1598 (weak) cm^{-1}; uv (95% ethanol) λ_{max} 282 mμ (ϵ 9700); 220 MHz nmr (CCl_4) δ 1.33 (t, J = 7 Hz, 3 H), 2.0–2.15 (m, 2 H), 2.45–2.60 (m, 4 H), 4.15–4.30 (m, 2 H), 5.95 (d, J = 12.5 Hz, 1 H), 6.50 (dd, J = 12.5 Hz, J = 5.5 Hz, 1 H), 7.30 (d, J = 5.5 Hz, 1 H).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.36; H, 7.34.

Registry No.—**1**, 24079-79-6; **2**, 25017-79-2; **3**, 25017-78-1; **7**, 25942-83-0; **9**, 2648-49-9; **12**, 25942-85-2; **13**, 25942-86-3; **14**, 25942-87-4; **16**, 25942-88-5; **17**, 25942-89-6; **19**, 25942-90-9; **22**, 24079-80-9; **23**, 24079-81-0; **24**, 24079-82-1; **25**, 25942-93-2; **26**, 25942-94-3; **27**, 25942-95-4.

Acknowledgments.—We are grateful to Professor R. L. Autrey and Mr. W. R. Anderson of Oregon Graduate Center, Portland, Oregon, for mass spectra, Mr. S. T. Bella for microanalyses, and Miss Luz Catan for expert technical assistance. The National Science Foundation (Grant No. GB-12278), The Research Corporation, and The Alfred P. Sloan Foundation generously provided funds which facilitated purchase of the 220-MHz nmr spectrometer.

Preparation and Reactions of 2,2-Dimethyl-4-cyclopentene-1,3-dione

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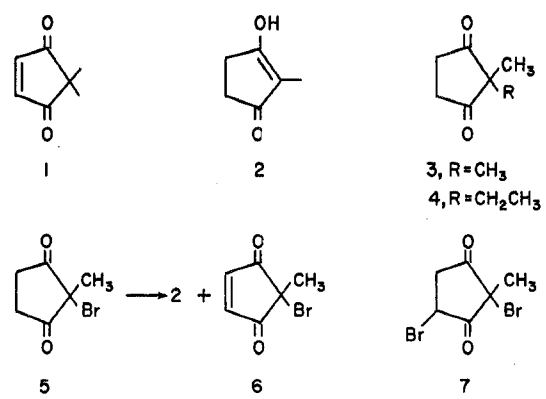
Treatment of **3** with *N*-bromosuccinimide yields **1**. Simple addition–elimination reactions of **1** and the related ketone **6** give **9**, **10**, **11**, and **14**. Enedione **1** is a sluggish dienophile relative to the parent compound **18**, but it behaves as a normal dipolarophile. The mechanistic implications of these observations are noted and the structure and stereochemistry of adducts of **1** with cyclopentadiene, three anthracenes, two aziridines (**24** and **25**), and diazomethane are recorded.

We describe here the preparation and a number of reactions of 2,2-dimethyl-4-cyclopentene-1,3-dione (**1**). These studies include simple addition–elimination reactions at the carbon–carbon double bond to provide substituted derivatives, as well as both Diels–Alder and 1,3-dipolar addition reactions. This compound (**1**) is a rather poor dienophile but a normal 1,3 dipolarophile, and we have previously discussed[2] the mechanistic implications of these observations for the 1,3-dipolar addition reaction.

Earlier investigators have described[3] methylation of the readily available enol **2**[4] to give 2,2-dimethylcyclopentane-1,3-dione (**3**) in 11% yield. By modification and careful control of the alkylating conditions we have improved this yield to 51%. Attempted use of similar conditions for ethylation, however, gave only a poor yield of the corresponding methylethyldione **4**. Reaction of **3** with *N*-bromosuccinimide in hot carbon tetrachloride gave the desired enedione **1** directly, presumably *via* α-bromination followed by dehydrobromination. The nuclear magnetic resonance (nmr) spectrum of the mixture during reaction showed only **3** and **1** with no evidence of the α-bromo ketone. Loss of hydrogen bromide from this intermediate under the reaction conditions then must be relatively rapid. Parallel behavior is apparent in a number of related transformations described below. The structure of **1** was confirmed by spectroscopic properties and its reduction back to **3** with zinc in acetic acid. The compound is a bright yellow liquid at room temperature and stable in the absence of base. Solutions of **1** exposed to amines, ammonia, or aqueous alkali quickly turn black.

An unexpected reaction similar to transformation of **3** to **1** occurs with the previously known[3] 2-bromo-2-methylcyclopentane-1,3-dione (**5**). On standing in the solid state at 4° this ketone undergoes slow conversion to a mixture of **2** and the bromoenedione **6**. Bromo ketone **5** apparently suffers bimolecular reaction with itself (perhaps through the intermediacy of molecular bromine) to give **2** and the unobserved dibromo ketone **7**, which then loses hydrogen bromide to form **6**.



We have followed the reaction of **1** with bromine in carbon tetrachloride solution by nmr and observed rapid formation of a dibromide which must be the trans isomer **8**, since its nmr spectrum consists of two singlets, one for the methyl groups and one for the ring protons. This substance can be obtained as a white solid by low temperature removal of solvent, but it fumes readily in air with formation of bromo ketone **9**. In similar fashion, but more slowly, **9** also reacts with bromine and yields dibromo ketone **10**. Absorption of bromine by **6** also proceeds at room temperature. In this case, however, addition of a second mole of halogen is relatively fast; the major product isolated, even with bromine as limiting reagent, is the fully brominated enedione **11**. This is accompanied by a small amount of **12**, which may be accounted for by reaction of liberated hydrogen bromide with the intermediate **13**.

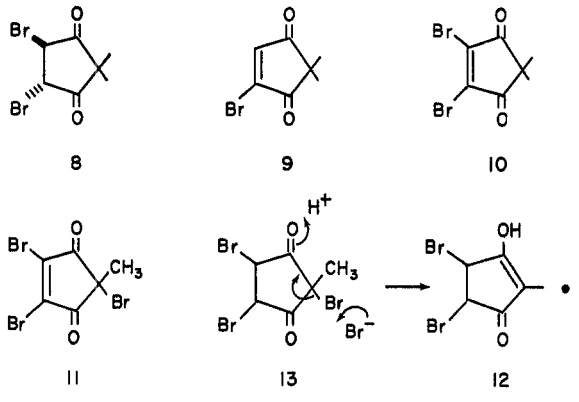
(1) Fellow of The Alfred P. Sloan Foundation. Author to whom correspondence should be addressed.

(2) W. C. Agosta and A. B. Smith, III, *Chem. Commun.*, 685 (1970).

(3) G. V. Kondrat'eva, G. A. Kogan, T. M. Fadeeva, and S. I. Saz'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1648 (1964).

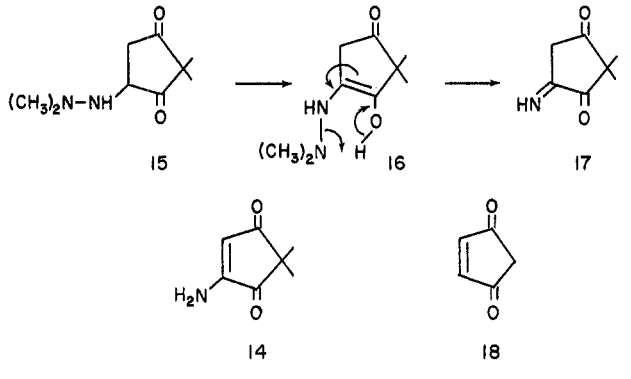
(4) H. Schick, G. Lehmann, and G. Hilgetag, *Ber.*, **102**, 3238 (1969), and references cited therein.

Since bromination of **1** gives **8** with no nmr evidence for the cis dibromide, it is probable that **12** also is the trans isomer.[5]



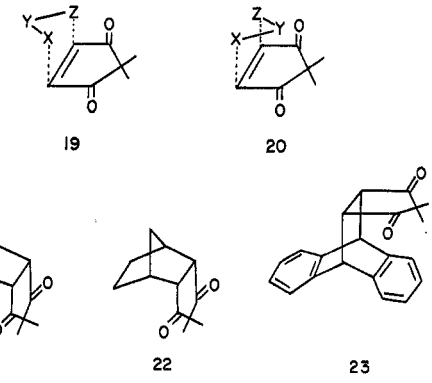
8 **9** **10** **11** **13** **12**

As noted above, attempts to add ammonia to **1** were unrewarding; this compound does react smoothly, however, with 1,1-dimethylhydrazine in dry ethanol to give enamine **14**. We may account for this rather unexpected result by assuming enolization of the initial Michael adduct **15** to form **16**, followed by elimination of dimethylamine and tautomerization of the resulting imine **17** to **14**. This sequence is mechanistically reminiscent of the long-known oxidation of α-hydroxy aldehydes and ketones by phenylhydrazine to yield osazones and aniline.[6] The amino ketone **14** was alternatively available in quantitative yield by Michael addition–elimination of ammonia with bromo ketone **9**. Reduction of **14** with zinc in acetic acid furnished **3**.



15 **16** **17** **14** **18**

The most interesting reactions we have carried out with **1** have been Diels–Alder and 1,3-dipolar additions. We have already reported[2] that **1** is a sluggish dienophile relative to the parent compound, 4-cyclopentene-1,3-dione (**18**),[7] but a normal 1,3 dipolarophile, and we have attributed this difference to steric retardation by the methyl groups in the transition state leading to Diels–Alder, but not dipolar, addition. These observations led to the conclusion that, if the generally accepted concerted mechanism[8] for 1,3-dipolar additions is operative here, the orientation of addends in the transition state must be that shown in **19** rather than **20**. We shall not present again the arguments involved, but simply note the assignment of structure and stereochemistry to the various adducts



19 **20** **21** **22** **23**

employed in our comparisons. Diels–Alder addition of **1** to cyclopentadiene affords adduct **21**. The endo configuration expected for this compound on the basis of the Alder–Stein rules[9] was confirmed by comparison of the nmr spectrum of **21** with that of its dihydro derivative **22** available on catalytic hydrogenation. Shielding of one methyl group by the double bond in **21**, an effect[10] possible only in the endo adduct, is indicated by the change in separation of the methyl singlets on hydrogenation. This separation ($\Delta\delta$) decreases from 0.20 ppm in **21** to 0.07 ppm in **22**. Also, the protons adjacent to the carbonyl groups show the upfield displacement ($\Delta\delta$ = 0.19 ppm) expected[11] for exo protons on passing from **21** to **22**. For endo protons the change anticipated[11] is smaller and in the opposite direction.[12] Addition of enedione **1** to anthracene proceeds smoothly with aluminum chloride catalysis[13] to form **23**. Similar adducts are formed with 2,6-dimethylanthracene[14] and 2,6-dichloroanthracene.[15] In each of these compounds the methyl group directly over the aromatic ring is quite shielded[16] magnetically and appears at about 0.2 ppm in the nmr spectrum.

As a dipolarophile, ketone **1** reacts normally and in good yield with the 1,3 dipoles formed in hot toluene from 1,2,3-triphenylaziridine (**24**)[17] and *trans*-1-cyclohexyl-2,3-dibenzoylaziridine (**25**).[18] In each case the adduct isolated (**26** and **27**, respectively), had trans disposed substituents on a cis-fused ring system, an assignment unambiguously clear from nmr spectra. In the spectra of **26** and **27** the protons at the ring junction

(5) As a result of rapid shift of the acidic proton, the ring hydrogen atoms are equivalent in **12** and in **2**, and they appear as a singlet in the nmr spectrum in both cases. This fact precludes an assignment of stereochemistry in **12** based on nmr measurements.

(6) A. Hassner and P. Catsoulacos, *Tetrahedron Lett.*, 489 (1967), and numerous references cited therein.

(7) C. H. DePuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **81**, 4920 (1959); C. H. DePuy and C. E. Lyons, *ibid.*, **82**, 631 (1960).

(8) R. Huisgen, *Angew. Chem.*, **75**, 742 (1963); R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968). For an opposing point of view, see R. A. Firestone, *ibid.*, **33**, 2285 (1968).

(9) A. S. Onishchenko, "Diene Synthesis," Daniel Davey and Co., New York, N. Y., 1964, Chapter 1, and references cited therein.

(10) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 83, and references cited therein.

(11) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(12) The more convenient distinction between endo and exo protons at these positions based (see ref 10, pp 288–289) on their observed coupling constants with the adjacent bridgehead protons fails with **19**. The four protons in question appear fortuitously as a sharp singlet even at 220 MHz. For successful application of this method in a closely related system, see M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).

(13) P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960).

(14) G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2203 (1929).

(15) Preparation of this compound by reduction of the known related quinone is detailed in the Experimental Section.

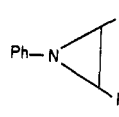
(16) Reference 10, p 94, and references cited therein.

(17) H. W. Heine, R. Peavy, and A. J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966).

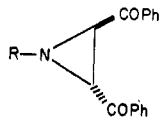
(18) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Amer. Chem. Soc.*, **87**, 1050 (1965); R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Lett.*, 397 (1966).

are coupled with a vicinal coupling constant of 10 Hz, indicating[19] cis rather than trans fusion of the two rings, just as expected on mechanistic grounds.[8] Furthermore, each proton on the pyrrolidine ring in **26** and **27** shows a unique chemical shift and unique coupling constants with its neighbors. This is possible only with trans disposition of phenyl (in **26**) or benzoyl (in **27**) groups, since both alternative isomers with these substituents cis possess structural symmetry inconsistent with four unique protons. The specific vicinal coupling constants derivable from the spectra are recorded in the Experimental Section and are fully consistent with the stereochemistry assigned.

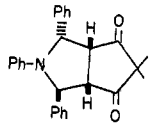
In similar fashion **1** adds diazomethane[20] at room temperature to give the rather unstable pyrazoline **28**. Also here the expected[8] cis-fused system is signaled[19] by the vicinal coupling constant (9 Hz) of the two methine protons. As predicted from previous observations,[21] **28** loses nitrogen on pyrolysis to give only the trimethyl ketone **29**, but yields a mixture of **29** and the isomeric cyclopropane **30** on photolysis.



24



25, R=cyclohexyl



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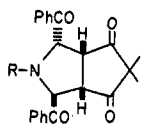
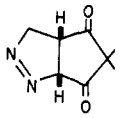
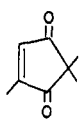


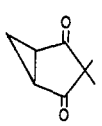
27, R=cyclohexyl



28



29



30

Experimental Section

Materials and Equipment.—Unless otherwise noted, both ir and nmr spectra were obtained for carbon tetrachloride solutions, the former on a Perkin-Elmer 237B spectrophotometer and the latter on a Varian A-60 (60 MHz) or HR-220 (220 MHz) nmr spectrometer. Spectra at 220 MHz are so marked; others are at 60 MHz. Ultraviolet spectra were obtained for solutions in 95% ethanol using a Cary Model 14PM spectrophotometer. Vpc was carried out using a Varian Aerograph Model 700 Autoprep equipped with a 20 ft × 0.25 in. stainless steel column packed with 30% FFAP on Chromosorb W and operated at 170° with a helium carrier gas flow rate of 100–150 ml/min. Photolysis was carried out at about 15° using a 450-W medium pressure mercury arc lamp, Hanovia type L, No. 679A-36, contained in a water-cooled quartz immersion well fitted with a Pyrex sleeve. Melting points are corrected.

2,2-Dimethylcyclopentane-1,3-dione (3).—A solution of 10 g of enone **2**,[4] 5 g of potassium hydroxide, and 13.4 g of methyl iodide was heated at reflux in 75 ml of dioxane and 25 ml of water. After 5 hr and again after 8.5 hr, 2.0 g of potassium hydroxide and 5.4 g of methyl iodide in 15 ml of dioxane and 5 ml of water was added to the refluxing mixture. After a total of 12 hr the mixture was cooled and extracted several times with ether. After removal of ether this extract was heated with 50 ml of 10% aqueous hydrochloric acid to the boiling point, cooled, and treated with excess 10% aqueous sodium carbonate. This solution was extracted four times with chloroform, and the organic extract was dried. The crude product remaining after removal of solvent was recrystallized from petroleum ether to give 51.5% **3** in two crops: ir ($CHCl_3$) 1770 (w), 1730 (s) cm^{-1}; nmr δ 1.05 (s, 6 H), 2.75 (s, 4 H). If no additional potassium hydroxide and methyl iodide were added during the reaction, the yield was 34%. The melting point of **3** was 45–47.

2-Ethyl-2-methylcyclopentane-1,3-dione (4).—This compound was prepared from **2**[4] and ethyl iodide as above. No additional base and ethyl iodide were added during the reaction. The crude yield was 14%. A sample was purified by vpc for analysis: ir (neat) 1765 (w), 1725 (s) cm^{-1}; nmr δ 0.77 (t, J = 7 Hz, 3 H), 1.00 (s, 3 H), 1.60 (q, J = 7 Hz, 2 H), 2.75 (s, 4 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.79; H, 8.66.

2,2-Dimethyl-4-cyclopentene-1,3-dione (1).—A mixture of 1.754 g of **3** and 2.44 g of *N*-bromosuccinimide in 40 ml of carbon tetrachloride was irradiated and heated with a 100-W incandescent bulb for 2 hr. The solution was cooled, filtered to remove succinimide, washed with sodium bicarbonate solution and then water, and dried. After removal of solvent there remained 1.28 g of yellow liquid product (74%), bp 90° (44 mm). On a larger scale the yield was 85%. Preparative vpc gave an analytical sample: ir 1750 (m), 1710 (vs), 1470 (m), 1315 (m), 1285 (m), 1135 (m), 1125 (m), 1038 (m), 845 (m) cm^{-1}; nmr δ 1.12 (s, 6 H), 7.15 (s, 2 H); uv λ_{max} 219 mμ (log ϵ 3.78), 345 (sh, 1.26), 389 (1.42).

Anal. Calcd for $C_7H_8O_2$: C, 67.74; H, 6.49. Found: C, 67.73; H, 6.66.

This compound could be stored at 4° for at least 1 year without change.

Reduction of 1 to 3.—A mixture of 200 mg of **1**, 2 g of zinc dust, and 10 ml of acetic acid was heated at 85° for 45 min. The solution was cooled and treated with excess 10% sodium carbonate solution and the product extracted into chloroform. This was washed with water and dried; removal of solvent gave 189 mg (92%) of **3**, identical with material prepared above by ir and nmr spectral comparisons.

2-Bromo-2-methyl-4-cyclopentene-1,3-dione (6).—A sample of **5** was stored at 4° for several months, during which time it turned quite yellow. It was treated with chloroform, and an insoluble white material was filtered off. Recrystallization of this material from water gave **2**, identical in ir spectrum, melting points and mixture melting point with authentic material. The chloroform filtrate yielded a yellow solid which was twice recrystallized from cyclohexane for analysis: mp 72–73°; ir 1760 (m), 1730 (s), 1715 (s), 1690 (w) cm^{-1}; nmr ($CDCl_3$) δ 1.80 (s, 3 H), 7.44 (s, 2 H).

Anal. Calcd for $C_6H_5O_2Br$: C, 38.13; H, 2.67. Found: C, 37.98; H, 2.66.

4-Bromo-2,2-dimethyl-4-cyclopentene-1,3-dione (9).—A solution of 380 mg of bromine in 5 ml of carbon tetrachloride was added dropwise to 300 mg of enedione **1** in 5 ml of carbon tetrachloride. Solvent and excess bromine were evaporated *in vacuo* to leave off-white crystals which fumed and turned to a yellow oil over 15 min. This oil crystallized spontaneously to give 434 mg (88%) of yellow crystals which could be recrystallized from petroleum ether. A sample was recrystallized for analysis: mp 75–76°; ir 1770 (w, sh), 1760 (w), 1715 (s) cm^{-1}; nmr δ 1.19 (s, 6 H), 7.40 (s, 1 H).

Anal. Calcd for $C_7H_7O_2Br$: C, 41.40; H, 3.48; Br, 39.36. Found: C, 41.33; H, 3.61; Br, 39.6.

In a similar experiment carried out in an nmr tube 100 mg of **1** was treated with 130 mg of bromine in 1 ml of carbon tetrachloride. The bromine color rapidly disappeared, and the nmr spectrum was then determined. This indicated that about 5% of both **1** and **9** was present and that the remaining material was the *trans*-dibromide **8** [δ 1.48 (s, 6 H), 4.72 (s, 2 H)]. Upon work-up the material described above was obtained.

4,5-Dibromo-2,2-dimethyl-4-cyclopentene-1,3-dione (10)—A mixture of 200 mg of bromo ketone **9** and 157 mg (1.0 equiv) of bromine was heated at reflux in 8 ml of carbon tetrachloride for 12 hr. From the nmr spectrum it was clear that starting material remained. The mixture was returned to reflux for an additional 36 hr with 100 mg more bromine. The crude product remaining on removal of solvent and excess bromine showed mp 135–142°. Three recrystallizations from carbon tetrachloride gave an analytical sample of yellow needles: mp 149–150.5°; ir (KBr disk) 1760 (s), 1735 (m), 1715 (vs), 1265 (s), 1210 (s),

(19) Reference 10, pp 286–288, and references cited therein.

(20) Dipolar additions of diazomethane are reviewed by R. Huisgen, *Angew. Chem.*, **75**, 604 (1963), and R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Wiley, New York, N. Y., 1964, Chapter 11, pp 806–878.

(21) Cyclopropane **30** is known to rearrange to **29** on pyrolysis: H. Stetter and H.-J. Sandhagen, *Ber.*, **100**, 2837 (1967). For decomposition of a related pyrazoline forming a thermally stable cyclopropane, see T. Sasaki and S. Eguchi, *J. Org. Chem.*, **33**, 4389 (1968).

1150 (s), 1110 (s) cm^{-1}; nmr δ 1.28 (s); uv λ_{max} 277 mμ (log ϵ 2.06), 325 (0.94).

Anal. Calcd for $C_7H_6O_2Br_2$: C, 29.82; H, 2.14; Br, 56.69. Found: C, 29.69; H, 2.16; Br, 57.0.

Bromination of 2-Bromo-2-methyl-4-cyclopentene-1,3-dione (6).—A solution of 200 mg of diketone 6 in 5 ml of chloroform was stirred at room temperature with 169 mg (1.0 equiv) of bromine. The color faded to yellow over 1.5 hr. The solvent was removed to leave a crystalline mass which was extracted with cyclohexane. This separated the reaction product into colorless needles (65 mg) insoluble in cyclohexane and a solution which yielded yellow needles (144 mg, 78% based on available bromine) on removal of solvent. Recrystallization of the colorless needles from benzene several times gave an analytical sample of **12**: mp 142.5–143.5°; ir ($CHCl_3$) 3450–2500 (m, broad), 1705 (m), 1625 (s, broad), 1395 (s), 1360 (m) cm^{-1}; nmr ($CDCl_3$) δ 1.83 (s), 4.86 (s).

Anal. Calcd for $C_6H_6O_2Br_2$: C, 26.70; H, 2.24. Found: C, 26.76; H, 2.25.

Recrystallization of the yellow needles from cyclohexane gave an analytical sample of **11**: mp 128–130°; ir 1770 (s), 1730 (vs), 1645 (s), 1545 (s), 1245 (m), 1120 (m), 1075 (m), 885 (m) cm^{-1}; nmr δ 1.87 (s).

Anal. Calcd for $C_6H_3O_2Br_3$: C, 20.78; H, 0.87. Found: C, 21.04; H, 0.93.

4-Amino-2,2-dimethyl-4-cyclopentene-1,3-dione (14). A. From 1,1-Dimethylhydrazine and Enedione 1.—A solution of 309 mg of enedione 1 and 174 mg of 1,1-dimethylhydrazine (freshly distilled and having ir identical with that reported[22]) in 5 ml of absolute ethanol stood at room temperature overnight. The solution was diluted with aqueous hydrochloric acid and the product extracted into ether. This was washed with water and brine and then dried. Removal of solvent gave 279 mg (80%) of solid. Recrystallization from benzene gave a sample with mp 169–170°, mmp (with material described below) 169–170°, ir and nmr spectra identical with those of material described below.

B. From Ammonia and Bromo Ketone 9.—A solution of 102 mg of bromo ketone 9 in 3 ml of ethanol and 1 ml of concentrated aqueous ammonia stood at room temperature for 3.5 hr. It was then evaporated to dryness, and the residue was extracted with ether to give 70 mg of product (100%). Recrystallization from benzene gave an analytical sample: mp 169–171°; ir 3510 (w), 3400 (w), 1745 (w), 1690 (m), 1635 (s) cm^{-1}; nmr ($CDCl_3$) δ 1.18 (s, 6 H), 5.50 (broad, 2 H, exchanges with D_2O), 5.90 (s, 1 H); uv λ_{max} 220 mμ (log ϵ 4.04), 309 (4.03).

Anal. Calcd for $C_7H_9O_2N$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.50; H, 6.48; N, 10.00.

Reduction of Amino Ketone 14 with Zinc in Acetic Acid.—A solution of 101 mg of amino ketone 14 in 5 ml of acetic acid containing 5 drops of concentrated hydrochloric acid and 1.00 g of zinc dust was stirred at room temperature for 2 hr. The solution was poured into water, neutralized with sodium bicarbonate solution, and extracted with chloroform. Removal of chloroform after drying left 29 mg of diketone **3** which was recrystallized from petroleum ether, mp and mmp (with authentic **3**) 46–48°, ir and nmr spectra identical with those of authentic **3**.

Reaction of Cyclopentadiene with Enedione 1.—A solution of 1.24 g of enedione 1 in 15 ml of benzene containing 1 ml of cyclopentadiene was heated at reflux under nitrogen for 19 hr. The mixture was concentrated *in vacuo*, treated with 10 ml of pentane, and then kept at −20° for several hours. Filtration then gave 900 mg (46%) of off-white crystals. Three recrystallizations from pentane at −20° gave an analytical sample of adduct **21**: mp 70–72°; ir 1770 (w), 1720 (s), 1112 (m), 1080 (m), 710 (m) cm^{-1}; nmr (220 MHz) δ 0.79 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.49 (d, J = 9 Hz, 1 H, CHH), 1.64 (d, J = 9 Hz, 1 H, CHH), 3.40 (s, $w_{1/2}$ = 3 Hz, 4 H), 5.98 (s, 2 H, olefinic H).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.67; H, 7.44.

Hydrogenation of Adduct 21.—A solution of 84 mg of adduct **21** in 5 ml of methanol containing 7 mg of 5% palladium on carbon was reduced with hydrogen at 1 atm. After removal of catalyst and solvent, the residue was treated with pentane and kept at −20° for several hours to give colorless crystals. Recrystallization from pentane gave an analytical sample of **22**: mp 60–61.5°; ir 1765 (m), 1720 (s) cm^{-1}; nmr (220 MHz) δ 0.99–1.23 (s, s, m, 8 H, CH_3, CH_3, bridge CH_2), 1.41–1.73 (m, 4 H, CH_2CH_2), 2.74 (broad, 2 H, bridgehead CH), 3.21 (s, $w_{1/2}$ = 7 Hz, 2 H, COCH).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.37.

Reaction of Anthracene with Enedione 1.—A solution of 140 mg of enedione 1 in 5 ml of dichloromethane containing 200 mg of anthracene and 140 mg of aluminum chloride was heated at reflux for 2 hr. The mixture was poured into 20 ml of water and the layers separated. The organic layer, plus two washings of the aqueous layer with dichloromethane, was washed with water and dried. Removal of solvent left a foam which crystallized from petroleum ether to yield 282 mg (82%) of adduct **23**. This was recrystallized from cyclohexane–benzene (3:1) to furnish an analytical sample: mp 176–177°; ir (Nujol) 1765 (m), 1715 (s), 755 (s), 740 (m) cm^{-1}; nmr (ppm downfield from external tetramethylsilane) 0.10 (s, 3 H), 0.97 (s, 3 H), 3.32 (m, 2 H), 4.83 (m, 2 H), 7.0–7.7 (m, 8 H).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.52; H, 5.91.

Reaction of 2,6-Dimethylanthracene with Enedione 1.—This reaction was carried out just as the preparation of **23** and gave an 82% yield. The product was best purified by elution from grade I neutral alumina with ethyl acetate. Two subsequent recrystallizations from ethanol gave an analytical sample of the desired adduct: mp 149.5–151.5°; ir (KBr disk) 1770 (w), 1730 (s), 1460 (m), 1120 (w), 1070 (m), 805 (w) cm^{-1}; nmr ($CDCl_3$, ppm downfield from external tetramethylsilane) 0.092 (s, CH_3), 0.95 (s, CH_3), 2.25 (s, $ArCH_3$), 2.35 (s, $ArCH_3$), 3.39 (m, COCH), 4.80 (m, ArCH), 6.85–7.50 (m, ArH).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.86; H, 6.70.

A bishydrazone was prepared using hydrazine and hydrazine hydrochloride in diethylene glycol at 130° (95%), mp 116–121° and 207–208° from ether.

Anal. Calcd for $C_{28}H_{26}N_4$: C, 77.06; H, 7.31; N, 15.63. Found: C, 77.14; H, 7.38; N, 15.75.

2,6-Dichloroanthracene.—A mixture of 2.74 g of 2,6-dichloro-9,10-anthraquinone,[23] 19.2 ml of concentrated aqueous ammonia, and 35.6 ml of water was heated on the steam bath for 7 hr and treated with 13.7 g of zinc dust in portions. The mixture was then filtered, and the product was extracted from the filter cake with several portions of hot acetone. This solvent was removed, and the crude product was dissolved in boiling 1-propanol, treated with a few drops of concentrated hydrochloric acid (to dehydrate any anthrol present), and allowed to cool. This gave 1.61 g of yellow plates. Several recrystallizations from benzene gave an analytical sample: mp 271–272°; ir (KBr disk) 1612 (m), 1440 (m), 1070 (m), 1055 (m), 920 (m), 895 (s), 790 (m) cm^{-1}.

Anal. Calcd for $C_{14}H_8Cl_2$: C, 68.05; H, 3.26. Found: C, 68.00; H, 3.41.

Reaction of 2,6-Dichloroanthracene with Enedione 1.—This reaction was carried out just as the preparation of **23** and gave an 83% yield. The adduct was purified by several recrystallizations from ethanol: mp 168–169.5°; nmr ($CDCl_3$, ppm downfield from external tetramethylsilane) 0.28 (s, CH_3), 1.07 (s, CH_3), 3.46 (m, COCH), 4.88 (m, ArCH), 7.08–7.51 (m, ArH).

Anal. Calcd for $C_{21}H_{16}O_2Cl_2$: C, 67.93; H, 4.35. Found: C, 68.04; H, 4.37.

Reaction of 1,2,3-Triphenylaziridine (24) with Enedione 1.—A solution of 124 mg of enedione 1 in 10 ml of toluene containing 271 mg of **24** was heated at reflux for 10 hr. Filtration of the cooled and somewhat concentrated solution gave 355 mg (90%) of solid product. One recrystallization from toluene gave 261 mg (66%) of adduct **26**. Two more recrystallizations furnished an analytical sample: mp 269–271°; ir (KBr disk) 1765 (w), 1725 (s), 1600 (m), 1500 (s), 1340 (s), 1330 (s), 735 (s), 680 (s) cm^{-1}; nmr ($CDCl_3$, 220 MHz) δ 0.080 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3), 3.46 (dd, J_{AB} = 10 Hz, J_{AC} = 1 Hz, 1 H, $COCH_A$), 4.16 (app t, J_{BA} = 10 Hz, J_{BD} = 10 Hz, 1 H, $COCH_B$), 5.66 (d, J_{DB} = 10 Hz, 1 H, $ArCH_D$), 5.84 (d, J_{CA} = 1 Hz, 1 H, $ArCH_C$), 6.34 (d, J = 8 Hz, 2 H, ArH), 6.52 (app t, J = 7 Hz, 1 H, ArH), 6.9–7.4 (m, 12 H, ArH).

Anal. Calcd for $C_{27}H_{25}O_2N$: C, 82.00; H, 6.37; N, 3.55. Found: C, 82.01; H, 6.46; N, 3.39.

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Reaction of *trans*-1-Cyclohexyl-2,3-dibenzoylaziridine (25) with Enedione 1.—A solution of 62 mg of enedione 1 in 5 ml of toluene containing 165 mg of aziridine **25** was heated at reflux for 2.75 hr. Concentration and filtration gave 181 mg (80%) of crude solid product. This was recrystallized several times from benzene to yield an analytical sample of adduct **27**: mp 175.5–177°; ir (KBr disk) 1765 (m), 1720 (s), 1675 (s), 1660 (s), 1230 (s) cm^{-1}; nmr ($CDCl_3$) δ 0.5–2.0 (m, 10 H, CH_2), 1.12 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 2.28–2.80 [broad, 1 H, C(1)H of cyclohexyl], 3.55 (dd, J_{BA} = 10.5 Hz, J_{BC} = 3 Hz, 1 H, $COCH_B$), 3.92 (dd, J_{AB} = 10.5 Hz, J_{AD} = 8 Hz, 1 H, $COCH_A$), 5.52 (d, J_{CB} = 3 Hz, 1 H, $ArCOCH_C$), 5.78 (d, J_{DA} = 8 Hz, 1 H, $ArCOCH_D$), 7.2–8.6 (m, 10 H, ArH).

Anal. Calcd for $C_{29}H_{31}O_4N$: C, 76.13; H, 6.84; N, 3.07. Found: C, 76.14; H, 6.91; N, 2.96.

Reaction of Diazomethane with Enedione 1.—A solution of 500 mg of enedione 1 in 20 ml of ether was treated with 30 ml of 0.14 *M* ethereal diazomethane. After 3 hr at room temperature excess diazomethane was distilled out on the steam bath and the solvent removed. The resulting crystals were washed with cyclohexane and filtered to give 514 mg (77%) of pyrazoline **28**. This was recrystallized by dissolution in benzene at room temperature, addition of cyclohexane, and subsequent cooling. Four such operations gave an analytical sample: mp 86–88°; ir 1770 (w), 1730 (s), 1545 (w) cm^{-1}; nmr ($CDCl_3$) δ 0.97 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 3.40 (six lines, 1 H, CH_2CH_BCO), 4.9–5.2 (m, 2 H, CH_XH_Y), 5.80 (broad dt, J_{AB} = 9 Hz, J_{AX} = 2.5 Hz, $J_{AY} \sim 0.5$ Hz, 1 H, NCH_ACO). This compound is light sensitive.

Anal. Calcd for $C_8H_{10}O_2N_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.91; H, 5.87; N, 16.76.

Pyrolysis of Pyrazoline 28.—A solution of 200 mg of adduct **28** in 10 ml of toluene was heated at reflux for 1.5 hr. The solvent was evaporated to leave 135 mg (81%) of crude product which was purified by preparative vpc to give an analytical sample of ketone **29**: ir 1750 (m), 1710 (s), 1620 (m), 1280 (m), 1120 (m) cm^{-1}; nmr δ 1.10 (s, 6 H), 2.10 (d, J = 1 Hz, 3 H), 6.84 (broad, 1 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.25; H, 7.25.

Photolysis of Pyrazoline 28.—A solution of 200 mg of adduct **28** in 400 ml of ether was photolyzed for 1 hr. Most of the solvent was removed and the product was purified by preparative vpc to give a small amount of **29** plus analytically pure cyclopropane **30**; ir 1763 (m), 1727 (s), 1265 (m), 1130 (m), 990 (m), 875 (m), 850 (m) cm^{-1}; nmr δ 1.03 (s, 3 H), 1.07 (s, 3 H), 1.17–1.92 (m, 2 H), 2.3–2.7 (m, 2 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.14; H, 7.22.

Registry No.—**1**, 26154-22-3; **3**, 3883-58-7; **4**, 25112-87-2; **6**, 26154-25-6; **9**, 26154-26-7; **10**, 26154-27-8; **11**, 26154-28-9; **12**, 26157-42-6; **14**, 26154-29-0; **21**, 26157-43-7; **22**, 26157-44-8; **23**, 26154-30-3; **26**, 26145-73-3; **27**, 26145-74-4; **28**, 26145-75-5; **29**, 15972-27-7; **30**, 15973-50-9; reaction product of 2,6-dimethylanthracene with **1**, 26154-33-6; reaction product of 2,6-dimethylanthracene with bishydrazone, 26154-34-7; 2,6-dichloroanthracene, 26154-35-8; reaction product of 2,6-dichloroanthracene with **1**, 26154-36-9.

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The Preparation and Properties of Cage Polycyclic Systems. I. Pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane and Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane Derivatives

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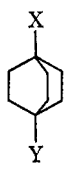
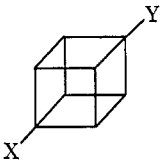
Reliable syntheses of some pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane (**22**) and pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (**23**) derivatives are described. The nmr spectra of several of them and the nmr spectra of the *endo*-dicyclopentadiene precursors are discussed; magnetic shielding of some of the cage methine protons is observed for certain ketones and ethylene ketals, a dimethyl ketal, and a hydrate, and even 5,9-dibromopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane has a two-proton absorption at higher field than that of the main group of protons. The cleavage of a nonenolizable α-bromo ketone, 5,9-dibromopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]deca-6,10-dione 6-ethylene ketal (**5**) to give a lactone (**17**), and several attempted Favorskii rearrangements on 5,9-dibromopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-deca-6,10-dione (**6**) and 1-bromopentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonan-9-one-4-carboxylic acid (**10**) are described.

Recently[1] we have prepared some 1,4-disubstituted bicyclo[2.2.2]octanes in order to study the polar effects of substituents X in a system such that they have no influence on the steric effect experienced by the reaction site Y. In these compounds the substituent is hidden from the reaction site by the bulk of the cyclic system and changing the substituent does not alter the steric effect at the reaction site. 1,4-Disubstituted cubanes[2] offer the same possibilities for studying polar effects without the intervention of steric effects,[3] and, after the preparation of 1,4-dimethoxy-





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