *N*-phenylmaleimide, norbornene, and norbornadiene all formed stable, crystalline 1:1 adducts with the pyrylium betaine **3**. With dimethyl fumarate only one product was isolated (47%) and the intensive tlc analyses of reaction mixtures never showed detectable amounts of isomeric material. The chemical shifts of the 6 and 7 protons suggest structure **27**, R = $COOCH_3$, for this product. Doublets at τ 5.75 and 5.95 (J = 3.0 Hz) and methyl singlets at τ 6.27 and 6.87 are consistent with the protons being in a 6-exo,7-endo configuration, this assignment being made on the basis of the chemical shifts of related protons in the adducts described below and on the assumption that, in an oxygen-bridged system of this type, exo protons would be deshielded relative to endo protons. In early stages of this work, it was noticed that these olefinic cycloadducts underwent thermal dissociation to their precursors. It was not surprising, then, that the stereochemically pure fumarate cycloadduct gave rise to an isomeric mixture of products on heating at 127° in anhydrous chlorobenzene for 12 hr. Nmr data indicated that a 3:1 ratio of isomers was produced and the minor product was assigned the 6-endo,7-exo configuration **27a** (R = $COOCH_3$) on the basis of nmr data (Experimental Section).

Fumaronitrile also gave a good yield (75%) of a 1:1 cycloadduct with **3** and this has been assigned structure **27a** (R = CN). In this case the 6 and 7 protons were magnetically equivalent, giving a sharp singlet at τ 6.03 in the nmr spectrum. When this cycloadduct was heated in chlorobenzene at 127° for 12 hr, it was converted completely into an isomeric product in which the 6 and 7 protons now appeared as two doublets (J = 3.0 Hz) at τ 6.32 and 6.75. Thus the cycloadduct from **3** and fumaronitrile formed at room temperature most likely had the protons in a 6-endo,7-exo configuration **27a** (R = CN). At reflux temperature a mixture of the two isomeric products was obtained.

A 1:1 cycloadduct was also formed (60%) from dimethyl maleate and **3** in refluxing benzene. The 6 and 7 protons appeared as two doublets at τ 5.72 and 6.13 with a cis coupling, J = 11.5 Hz. In contrast to the fumarate adduct, the two ester methyl groups were equivalent. *N*-Phenylmaleimide also formed (44%) a 1:1 adduct with J = 9.5 Hz between the 6 and 7 protons which appeared as doublets at τ 5.70 and 5.93. These chemical shifts indicate an endo configuration for these two adducts, which have been assigned structures **28** (R = $COOCH_3$ and –CONPhCO–, respectively).

The electron-rich, olefinic dipolarophile ethyl vinyl ether and **3** formed a 1:1 cycloadduct (46%). The 6 and 7 protons formed a typical ABX pattern (J_{AB} = 13.0, J_{AX} = 8.75, and J_{BX} = 4.75 Hz) which was consistent with the calculated spectrum. Proton B at τ 7.32 has to have an endo configuration, which requires the ethoxyl group also to have an endo configuration. Though it cannot be established rigorously, the ether group is most likely at position 6, and the structure of the product is represented by **29**.

The stereochemistry represented in the structures **27**–**29** is consistent with that recently described for analogous adducts of the benzo analog[4d] of **3**, and for other oxygen-bridged[4d] systems. Experiments aimed at verifying these assignments by chemical methods are currently underway.

Highly strained olefins also reacted with the pyrylium oxide **3**. The 1:1 adduct from norbornene was assigned the exo,exo structure **30** on the basis of its nmr spectrum. A deshielding effect on the syn proton and a corresponding shielding effect on the anti proton of the methylene-bridge protons of norbornene by an oxide bridge has been found in adducts from diphenylisobenzofuran and norbornene (τ 7.73 and 9.40, respectively),[21] and also in *exo*-1,2-epoxynorbornene (τ 8.65 and 9.30, respectively).[22] In the nmr spectrum of **30**, the 7-anti proton of the norbornane moiety appeared as one-half of an AB quartet (J = 10.0 Hz), centered at τ 9.43, while the 7-syn proton was hidden amidst the methylene resonances of the norbornane moiety. There are four possible structures for this adduct (exo,exo, exo,endo, endo,exo, endo,endo), and only the exo,exo product is compatible with this observation. The protons at C_6 and C_7 of the bicyclo[3.2.1] system were assigned resonances at τ 7.32 and 7.50 (J = 6.0 Hz), respectively, these chemical shifts clearly requiring these protons to be in the endo configuration.

When excess norbornadiene was treated with **3**, a 1:1 adduct formed in 42% yield and, from five possible isomers (exo,exo, exo,endo, endo,endo, endo,exo, and 1,5 addition), this was assigned structure **31** on the basis of its nmr spectrum and its conversion into **30**. The exo configuration of the adduct was demonstrated by the protons at C_7 of the norbornene system appearing as an AB doublet, with the 7-anti proton at τ 9.20 and the 7-syn proton at τ 8.12 (J = 9.0 Hz). In

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[21] M. P. Cava and F. M. Scheel, *J. Org. Chem.*, **32**, 1304 (1967).

[22] K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 559 (1964).

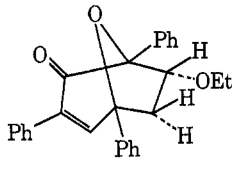
this adduct the norbornene bridgehead protons (at C_1 and C_4 of the norbornene system) were found as broad singlets at τ 7.82 and 7.50, and the endo protons at C_6 and C_7 of the bicyclo[3.2.1]heptane system occurred as an AB doublet (J = 7.0 Hz) at τ 7.17 and 7.27. Reduction of the adduct **31** with hydrogen and palladium gave the adduct **30**, establishing the close interrelationship of the two adducts.

Reaction of norbornene with 2 equiv of the pyrylium betaine **3** gave a mixture of two bis adducts (41% yield) which has not yielded to chromatographic separation. The nmr spectrum showed 2-methylene protons as a broad singlet at τ 9.07; no protons were observed at higher fields. The 4-endo protons, *i.e.*, the protons at C_6 and C_7 of the bicyclo[3.3.2]heptane system, appeared as an A_2B_2 quartet (J = 7.0 Hz) centered at τ 7.50 and 7.30. The most likely structures for these bis adducts are represented by **32** and **33**, respectively, and the nmr data may be rationalized on the basis of these structures. The bridgehead protons in **32** (*i.e.*, those at C_1 and C_4 of the norbornane system) should appear as two broad singlets (τ 8.63 and 8.00), whereas the corresponding bridgehead protons in **33** would be anticipated to be a broad singlet. These last protons were assigned to a resonance at τ 8.30.

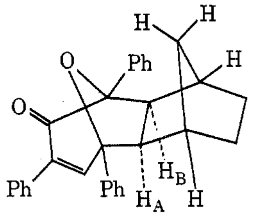
There has been considerable interest of late in the use of three-membered rings as dipolarophiles in cycloadditions. 2,3-Diphenylthiirene 1,1-dioxide and phenyldiazomethane at room temperature have been found to give 3,4,5-triphenylpyrazole (6%), arising from the loss of SO_2 from the initial 1,3-dipolar adduct,[23] and various cyclopropane derivatives have also been shown to form interesting adducts in cycloaddition reactions.[24]

The pyrylium betaine **3** and 1,1-diphenylthiirene 1,1-dioxide reacted slowly at room temperature with the loss of SO_2, and the presence of diphenylacetylene was detected after a few hours. After 3 days diphenylacetylene, 4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**4**), and unchanged pyrylium betaine **3** were present in the reaction mixture. While the adduct **4** might conceivably have been obtained from diphenylacetylene and **3**, it was shown independently that these reactants did not give **4** under these reaction conditions. The adduct **4**, obtained in 25% yield, is thought to arise from the loss of SO_2 from the initially formed adduct **34**. In hot benzene solution, only minor reaction occurred between **3** and the thiirene 1,1-dioxide, the latter undergoing complete loss of SO_2 in less than 2 hr.

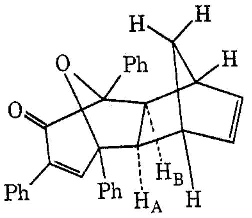
2,3-Diphenylcyclopropenethione has also received considerable attention lately as a dipolarophile[25] and its reaction with 1,3 dipoles offers a convenient method of annelation of a 3-carbon unit. With the pyrylium betaine **3**, a 1:1 adduct (50%) was formed in dry benzene at room temperature over a four-day period. Analytical and spectral data were consistent with the molecular formula represented by structure **35**, 4-oxo-1,3,5,7,8-pentaphenyl-8-thiocarbonyl-9-oxabicyclo[3.3.1]nona-2,6-diene. This assignment can only be regarded as tentative, as the alternative structure **36** cannot be excluded on the basis of the available data. However, such a mode of addition is consistent with the known characteristics of the thione and, on the basis of its reactions with other mesoionic systems,[26] structure **35** appears to be the more likely one.



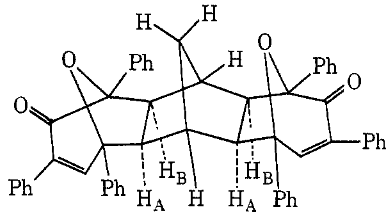
29



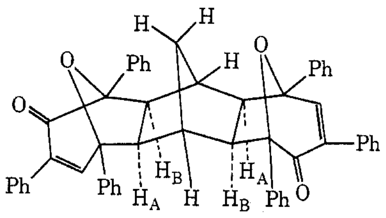
30



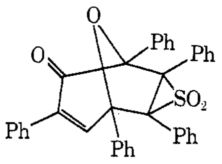
31



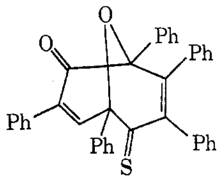
32



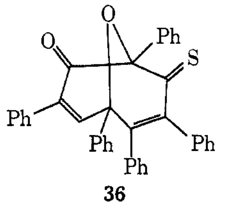
33



34



35



36

In contrast to the above reaction, diphenylcyclopropenone and **3** gave only 4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**4**) arising from addition across the carbon–carbon double bond with subsequent loss of carbon monoxide. Similar behavior has been observed with the benzo[*c*] analog[4d] of **3**. There was no evidence of any other mode of addition which would afford a compound analogous to **36**.

A structural ambiguity also exists with the 1:1 ad-

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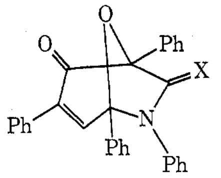
[23] L. A. Carpino, L. V. Mc Adams, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, **93**, 476 (1971).

[24] For references see R. Grigg and J. L. Jackson, *J. Chem. Soc. C*, 552 (1970).

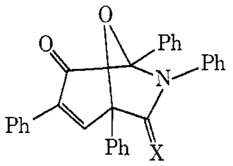
[25] J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **49**, 3119 (1971).

[26] K. T. Potts, J. Baum, and E. Houghton, unpublished results.

ducts formed from **3** and phenyl isocyanate, and also from phenyl isothiocyanate. These adducts, formed in good yield, may be represented by **37** or **38**.



37



38, X = O, S

An alternative to the use of the pyrylium oxide **3** in these cycloadditions is to carry out the reactions with its perchlorate in the presence of triethylamine. Generation of the pyrylium oxide **3** *in situ* in this fashion has little effect on the yield of purified cycloadduct; it offers considerable experimental convenience over the large-scale preparation of **3** which, unless the conditions described in the Experimental Section are adhered to, often leads to extremely impure products.[27]

In contrast to the adducts with a double bond in the 6,7 positions, the above adducts did not undergo thermal isomerization. Rather, fission of the 5,6 and 7,1 bonds occurred with regeneration of the pyrylium oxide **3** and the dipolarophile. This ready reversion to the initial components was also observed in the mass spectra of these adducts, with a relatively intense ion corresponding to the molecular ion of **3** being observed in all the spectra. It is most likely that this is a thermal process initiated in the ion source. Apart from the diphenylthiocyclopropenone adduct **35** (or **36**), the products described above all gave mass spectra with molecular ions of sufficient intensity to be measured. These established the stoichiometry of the adducts whose fragmentation patterns were consistent with the assigned structures.[28]

Experimental Section[29]

***anhydro*-3-Hydroxy-2,4,6-triphenylpyrylium Hydroxide**[12] (**3**).—Chalcone (41.6 g) and phenacyl acetate (35.6 g) were dissolved in acetic anhydride (300 ml) and the solution was cooled in an ice bath. Perchloric acid[30] (100 ml, 70%) in acetic acid (50 ml) and acetic anhydride (50 ml) (*Caution: vigorously exothermic*) was then added to the stirred solution during 10–15 min. Stirring was continued for 5 min at 0°, and the reaction mixture was then heated on a steam bath for 10–15 min, after which it was a dark-red color. After cooling (30–60 min) it was poured with stirring into ether (4 l.). A dirty-yellow solid separated which was collected and triturated with acetic acid, giving a bright-yellow product which, on crystallization from acetic acid, separated as canary-yellow plates, mp 230–231°. This perchlorate was dissolved in the minimum amount of dry, cold pyridine and poured onto ice and water. After 2–3 hr the purple solid was collected, washed well with water, and, after drying *in vacuo*, crystallized from acetone from which it separated as purple needles, mp 187–191° (lit[12] mp 193.5–195°).

Dimethyl 4-Oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene-6,7-dicarboxylate (**7**).—*anhydro*-3-Hydroxy-2,4,6-triphenylpyrylium hydroxide (**3**) (0.2 g, 0.618 mmol), dimethyl acetylenedicarboxylate (0.2 g, 1.24 mmol), and benzene (10 ml) were refluxed for 1 hr. The solvent was then removed *in vacuo* and the residue was triturated with methanol and finally recrystallized from methanol, giving pale-cream prisms: yield 84%; mp 132–133°; ir (KBr) 3025, 2960, 1720, 1650 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 315 nm (log ε 3.73), 255 (4.00), 217 (4.87); nmr ($CDCl_3$) τ 6.32 (s, 3, C_6 $COOCH_3$), 6.29 (s, 3, C_7 $COOCH_3$), 2.67–2.18 (m, 15, aromatic), 2.07 (s, 1, C_4 H); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 466 (6).

Anal. Calcd for $C_{29}H_{22}O_6$: C, 74.75; H, 4.79. Found: C, 74.62; H, 4.75.

4-Oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**4**) was obtained from **3** and diphenylacetylene in refluxing benzene over 50 hr. The crude product was triturated with ether and recrystallized from ethanol, separating as pale-yellow prisms: yield 62%; mp 187–189°; ir (KBr) 3025, 3060, 1690 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 315 nm (log ε 3.43), 277 (3.97), 225 (4.52); nmr ($CDCl_3$) τ 3.32–2.30 (m, 25, aromatic), 2.0 (s, 1, C_2 H); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 502 (13).

Anal. Calcd for $C_{37}H_{26}O_2$: C 88.42; H, 5.21. Found: C, 88.19; H, 5.22.

Similarly, **6,7-dibenzoyl-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene** (**12**) was obtained when the pyrylium betaine **3** (1.61 g, 0.5 mmol), dibenzoylacetylene (1.17 g, 0.5 mmol), and dry benzene (100 ml) were stirred together for 30 min at room temperature. The solvent was removed *in vacuo* and the residue was chromatographed on Florisil using benzene as eluent. The product separated as yellow needles from hexane: yield 57%; mp 84–85°; ir (KBr) 3075, 3045, 2960, 2940, 1710, 1660 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 315 nm (log ε 3.35), 267 sh (3.83), 230 (4.29); nmr ($CDCl_3$) τ 3.00–2.00 (m, 25, aromatic), 1.13 (s, 1, C_2 H); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 558 (5).

Anal. Calcd for $C_{39}H_{26}O_4$: C, 83.85; H, 4.69. Found: C, 83.46; H, 4.99.

Thermal Isomerization of 4-Oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**4**).—The above adduct (0.502 g, 0.001 mol) was heated at 280° for 1 hr in a vacuum (*ca.* 8 mm) and the product, after cooling, was chromatographed on silica gel using petroleum ether (bp 30–60°)–benzene (1:1) as eluent. Crystallization from ethanol afforded **6-benzoyl-2,4,5,6-tetraphenyl-2,4-cyclohexadienone** (**5**) as colorless needles: yield 60%; mp 192–194°; ir (KBr) 3050, 1735 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 260 nm (log ε 4.58), 243 (4.74); nmr ($CDCl_3$) τ 2.2–3.1 (m, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 502 (15).

Anal. Calcd for $C_{37}H_{26}O_2$: C, 88.42; H, 5.21. Found: C, 88.25; H, 5.13.

Hydrolysis of 6-Benzoyl-2,4,5,6-tetraphenyl-2,4-cyclohexadienone (**5**).—The dienone (0.15 g, 0.29 mol), KOH (0.15 g), ethanol (20 ml), and water (3 ml) were refluxed for 3 hr. The cold mixture was acidified with dilute HCl and the solvent was then evaporated *in vacuo*. The residue was washed with water, dried, and recrystallized from cyclohexane, giving colorless prisms of 2,4,5,6-tetraphenylphenol (**6**): yield 76%; mp 244–246°; ir (KBr) 3540, 3040 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 295 nm sh (log ε 4.07), 265 sh (4.58), 247 (4.82), 204 (4.94); nmr ($CDCl_3$) τ 4.75 (s, 1, OH, exchanged with D_2O), 3.1–2.2 (m, 21, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 398 (100).

Anal. Calcd for $C_{30}H_{22}O$: C, 90.45; H, 5.56. Found: C, 90.16; H, 5.62.

Thermal Isomerization of Dimethyl 4-Oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene-6,7-dicarboxylate (**7**).—The adduct **7** (0.35 g, 0.785 mmol) was heated at 190° for 2 hr under vacuum (*ca.* 8 mm) and the product was then chromatographed on silica gel using benzene–ether (95:5) as eluent. The first fraction, after recrystallization from methanol, afforded colorless prisms of **dimethyl 3,4,6-triphenylphthalate** (**9**): yield 13%; mp 205–206°; ir (KBr) 3040, 2960, 1730, 1720 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 247 nm (log ε 4.64), 204 (4.72); nmr ($CDCl_3$) τ 6.50 (s, 3, C_2 $COOCH_3$), 6.40 (s, 3, C_1 $COOCH_3$), 2.89–2.48 (m, 16, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 422 (100).

Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.56; H, 5.28. Found: C, 79.57; H, 5.27.

The second fraction crystallized from methanol as colorless needles of **dimethyl 6-benzoyl-2,4-diphenyl-2,4-cyclohexadien-1-one-5,6-dicarboxylate** (**8**): yield 43%; mp 189–190°; ir

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[27] If the crude pyrylium oxide **3** melts above 140°, it may be used without extensive purification and will yield reasonable adducts.

[28] The mass spectra were all determined utilizing the direct inlet probe of the Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV, with a source temperature of *ca.* 150°.

[29] Spectral characterizations were carried out on the following instrumentation: infrared spectra, Perkin-Elmer Model 421 and 331 spectrophotometers; ultraviolet spectra, Cary 14 spectrophotometer; nmr spectra, Varian A-60 and T-60 spectrometers, using TMS as internal standard. Melting points were determined in capillaries and all evaporations were carried out using a Rotovap apparatus. Microanalyses were performed by Instranal Laboratories, Inc., Rensselaer, N. Y.

[30] Use of perchloric acid below 70% strength will prevent separation of the perchlorate when the reaction mixture is added to ether. This perchlorate must be bright yellow and reasonably pure for effective conversion into the pyrylium oxide **3**. The latter should be collected using gravity filtration only.

(KBr) 3040, 2960 1735 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 235 nm (log ϵ 4.83), 200 (5.07); nmr (CDCl$_3$) τ 6.40 (s, 3, C$_5$ COOCH$_3$), 6.09 (s, 3, C$_5$ COOCH$_3$), 2.90–2.26 (m, 15, aromatic), 1.84 (s, 1, C$_3$ H); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 466 (14).

Anal. Calcd for $C_{29}H_{22}O_6$: C, 74.80; H, 4.74 Found: C, 74.78; H, 4.79.

6-Benzoyl-2,4-diphenyl-2,4-cyclohexadiene-2,6-dicarboxylic Acid Anhydride (**10**).—Dimethyl 6-benzoyl-2,4-diphenyl-2,4-cyclohexadien-1-one-5,6-dicarboxylate (**8**) (0.4 g), acetic acid (3.5 ml), and H_2SO_4 (0.35 ml) were refluxed for 3 hr. After cooling, the reaction mixture was treated with water, and the solid which precipitated was collected, washed with water, and dried *in vacuo*. Crystallization from ether gave colorless prisms of the anhydride: yield 100%; mp 220°); ir (KBr) 3050, 2875, 1850, 1790, 1750, 1730 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 302 nm (log ϵ 4.25), 244 sh (4.80); nmr (CDCl$_3$) τ 2.8–2.2 (m, 15, aromatic), 1.9 (s, 1, C$_3$ H); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 420 (5).

Anal. Calcd for $C_{27}H_{16}O_5$: C, 77.14; H, 3.84. Found: C, 76.69; H, 3.98.

3-Hydroxy-4,6-diphenylphthalic Acid (**11**).—The above anhydride (0.1 g) was refluxed for 2 hr with excess alcoholic NaOH. The solvent was removed *in vacuo* and the residue was treated with dilute HCl. The solid precipitate was extracted with ether, and the ether solution was washed with water, dried (MgSO$_4$), and evaporated to dryness. The residue was recrystallized from aqueous ethanol affording colorless prisms: yield 100%; mp 231–232°; ir (KBr) 3509, 3200–2300, 1730, 1685 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 287 sh nm (log ϵ 3.56), 257 sh (4.19), 241 (4.49); mass spectrum *m/e* (rel intensity) 316 (37) ($M\cdot^+$ of anhydride), 272 (12), 271 (12), 250 (20), 249 (100), 244 (12), 217 (18), 147 (23), 146 (25), 118 (22), 105 (45), 104 (50), 93 (14), 77 (54).

Anal. Calcd for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.43; H, 4.43.

Thermal Isomerization of 6,7-Dibenzoyl-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**12**).—The adduct **12** (2.0 g) was heated at 190° for 1 hr under vacuum (*ca.* 1 mm) and the product, after cooling, was chromatographed on silica gel using benzene as eluent. Crystallization from hexane–benzene afforded **2,4-diphenyl-5,6,6-tribenzoyl-2,4-cyclohexadienone** (**13**) as colorless needles: yield 29%; mp 194–195°; ir (KBr) 3060, 2920, 2850, 1750, 1660 cm^{-1}; λ_{max}^{MeOH} 255 nm (log ϵ 4.69), 202 (5.17); nmr (CDCl$_3$) τ 3.0–2.0 (m, aromatic); mass spectrum (rel intensity) $M\cdot^+$ 558 (9).

Anal. Calcd for $C_{39}H_{26}O_4$: C, 83.85; H, 4.69. Found: C, 83.45; H, 4.61.

Catalytic Hydrogenation of 4-Oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**4**).—The diene **4** (0.65 g, 1.3 mmol) dissolved in THF (20 ml) and a catalytic amount of PtO$_2$ were shaken with hydrogen (30 psi) for 6 hr. The catalyst was filtered, the solvent was evaporated, and the residue was recrystallized from ethanol, affording colorless prisms of **4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]oct-6-ene** (**22**): yield 76%; mp 210–212°; ir (KBr) 3060, 3030, 2945, 2865, 1720 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 265 sh nm (log ϵ 3.70), 240 (4.00), 292–335 (end absorption); nmr (CDCl$_3$) τ 7.18 (qt, 1, H$_2$ exo, $J_{2\text{-exo},2\text{-endo}}$ = 14 Hz; $J_{2\text{-exo},3\text{-endo}}$ = 10 Hz); 6.72 (qt, 1, H$_2$ endo; $J_{2\text{-endo},3\text{-endo}}$ = 9 Hz), 5.38 (qt, 1, H$_3$ endo), 3.20–2.32 (m, 25, aromatic); mass spectrum *m/e* (rel intensity) 374 (32), 372 (100), 207 (11), 105 (25), 77 (13).

Anal. Calcd for $C_{37}H_{28}O_2$: C, 88.01; H, 5.60. Found: C, 87.87; H, 5.64.

Lithium Aluminum Hydride Reduction of 4-Oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]oct-6-ene (**22**).—The above ketone **22** (0.7 g, 1.39 mmol), LiAlH$_4$ (0.15 g, 4.0 mmol), and THF (20 ml) were refluxed under N$_2$ for 5 days. The reaction mixture was cooled, treated with water, and filtered. The filtrate was evaporated *in vacuo* and the solid residue was chromatographed on silica gel. The petroleum ether (bp 60–80°) effluent was recrystallized from acetonitrile, giving colorless prisms of **1,2,3,4,6-pentaphenylcyclohepta-1,3-diene** (**24**): yield 30%; mp 198–200°; ir (KBr) 3060, 3030, 2950, 2925 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 295 sh nm (log ϵ 4.15), 268 (4.24), 222 (4.21); nmr (CDCl$_3$) τ 6.82 (d, 4, CH$_2$), 6.08 (quintet, 1, CH, $J_{CH_2,CH}$ = 6.5 Hz), 3.13–2.80 (m, 25, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 474 (45).

Anal. Calcd for $C_{37}H_{30}$: C, 93.63; H, 6.37. Found: C, 93.38; H, 6.45.

The petroleum ether–benzene (7:3) effluent, after crystallization from acetonitrile, gave colorless plates of **2-hydroxy-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]oct-6-ene** (**23**): yield 22%; mp 227–229°; ir (KBr) 3580, 3065, 3040, 2900 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 298 nm (log ϵ 3.82), 244 (3.82); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 506 (20).

Anal. Calcd for $C_{37}H_{30}O_2$: C, 87.55; H, 5.94. Found: C, 87.43; H, 6.00.

Formation of 1,3,4,5,6-Pentaphenyl-1,3,5-cycloheptatriene (**25**).—2-Hydroxy-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.3.1]oct-6-ene (**23**) (0.506 g, 0.001 mol), *p*-toluenesulfonic acid (0.191 g, 0.001 mol), and toluene (20 ml) were refluxed for 6 hr. After cooling, *p*-toluenesulfonic acid separated and was filtered. The filtrate was washed with NaHCO$_3$ (5% solution), dried (CaCl$_2$), and evaporated *in vacuo*. The residue was recrystallized from acetonitrile and from cyclohexane, affording colorless prisms: yield 85%; mp 218–220°; ir (KBr) 3030, 2900, 1600, 1500, 1490 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 373 sh nm (log ϵ 4.08), 358 (4.26), 259 (4.45), 219 sh (4.50), 208 sh (4.62), 202 (4.66); nmr (CDCl$_3$) τ 8.58 (s, 2, CH$_2$), 4.89 (s, 1, CH), 3.5–2.0 (m, 25, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 472 (10).

Anal. Calcd for $C_{37}H_{28}$: C, 94.01; H, 5.97. Found: C, 94.19; H, 5.55.

Reaction of 3 with Dimethyl Fumarate.—The pyrylium betaine **3** (1.62 g, 0.5 mmol), dimethyl fumarate (0.72 g, 0.5 mmol), and dry benzene were heated under reflux for 3 hr. The solvent was evaporated *in vacuo*, and the residue was chromatographed on silica gel (benzene) and crystallized from cyclohexane to give colorless plates of **6,7-dicarbomethoxy-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]oct-2-ene** (**27, R = COOCH$_3$**): yield 47%; mp 184°; ir (KBr) 3075, 3050, 3020, 2945, 1730, 1720, 1710 cm^{-1}; nmr (CDCl$_3$) τ 6.87 (s, 3, COOCH$_3$), 6.27 (s, 3, COOCH$_3$), 5.95 (d, 1, J = 3.0 Hz), 5.75 (d, 1, J = 3.0 Hz), 2.77–2.00 (m, 16, aromatic); $\lambda_{max}^{CH_3OH}$ 255 nm (log ϵ 3.93), 216 sh (4.70); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 468 (2).

Anal. Calcd for $C_{29}H_{24}O_6$: C, 74.34; H, 5.16. Found: C, 74.24; H, 5.22.

Similarly, the pyrylium betaine **3** and dimethyl maleate on reflux for 4 hr in benzene and reaction work-up as above gave **6,7-dicarbomethoxy-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]oct-2-ene** (**28, R = COOCH$_3$**) as colorless plates from cyclohexane: yield 60%; mp 176–178°; ir (KBr) 3075, 3050, 3010, 2950, 1745, 1700 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 255 nm (log ϵ 3.87), 216 sh (4.64); nmr (CDCl$_3$) τ 6.23 (s, 6, 2 COOCH$_3$), 6.13 (d, 1, J = 11.5 Hz), 5.72 (d, 1, J = 11.5 Hz), 2.67–2.20 (m, 16, aromatic), 2.07 (s, 1, C$_2$ H); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 468 (5).

Anal. Calcd for $C_{29}H_{24}O_6$: C, 74.34; H, 5.16. Found: C, 74.43; H, 5.08.

6,7-Dicyano-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]oct-2-ene (**27**, R = CN) was obtained from equivalent amounts of the pyrylium betaine **3** and fumaronitrile in benzene at room temperature. After 6 hr, the solvent was removed *in vacuo* and methanol was added to the liquid residue, causing it to crystallize. Crystallization from cyclohexane gave colorless prisms: yield 75%; mp 217–218°; ir (KBr) 3075, 3045, 2945, 2260, 1710 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 285 nm (log ϵ 3.80), 215 sh (4.58); nmr (CDCl$_3$) τ 6.03 (s, 2, C$_6$ + C$_7$), 2.80–2.33 (m, 16, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 402 (6).

Anal. Calcd for $C_{27}H_{18}N_2O_2$: C, 80.58; H, 4.51; N, 6.96. Found: C, 80.36; H, 4.49; N, 6.85.

6-Ethoxy-4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]oct-2-ene (**29**).—The pyrylium betaine **3** (1.62 g, 0.5 mmol), ethyl vinyl ether (5 ml), and dry benzene (100 ml) were heated under reflux for 6 hr. The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel in benzene. Crystallization from hexane gave colorless prisms: yield 46%; mp 117–118°; ir (KBr) 3075, 3045, 2975, 2890, 1690 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 267 nm (log ϵ 3.76), 215 sh (4.41); nmr (CDCl$_3$) τ 8.60 (t, 3, J = 7.0 Hz), 6.30 (qt, 2, J = 7.0 Hz), 7.60–6.80 (m, 2, C$_7$ H, AB portion of ABX), 5.80–5.40 (m, C$_6$ H, X portion of ABX; ABX calcd ν_A τ 6.93, ν_B 7.32, ν_X 5.53, J_{AB} = 13.0, J_{AX} = 8.75, J_{BX} = 4.75 Hz), 3.0–2.0 (m, 16, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 396 (10).

Anal. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10. Found: C, 81.60; H, 6.13.

Reaction of 3 with Norbornene.—The pyrylium betaine **3** (0.972 g, 0.003 mol) and norbornene (0.31 g, 0.0033 mol) in toluene (10 ml) were refluxed for 30 min. The solvent was removed *in vacuo* and the semisolid residue was chromatographed on silica gel in benzene. Crystallization of the initial fraction from cyclohexane afforded colorless needles of the adduct **30**: yield 32%; mp 202–203°; ir (KBr) 3075, 3045, 2975, 2945, 2885, 1700 cm^{-1}; nmr (CDCl$_3$) τ 9.43 (d, 1, C$_7$ anti H, J = 10.0

Hz), 8.4–9.2 (m, 5, CH_2 + C_7 syn H), 8.25 (broad s, 1, $C_{1(4)}$ H), 7.95 (broad s, 1, $C_{1(4)}$ H), 7.54 (d, 1, H_A), 7.32 (d, 1, H_B, J_{AB} = 7.0 Hz), 2.0–3.0 (m, 16, aromatic); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 268 nm (log ϵ 3.10), 218 sh (3.80); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 418 (82).

Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.20; H, 6.26. Found: C, 85.94; H, 6.31.

Similarly, the pyrylium betaine **3** and a tenfold excess of norbornadiene afforded the 1:1 adduct **31**, which separated as colorless needles from cyclohexane: yield 42%; mp 157–158°; ir (KBr) 3075, 3045, 2960, 2940, 1690 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 270 nm (log ϵ 3.54), 218 sh (4.28); nmr ($CDCl_3$) τ 9.20 (d, 1, C_7 anti H, J = 9.0 Hz), 8.12 (d, 1, C_7 syn H, J = 9.0 Hz), 7.82 (broad s, 1, $C_{1(4)}$ H), 7.50 (broad s, 1, $C_{1(4)}$ H), 7.27 (d, 1, H_A), 7.17 (d, 1, H_B, J_{AB} = 7.0 Hz), 3.92 (broad m, 2, olefinic), 3.0–2.0 (m, 16, aromatic); mass spectrum *m/e* (rel intensity) 416 (2).

Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.12; H, 5.84.

Catalytic reduction of a sample of the above 1:1 adduct (**31**) in ethyl acetate solution (10% palladium on charcoal catalyst) afforded a product identical[31] with that prepared from norbornene.

The 2:1 Adduct with Norbornadiene (32 and 33).—The pyrylium betaine **3** (3.24 g, 0.01 mol), norbornadiene (0.45 g, 0.005 mol), and dry benzene (120 ml) were refluxed for 2 hr. Removal of the solvent *in vacuo* gave a semisolid residue which crystallized on the addition of methanol. Crystallization from *n*-butyl alcohol gave the bis adducts **32** and **33** as colorless needles: yield 41%; np 333–335°; ir (KBr) 3075, 3045, 2940, 1710 cm^{-1}; nmr ($CDCl_3$) τ 9.07 (broad s, 2, C_7 H), 8.63, 8.30, 8.00 (3 broad s, 2, $C_{1(4)}$ H), 7.50 (d, 2, H_A), 7.30 (d, 2, H_B, J_{AB} = 7.0 Hz), 2.9–2.4 (m, 30, aromatic); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 270 nm (log ϵ 4.06), 215 sh (4.68); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 740 (4).

Anal. Calcd for $C_{53}H_{40}N_4$: C, 85.91; H, 5.44. Found: C, 85.67; H, 5.44.

Reaction of 3 with 2,3-Diphenylthirene 1,1-Dioxide.—The pyrylium betaine **3** (1.62 g, 0.05 mmol), 2,3-diphenylthiirene dioxide (1.81 g, 0.75 mmol), and dry benzene (50 ml) were stirred together at room temprature for 3 days. The solvent was removed *in vacuo* and the pale yellow solid was crystallized twice from methanol, giving pale yellow prisms of **4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene**[31] (4), yield 25%, mp 186–189°.

Reaction of 3 with 2,3-Diphenylcyclopropenethione.—Equivalent amounts of the pyrylium betaine **3** and 2,3-diphenylcyclopropenethione were stirred together at room temperature in dry benzene. Chromatography on silica gel (benzene) followed by recrystallization from ethyl acetate afforded **4-oxo-1,3,5,6,7-pentaphenyl-8-thioxo-9-oxabicyclo[3.3.1]nona-2,6-diene (35)** as pale yellow needles: mp 228°; ir (KBr) 3075, 3045, 2940, 1695 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 335 nm (log ϵ 4.16), 280 sh (4.21), 232 (4.66); nmr ($CDCl_3$) τ 3.73 (s, 1, C_2 H), 2.80–2.17 (m, 25, aromatic); mass spectrum *m/e* (rel intensity) 441 (88), 105 (100).

Anal. Calcd for $C_{38}H_{26}O_2S$: C, 83.50; H, 4.79. Found: C, 82.99; H, 4.68.

4,6-Dioxo-1,3,5,7-tetraphenyl-7-aza-8-oxabicyclo[3.2.1]oct-2-ene (37, X = O).—The pyrylium betaine **3** (0.2 g, 0.618 mmol), phenyl isocyanate (0.081 g, 0.68 mmol), and dry benzene (12 ml) were refluxed for 5 hr. After removal of the solvent *in vacuo*, a small volume of methanol was added to the liquid residue, causing it to crystallize. Crystallization from methanol afforded yellow prisms: yield 80%; mp 178–179°; ir (KBr) 3040, 1760, 1630, 1600, 1580, 1500 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 345 nm (log ϵ 3.91), 265 (4.31), 216 sh (4.37); nmr ($CDCl_3$) τ 3.17–2.10 (m, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 443 (2).

Anal. Calcd for $C_{30}H_{21}NO_3$: C, 81.35; H, 4.78; N, 3.16. Found: C, 81.32; H, 4.77; N, 3.09.

Similarly **4-oxo-1,2,5,7-tetraphenyl-6-thioxo-7-aza-8-oxabicyclo[3.2.1]oct-2-ene (37, X = S)** prepared from **3** and phenyl isothiocyanate crystallized from methanol as yellow prisms: yield 75%; mp 194–195°; ir (KBr) 3050, 1640, 1600, 1580, 1500 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 348 nm (log ϵ 3.46), 272 (4.01), 218 sh (4.19); nmr ($CDCl_3$) τ 3.17–2.10 (m, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 459 (9).

Anal. Calcd for $C_{30}H_{21}NO_2S$: C, 78.49; H, 4.60; N, 3.03. Found: C, 78.33; H, 4.62; N, 2.97.

The adduct formed from *N*-phenylmaleimide and **3** under the above conditions also crystallized from methanol, and cyclohexane, separating as colorless, irregular prisms: yield 44%; mp 203–205°; ir (KBr) 3040, 2930, 1700, 1600, 1500 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 258 nm (log ϵ 3.76), 216 sh (4.52); nmr ($CDCl_3$) τ 5.93 (d, 1, C_7 exo H, J = 9.5 Hz), 5.70 (d, 1, C_6 exo H, J = 9.5 Hz), 3.07–1.83 (m, 21, aromatic); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 497 (13).

Anal. Calcd for $C_{33}H_{23}NO_4$: C, 79.66; H, 4.66; N, 2.82. Found: C, 79.52; H, 4.76; N, 2.65.

Thermal Isomerization of the Dimethyl Fumarate Adduct (27, R = $COOCH_3$).—The adduct **27** in anhydrous chlorobenzene was heated in a sealed nmr tube at 127° for 12 hr. The red coloration which developed during this period was lost on cooling. The nmr (before heating) showed τ 6.23 (d, 1, J = 3.0 Hz), 5.95 (d, 1, J = 3.0 Hz), 7.40 (s, 3), 6.90 (s, 3); after heating, in addition to the above, new peaks appeared at τ 6.50 (d, 1, J = 3.0 Hz), 6.05 (d, 1, J = 3.0 Hz), 7.25 (s, 3), and 6.90 (s, 3); isomer ratio by integration was shown to be 3:1.

Thermal Isomerization of the Fumaronitrile Adduct (27a, R = CN).—The adduct was heated as above and, after 12 hr, all the initial product had isomerized: nmr (before heating) ($CDCl_3$) τ 6.03 (s, 2); after heating (C_6H_5Cl) τ 6.75 (d, 1, J = 3.0 Hz), 6.32 (d, 1, J = 3.0 Hz).

Reaction of 3 with 2,3-Diphenylcyclopropenone.—Equivalent amounts of the pyrylium betaine **3** and 2,3-diphenylcyclopropenone were boiled under reflux in dry toluene for 6 hr. Chromatography on silica gel (benzene) followed by crystallization from methanol afforded pale yellow prisms of 4-oxo-1,3,5,6,7-pentaphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene[31] (**4**), yield 61%, mp 186–189°.

Registry No.—**3,** 31994-72-6; **4,** 35740-90-0; **5,** 35867-16-4; **6,** 913-58-6; **7,** 35740-92-2; **8,** 35740-93-3; **9,** 35740-94-4; **10,** 35740-95-5; **11,** 35740-96-6; **12,** 35740-97-7; **13,** 35740-98-8; **22,** 35740-99-9; **23** (*exo*-OH), 35741-00-5; **23** (*endo*-OH), 35741-01-6; **24,** 35741-02-7; **25,** 35741-03-8; **27** (R = $COOCH_3$), 35741-04-9; **27** (R = CN), 35820-74-7; **27a** (R = $COOCH_3$), 35741-05-0; **27a** (R = CN), 35741-06-1; **28** (R = $COOCH_3$), 35741-07-2; **28** (R = CONPhCO), 35741-08-3; **29,** 35741-09-4; **30,** 35741-10-7; **31,** 35820-75-8; **32,** 35741-11-8; **33,** 35741-12-9; **35,** 35741-13-0; **37** (X = O), 35741-14-1; **37** (X = S), 35741-15-2; **38** (X = O), 35741-16-3; **38** (X = S), 35741-17-4.

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[31] Criteria used for establishing identity were superimposable infrared spectra, no depression in mixture melting point, and identical R_f values.