and 0.88 (t, 3, J = 7 Hz, CH_3CH_2). Irradiation of the methylene region, in a double resonance experiment, collapsed the two terminal methyl triplets (δ 0.92 and 0.88) into two singlets. The ratio of the two singlets was 70:30 as observed previously for the two triplets.

The structure of 1-methano-2-methyl-3-acetoxy-3-butene (4.3 min) was tentatively assigned to product E on the following data: ir (CCl_4) 1780 (C=O), 1670 (C=C), 1220, 1150, 1020, 965, 955, and 900 cm^{-1}. In the mass spectrum, peaks were observed at m/e of 140, 125, 112, 98 (B), and 83. Injection of the enol acetate on the Carbowax–KOH column (hydrolysis) gave a peak which corresponded to the retention time of the starting cyclopropyl ketone **3**.

Registry No.—**4**, 24471-77-0; **5**, 24471-78-1; **6**, 24471-79-2; **7**, 24471-80-5; **8**, 24471-81-6; **10**, 24471-82-7; **11**, 24471-83-8; **13**, 24471-84-9; **14**, 10499-83-9; **15**, 1541-05-5; **16**, 15984-03-9; **17**, 10500-08-0; **18**, 15984-02-8.

Cyclopentadienones from 1,2,4-Cyclopentanetriones, 2-Cyclopentene-1,4-diones, and 3-Cyclopentene-1,2-diones

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Received September 11, 1969

Cyclopentadienones may be prepared by enolization of 1,2,4-cyclopentanetriones, 2-cyclopentane-1,4-diones, and 3-cyclopentene-1,2-diones. 2,5-Diphenyl-1,2,4-cyclopentanetrione (**1b**) reacts with 1 and with 2 equiv of sodium hydride to give the corresponding mono- (**5b**) and dianions (**4b**). Dienolate **4b** is converted by benzoyl chloride into 3-benzoyloxy-2,5-diphenyl-2-cyclopentene-1,4-dione (**6**). 3,4-Dibenzoyloxy-2,5-diphenylcyclopentadienone (**10a**), 3,4-di-*p*-anisoyloxy-2,5-diphenylcyclopentadienone (**10b**), and 3,4-diacetoxy-2,5-diphenylcyclopentadienone (**10c**) result from reactions of **1b** with the appropriate acid chlorides in triethylamine. The structures of **10a–c** are established by reaction with N-phenylmaleimide and from the nmr of the resulting 2-norbornen-7-ones (**12a, d, e**). Cyclopentadienone **10b** and benzyne yield 2,3-di-*p*-anisoyloxy-1,4-diphenyl-naphthalene (**18**). 3-Methoxy-2,5-diphenyl-2-cyclopentene-1,4-dione (**19**), prepared from **1b** and diazomethane, reacts with sodium hydride to give monoanion **20**, which with *p*-anisoyl chloride results in 4-*p*-anisoyloxy-3-methoxy-2,5-diphenylcyclopentadienone (**10d**). 3-Phenyl-1,2,4-cyclopentanetrione (**1c**), 3-methyl-1,2,4-cyclopentanetrione (**1d**), and 1,2,4-cyclopentanetrione (**1a**) are converted by diazomethane into their corresponding 3-methoxy-2-cyclopentene-1,4-diones (**21, 24,** and **25**). Acid- and base-catalyzed deuterium exchange into **19, 21, 24,** and **25** reveal that the 2-cyclopentene-1,4-diones are converted into hydroxycyclopentadienones and their conjugate bases. Enolization of 3-cyclopentene-1,2-diones has been investigated. Deuterium incorporation into 4-phenyl-3-cyclopentene-1,2-dione (**29a**), 3,4-diphenyl-3-cyclopentene-1,2-dione (**29b**), and 4-methyl-3-cyclopentene-1,2-dione (**29c**) in acid solution and into **29a** and **20b** in basic environments indicate that these systems are converted into their 2-hydroxycyclopentadienones (**31a–c**) and their cyclopentadienone enolates (**30a,b**). Dione **29b** has been prepared by nitrosation of 3,4-diphenyl-2-cyclopentene-1-one (**32**) to 1-oximino-4,5-diphenyl-3-cyclopentene-1,2-dione (**33**), conversion of **33** by formaldehyde in acid solution into 4,5-diphenyl-3-cyclopentene-1,2-dione (**34**), and isomerization of **34** by hot hydrochloric acid to **29b**. The previous structural assignment to 2-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione is incorrect and **34** is a new cyclopentene-1,2-dione.

Cyclopentadienone is a highly reactive monomer whose isolation is yet to be accomplished.[2] Many tetraaryl- and tetraalkylcyclopentadienones[2c,d] and certain tri- and disubstituted cyclopentadienones such as 2,3,5-triphenylcyclopentadienone, 2,3,5-tri-*t*-butyl-cyclopentadienone,[3a] cyclooctatetraeno-4-methylcyclo-pentadienone,[3b] 2,5-diphenylcyclopentadienone,[3c] and 2,4-di-*t*-butylcyclopentadienone,[3d] cyclopentadienones containing delocalizing or bulky groups in 2 and/or 5 positions, are stable at 20–30° or may be generated at moderately elevated temperatures. 3-*t*-Butylcyclopentadienone has been prepared; it dimerizes rapidly, however, at −20°.[3d]

A variety of approaches have been used for synthesis or generation of cyclopentadienones.[2d] Of present interest is that cyclopentenediones and cyclopentanetri-ones are potentially capable of enolizing to substituted cyclopentadienones.[4,5] DePuy, *et al.*, reported on the synthesis and reactions of 2-cyclopentene-1,4-dione[5] and presented evidence for its enolization to 3-hydroxy-cyclopentadienone and its enolate.[5] Such enolizations to give cyclopentadienone derivatives have had little other study and, as a consequence, serve as the basis for the present investigation.

1,2,4-Cyclopentanetrione (**1a**)[6] exists as its monoenol (**2a**) and as such is a moderately strong acid (pK_a = 3.0), undergoing conversion into its monoenolate (**5a**). A second enolization would give 3,4-dihydroxycyclo-pentadienone (**3a**) and in a sufficiently basic environment its cyclopentadienone dianion **4a**. Strong electron-donating groups are expected to stabilize cyclo-pentadienones. Present attempts to demonstrate the existence of **3a** spectroscopically and of **4a** by reaction of **2a** with strong bases have been ambiguous (see Experimental Section). Additional experiments with this system have been deferred, and work with 3,4-diphenyl-

(1) (a) Abstracted in part from the Ph.D. dissertation of C. F. S., The Ohio State University, Columbus, Ohio, 1966. (b) This research was supported by grants from the Union Carbide Chemical Corp., the American Oil Co., the National Science Foundation, and The Ohio State University.

(2) (a) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964). (b) For reviews of cyclopentadienones, see (c) C. F. H. Allen and S. A. VanAllan, *J. Amer. Chem. Soc.*, **72**, 5165 (1950); (d) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

(3) (a) C. Hoogzand and W. Hübel, *Tetrahedron Lett.*, 639 (1961); (b) R. Breslow, W. Vitals, and K. Wandell, *ibid.*, 365 (1965); (c) V. Kruerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961); (d) E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433 (1966).

(4) (a) F. Kögl, H. Becker, G. deVoss, and E. Wirth, *Justus Liebigs Ann. Chem.*, **465**, 243 (1928); (b) C. F. Koelsch and T. A. Geissman, *J. Org. Chem.*, **3**, 480 (1938).

(5) C. H. DePuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **79**, 3923 (1957); C. H. DePuy and E. F. Zaweski, *ibid.*, **81**, 4920 (1959); C. H. DePuy and P. R. Wells, *ibid.*, **82**, 2909 (1960).

(6) J. H. Boothe, R. G. Wilkinson, S. Kushner, and J. H. Wilkinson, *ibid.*, **75**, 1732 (1953).

1,2,4-cyclopentanetrione (**1b**)[7] was initiated on the assumption that its phenyl substituents would confer

a, $R_1 = R_2 = H$
b, $R_1 = R_2 = C_6H_5$
c, $R_1 = C_6H_5$; $R_2 = H$
d, $R_1 = CH_3$; $R_2 = H$
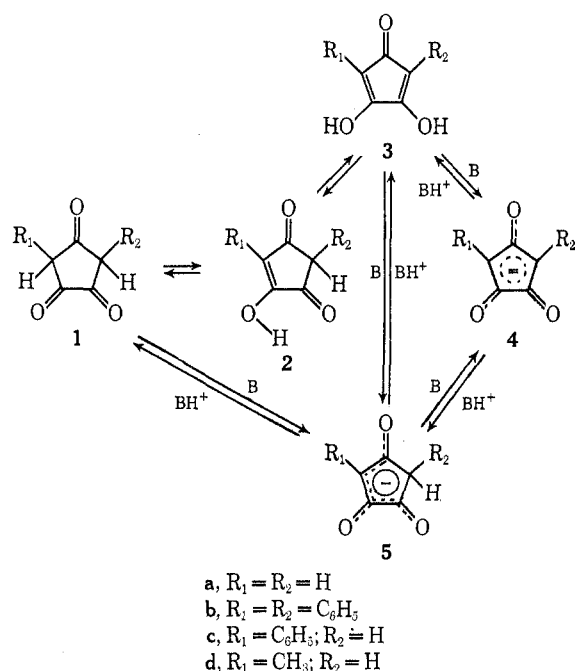
stability to dianion **4b**. It has been reported[7] that **1b** dissolves in aqueous sodium carbonate and in strong alkali to give yellow and deep blue solutions, respectively. It has now been established that these reactions correspond to removal of one and two active hydrogens from **1b–2b** to give **5b** and **4b**. The deep blue dianion **4b** is produced along with 1.96 equiv of hydrogen upon reaction of **1b–2b** with excess sodium hydride in anhydrous tetrahydrofuran. Acidification of **4b** results in generation of **1b–2b**.

The chemistry of dianion **4b** has been studied. Reaction of **4b** with benzoyl chloride yields, after work-up, 3-benzoyloxy-2,5-diphenyl-2-cyclopentene-1,4-dione (**6**) rather than the desired 3,4-dibenzoyloxy-2,5-diphenylcyclopentadienone (**10a**). Monoester **6** is distinguished from its C-benzoyl isomeric possibilities, **7** and **8**, by its ester carbonyl absorption at 1750 cm^{-1},
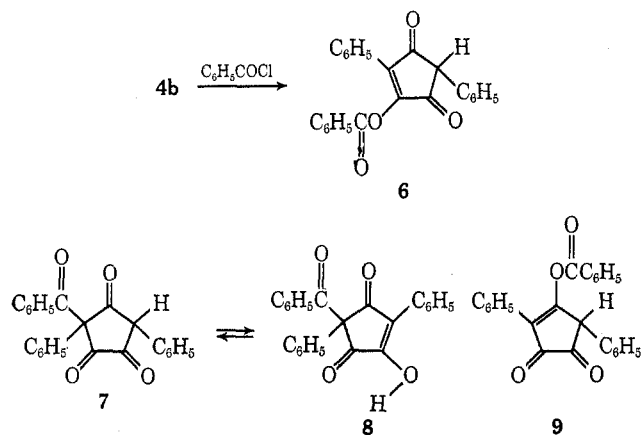
the product isolated shows no enolic properties either by ferric chloride or by its infrared absorption (tetraketone **7** is expected to enolize strongly), and its pmr spectrum shows a sharp singlet of relative area 1 at τ 5.8 for a

benzylic proton. The possibility that the product is **9** is excluded by experiments to be described.

Triketone **1b** undergoes reaction with excess benzoyl chloride and triethylamine in benzene. Immediately after the reactants are mixed at *ca.* 20°, the solution becomes deep purple, precipitation of triethylamine hydrochloride is rapid, and a material was isolated which crystallizes from ethyl acetate in deep purple needles. The product of dibenzoylation of **1b** is **10a** and not 2,4-dibenzoyloxy-3,5-diphenylcyclopentadienone (**11**) as subsequently proven. Reaction of **6** with
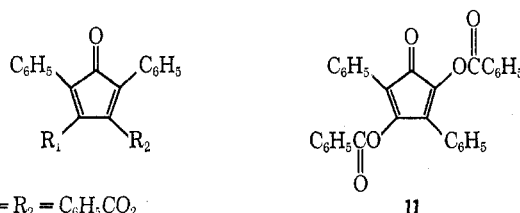
10a, $R_1 = R_2 = C_6H_5CO_2$
b, $R_1 = R_2 = p\text{-}CH_3OC_6H_4CO_2$
c, $R_1 = R_2 = CH_3CO_2$
d, $R_1 = CH_3O$; $R_2 = p\text{-}CH_3OC_6H_4CO_2$

benzoyl chloride and triethylamine also give **10a** and thus is consistent with its assigned structure. The infrared spectrum of **10a** shows a broad carbonyl band centered at 1740 cm^{-1} which is probably a composite of aromatic ester and substituted cyclopentadienone frequencies and conjugated carbonyl at 1705 cm^{-1}. The ultraviolet spectrum of **10a** in tetrahydrofuran exhibits maxima at 245 (ϵ 60,000) and 485 mμ (ϵ 7000). For comparison, 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) absorbs at 262 (ϵ 27,800), 342 (ϵ 6780), and 512 mμ (ϵ 1320).[8]

The pmr spectrum of **10a** shows only aromatic multiplets centered at τ 2.65, 2.35, and 2.0. In contrast, the pmr spectra of many other tetraarylcyclopentadienones exhibit a characteristic sharp singlet at *ca.* τ 2.76 which is attributed to the protons of the unsubstituted 2- and 5-phenyl groups.[9] The nature of the substituents on the phenyl groups at the 3 and 4 positions of a cyclopentadienone has little effect on this signal, even though the substituents may be varied from *p*-N,N-diethylamino to *p*-nitro and *p*-cyano. The hypothesis has been advanced that electron depletion of the 2- and 5-phenyl groups is responsible for this singlet characteristic.[9] If this is correct, the inductive and/or resonance effects responsible for this electron depletion are radically altered by substitution of benzoyloxy for phenyl as in **10a**.

Substituted cyclopentadienones undergo Diels–Alder reactions as dienes to give norbornene derivatives.[10] Structural proof of **10a** was attempted *via* its addition to dienophiles. Attempts to condense excess tetracyanoethylene with **10a** or with tetracyclone for 4 days at 80° resulted in complete recovery of initial reactants. A possible explanation for the lack of reactivity of the cyclopentadienones is that the adducts suffer severe intramolecular strain. In contrast, both **10a** and tetracyclone react in refluxing benzene with N-phenyl-

(7) L. Claisen and T. Ewan, *Justus Liebigs Ann. Chem.*, **284**, 245 (1885).

(8) S. B. Coan, D. E. Trucker, and E. I. Becker, *J. Amer. Chem. Soc.*, **75**, 900 (1953).

(9) Unpublished results as summarized in ref 2d.

(10) (a) C. F. H. Allen, R. W. Ryan, and J. A. VanAllan, *J. Org. Chem.*, **27**, 778 (1962); R. F. Doering, R. S. Miner, L. Rothman, and E. I. Becker, *ibid.*, **23**, 520 (1958).

maleimide, a good dienophile but usually less reactive than tetracyanoethylene, to give **12a** and **12b**. These reactions are easy to follow because of the gradual discharge of the intense purple color of the initial cyclopentadienones.
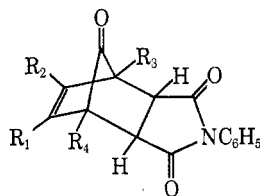

12a, $R_1 = R_2 = C_6H_5CO_2$; $R_3 = R_4 = C_6H_5$
  b, $R_1 = R_2 = R_3 = R_4 = C_6H_5$
  c, $R_1 = R_3 = C_6H_5CO_2$; $R_2 = R_4 = C_6H_5$
  d, $R_1 = R_2 = p\text{-}CH_3OC_6H_4CO_2$; $R_3 = R_4 = C_6H_5$
  e, $R_1 = R_2 = CH_3CO_2$; $R_3 = R_4 = C_6H_5$

The pmr spectrum of **12a** shows a sharp singlet of relative area 2 at τ 5.4 (2,3 protons) and multiplets at τ 2.9–2.2 (aromatic protons). The singlet character of the 2,3 protons of **12a** supports the symmetrical structure assigned. If the initial dibenzoyloxydiphenyl-cyclopentadienone possessed the unsymmetrical structure **11** and consequently gave the Diels–Alder adduct **12c**, the 2,3 protons would likely exhibit different chemical shifts and appear as a doublet.

Present data permit no definite assignment of the stereochemistry of **12a** or **12b**. The Alder rule[11] predicts the product to be *endo* (the 2,3 protons of **12a** and **12b** are thus *exo,exo*). However, *exo* additions of maleic anhydride to 6,6-dimethylfulvene and 6,6-di-phenylfulvene have been observed.[12] The stereochemistry of these latter systems presumably results from isomerization of the initial labile *endo* adducts to the more stable *exo* products. A thermodynamic factor in the isomerization apparently involves overlap of the apical double bond with the succinic anhydride moiety in the adducts.

The model compounds possessing some of the steric aspects of **12a** and **12b** were prepared. 1,4-Diphenyl-cyclopentadiene reacts readily with N-phenylmaleimide and with tetracyanoethylene to form stable adducts (**13** and **14**). The stereochemistry of **13** is assigned as *endo* on the basis of the pmr spectrum shift of the 2,3

13   **14**
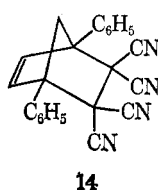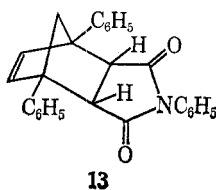
protons of the succinimide moiety from τ 6.2 to 6.65 following hydrogenation of the norbornene double bond, whereas 2,3 *endo*-proton signals shift downfield.[13] These results thus indicate that in this system the 1,6-bridgehead phenyls do not lead to reaction in which the Alder rule of addition is flouted.

Adduct **14** exhibits the interesting property of reversible color change from colorless to intense blue[14]

during recrystallization from ethyl acetate. In this system the phenyl groups at the 1,6-bridgehead positions do not impose sufficient steric strain on the 2,3-*endo,cis* cyano groups to prevent formation of the adduct.

Triketone **1b** reacts with excess *p*-anisoyl chloride and with acetyl chloride in triethylamine to give the substituted cyclopentadienones **10b** and **10c**. The pmr spectrum of **10b** exhibits a sharp singlet at τ 6.17 of relative area 6 (methoxy protons). Hydrogens *ortho* to the methoxy group appear as a doublet at τ 3.07 ($J = 8.0$ cps) and those *ortho* to the carboxyl group appear as a doublet at τ 1.92. Protons of the 2- and 5-phenyl groups occur as two sets of doublets at τ 2.63 and 2.25. The narrow singlet for the methoxy protons and the simple doublet character of the anisoxy ring protons support the symmetrical structure assigned as **10b**.
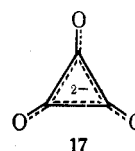
The pmr spectrum of **10c** shows a sharp singlet at τ 7.70 of relative area 6 (acetate methyls) and aromatic multiplets centered at τ 2.5. The singlet properties of the methyl protons are in agreement with the symmetrical structure of **10c** rather than the unsymmetrical possibility (the acetoxy analog of **11**).

Cyclopentadienones **10b** and **10c** react with N-phenylmaleimide to give adducts **12d** and **12e**. The pmr spectrum of **12e** shows acetate methyls as a sharp singlet at τ 8.0 of relative area 6 and the 2,3-succinimide protons as a singlet at τ 5.4 of relative area 2. The magnetic resonance of **12e** thus confirms the symmetrical diacetoxy structure assigned as **10c**. No definite stereochemistry is assignable as yet to **12d** and **12e**.

Saponification of adducts **12a**, **10b**, and **10c** is of interest as a possible source of ketol **15** and in particular dianion **16**. Dianion **16** is a homoanalog of deltic acid dianion, $C_3O_3^{2-}$ (**17**), an oxy anion calculated to be of real stability.[15] As yet, however, conversions of **12a**, **10b**, and **10c** into **15** and/or **16** have been unsuccessful.

15

16   **16**
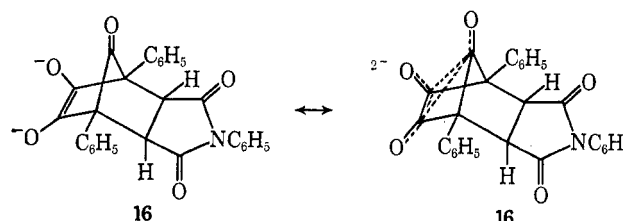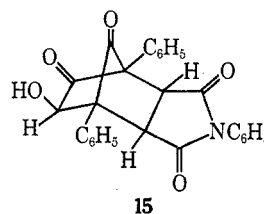
The structure of the blue product arising from saponification of the above Diels–Alder adducts remains to be determined.

17

(11) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(12) J. A. Norton, *Chem. Rev.*, **31**, 319 (1942); (b) R. B. Woodward and H. Baer, *J. Amer. Chem. Soc.*, **66**, 645 (1944).

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

(14) The nature of the chromophoric intermediate, possibly a charge-transfer complex, is unknown.

(15) R. West and D. L. Powell, *J. Amer. Chem. Soc.*, **85**, 2577 (1963).

Substituted cyclopentadienones react with benzyne with loss of carbon monoxide to yield naphthalene derivatives.[16] Cyclopentadienone **10b** behaves analogously to benzyne to give 2,3-di-*p*-anisoxy-1,4-diphenylnaphthalene (**18**, 90%). The structure of **18** is established by its elemental analysis and by its pmr and infrared spectra. The latter shows a very narrow carbonyl band at 1735 cm^{-1} (aromatic ester), substituted naphthalene bands at 770–700 cm^{-1}, and no bridged absorption. Saponification of **18** yields the known 1,4-diphenylnaphthalene-2,3-diol.[17]

18
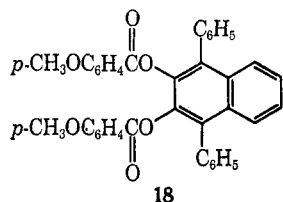
The cyclopentadienone **1b**–enol **2b** system is methylated by diazomethane to 3-methoxy-2,5-diphenyl-2-cyclopentene-1,4-dione[7] (**19**). The pmr spectrum of **19** exhibits a narrow singlet at τ 5.65 of relative area 3 (methoxy protons) and at τ 5.9 of relative area 1


19   **20**
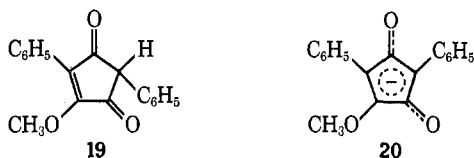
(benzyl proton). The infrared spectrum of **19** exhibits carbonyl absorption at 1750 and 1690 cm^{-1}, double-bond absorption at 1600 cm^{-1}, and vinyl ether absorption at 1200 cm^{-1}. It is of note that monoalkylation and acylation of **1b**–**2b** occur on oxygen at C-3 rather than C-1 of the cyclopentadienone.

Reaction of **19** with excess sodium hydride results in release of 1.09 equiv of hydrogen to form the blue monoanion **20**. Acylation of **20** with *p*-anisoyl chloride yields 4-*p*-anisoxy-3-methoxy-2,5-diphenylcyclopentadienone (**10d**) as scarlet needles. The pmr spectrum of **10d** shows a pair of narrow singlets of equal intensity, both of relative area 3, at τ 6.38 and 6.17, attributable to methoxy and to anisoxy protons, respectively. Protons of the 2- and 5-phenyl rings occur as a sharp singlet at τ 2.67 and a multiplet at τ 2.3. The ring proton of the *p*-anisoxy substituent gives the same pattern as that for **10b**; the overall pmr properties of **10d** are thus in agreement with the structural assignment.

Reactions of diazomethane with 1,2,4-cyclopentanetriones which are less substituted than **1b** have been investigated. The orientation in methylation of these systems and deuterium exchange of the products thereof are of present interest. 3-Phenyl-1,2,4-cyclopentanetrione (**1c**)[18] exists extensively as a yellow enol whose infrared absorption indicates that its hydroxyl group is highly intramolecularly hydrogen bonded. The principal enol of **1c** is apparently **2c** and it reacts

with diazomethane to yield a yellow solid assigned as 3-methoxy-2-phenyl-2-cyclopentene-1,4-dione (**21**). The pmr spectrum of the product exhibits a narrow

21, R = C$_6$H$_5$
24, R = CH$_3$
**25**, R = H

22   **23**
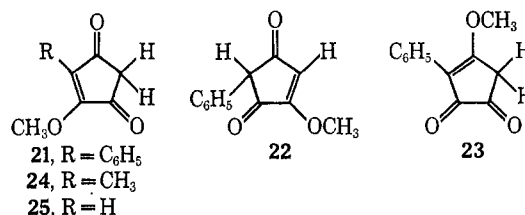
singlet at τ 7.05 of relative area 2 (methylene protons) and at τ 5.70 (methoxy protons), and two sets of multiplets centered at τ 2.6 and 2.1 (phenyl protons). The pmr results (vinyl protons are absent) discount **22** as the structure of the product. There is no direct evidence which eliminates **23** as the methylation product; however, on the basis of the structure of the parent enol (**2c**), possible minimum change during reaction of **2c**, and previous experience in methylation and acylation of **1b**–**2b**, it is very likely that the methyl ether is **22**.

3-Methyl-1,2,4-cyclopentanetrione (**1d**)[19] is also highly enolic and intramolecularly hydrogen bonded. Its enol is apparently principally **2d**. Diazomethane rapidly methylates the **1d**–**2d** system, yielding a white solid assigned as 3-methoxy-2-methyl-2-cyclopentene-1,4-dione (**24**). The pmr spectrum of **24** reveals methylene protons at τ 7.05 and methoxy protons at τ 5.65; there is no absorption for vinyl hydrogen. The structure is indicated as **24** rather than as 4-methoxy-3-methyl-3-cyclopentene-1,2-dione because of precedent with **19** (and **21**) and because of mechanistic considerations.

Methylation of the parent 1,2,4-cyclopentanetrione system, **1a**–**2a**, also occurs efficiently to give the white solid, presumably 3-methoxy-2-cyclopentene-1,4-dione (**25**). The infrared spectrum of the ether indicates carbonyl absorption at 1760 and 1695 cm^{-1}; olefinic absorption occurs at 1600 cm^{-1} and vinyl ether absorption occurs at 1220 cm^{-1}. The pmr spectrum of the product shows methylene protons at τ 7.05, methoxy protons at τ 6.0, and a vinyl proton at τ 3.6, all as sharp singlets. The possible structure, 4-methoxy-3-cyclopentene-1,2-dione, is eliminated for reasons cited previously for **23**.

Introduction of deuterium into the methoxy ethers **19**, **21**, **24**, and **25** from deuterium oxide has been examined in basic and in acidic environments. Rapid exchange of benzyl hydrogen occurs in **19** in mixtures of deuterium oxide, triethylamine, and tetrahydrofuran. The deuterium content in recovered **26a** is determined

26   **27**   **28**
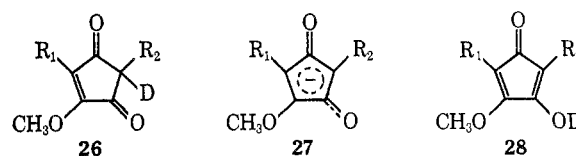
a, R$_1$ = R$_2$ = C$_6$H$_5$
b, R$_1$ = C$_6$H$_5$; R$_2$ = H
c, R$_1$ = CH$_3$; R$_2$ = H
d, R$_1$ = R$_2$ = H

(16) F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).

(17) M. S. Newman, personal communication of unpublished results and gift of comparison sample.

(18) W. Wislicenus and F. Melms, *Justus Liebigs Ann. Chem.*, **436**, 101 (1924).

(19) M. Orchin and L. W. Butz, *J. Amer. Chem. Soc.*, **65**, 2296 (1943).

from the residual benzyl pmr signal at τ 5.9. During the exchange experiment the tetrahydrofuran solution is dark violet. The color may be due to perceptible concentrations of its enolate **27a**. The ethers **21** and **24** exchange their methylene protons completely in deuterium oxide–triethylamine; pmr signals for methylene protons in recovered **26b** and **26c** are absent. It is thus clear that **19**, **21**, and **24** are converted into their cyclopentadienone-3-oxide anions **27a–c** and that the enolization behavior of these 2-cyclopentene-1,4-dione derivatives parallels that of the parent diketone.[5] Study of base-catalyzed deuterium incorporation in **26** is inconclusive as yet, because the diketone is rapidly destroyed in the alkaline environment.

Deuterium exchange into benzyl or methylene positions in **19**, **21**, **24**, aud **25** occurs extensively (>85%) in deuterium oxide containing catalytic quantities of hydrochloric acid. The deuterium content of the recovered diketones was determined by pmr methods. It is reasonable to infer that 3-deuterioxy-4-methoxy-cyclopentadienones (**28a–d**) are generated as intermediates in these experiments.

A study has been initiated of enolization of 3-cyclopentene-1,2-diones (**29a–c**) in the presence of bases and of acids. Such diones might be expected to undergo facile conversion into their cyclopentadienone monoanions (**30a–c**), because these enolates contain a powerful electron-donating group (0) in the 2 position and allow extended delocalization effects.[20] Enols (**31a–c**) derived from these diones also have the possible advantages of strong electron release at C-2 and of extended conjugation[21] along with contributions involving intramolecular hydrogen bonding.

a, $R_1 = R_3 = H; R_2 = C_6H_5$
b, $R_1 = R_2 = C_6H_5; R_3 = H$
c, $R_1 = R_2 = H; R_3 = CH_3$
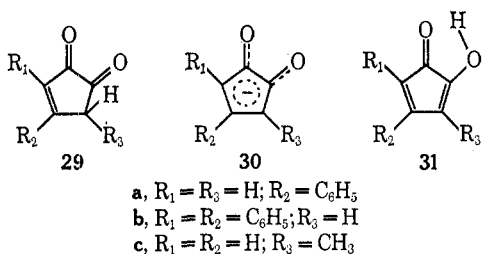
4-Phenyl-3-cyclopentene-1,2-dione (**29a**)[21] undergoes deuterium exchange for its methylene hydrogens when suspended in deuterium oxide containing sodium acetate, and thus appears to involve enolate **30a** as an intermediate.[22] Deuterium is also exchanged for methylene hydrogens in **29a** in hot solutions of deuterium oxide and deuterioacetic acid containing traces of hydrochloric acid. The slow exchange of deuterium into **29a** presumably occurs *via* enol **31a** or its tautomer.

Study of enolization of 3,4-diphenyl-3-cyclopentene-1,2-dione (**29b**) then became of interest. This diketone has been previously reported[23] as the product of hydrolysis of 2-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione as obtained from 3,4-diphenyl-3-cyclopentene-1-one,[24a] butyl nitrite, and hydrochloric acid. It later

became apparent,[24b] on the basis of its ultraviolet absorption, that the initial cyclopentenone is 3,4-diphenyl-2-cyclopenten-1-one (**32**), and thus the structural assignment to **29b** is subject to question.

It has now been found that **32** reacts with butyl nitrite and hydrochloric acid to give 1-oximino-4,5-diphenyl-3-cyclopentene-1,2-dione (**33**). Exchange of **33** with formaldehyde in hydrochloric acid–glacial acetic acid at 30° yields 4,5-diphenyl-3-cyclopentene-1,2-dione (**34**). In refluxing hydrochloric acid–acetic acid **34** is converted into **29b**; similarly, **33** is deoximated and isomerized to **29b** by formaldehyde in hot hydrochloric acid–acetic acid. The previous structural assignment to **29b** is thus correct; however, that to 2-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione is in error and **34** is a new diphenylcyclopentene-1,2-dione.[25]
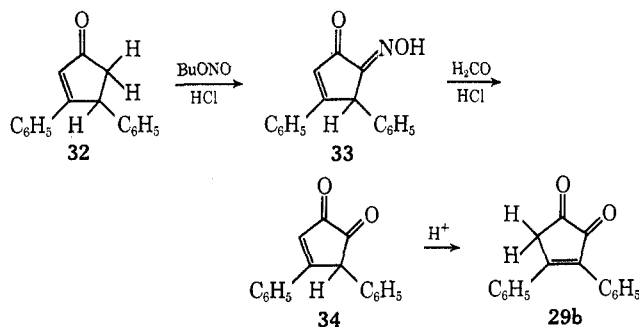
Dione **34** is refluxing deuterium oxide–deuterioacetic acid containing a trace of hydrochloric acid yields the rearranged diketone **29b** completely deuterated in the methylene position. Undeuterated **29b** under the same conditions also shows complete exchange of methylene protium for deuterium. These observations, along with the isomerization of **34** to **29b**, indicate that **34** and **29b** undergo enolization to **31b** and its enol isomer. The results, however, do not indicate whether **34** exchanges deuterium to give deuterated **34** prior to isomerization to deuterated **29b**.

4-Methyl-3-cyclopentene-1,2-dione (**29c**) is important to the development of the present theory of stabilized cyclopentadienones, since it is reported to give a ferric chloride test[26a] and is presumed to have enolic properties.[26b] It has been presently observed that **29c** does indeed give a positive ferric chloride reaction in aqueous solution and loses its protium in deuterium oxide containing traces of hydrochloric acid. The detailed chemistry of **29c** is not yet completely clear, particularly in alkaline solution. Study of **29c**, 3-cyclopentene-1,2-dione, and 1,2,3-cyclopentanetrione is in progress.

Experimental Section

Properties of 1a.—Solutions of **1a**[27] in water or methanol give positive ferric chloride tests and show strong broad enolic absorption (hydrogen bonded) at 3100 cm^{-1} and ultraviolet maxima at 305 and 225 mμ (ϵ 48,500). The triketone survives hot concentrated hydrochloric acid and reacts rapidly with aqueous sodium bicarbonate with evolution of carbon dioxide to give solutions, λ_{max} 308 mμ (ϵ 12,900). In excess 10% aqueous sodium

(20) Enolates and enols of 2-cyclopentene-1,4-diones are cross conjugated.

(21) S. Wawzonek and C. E. Morreal, *J. Amer. Chem. Soc.*, **82**, 439 (1960).

(22) In homogenous solution in deuterium oxide–tetrahydrofuran mixtures containing triethylamine, sodium carbonate, or sodium bicarbonate, **29a** is converted into products other than its simple deuterated analog.

(23) T. A. Geissman and C. F. Koelsch, *J. Org. Chem.*, **3**, 489 (1938).

(24) (a) F. R. Japp and E. Miller, *J. Chem. Soc.*, **47**, 27 (1885); (b) C. F. H. Allen and J. A. VanAllan, *J. Amer. Chem. Soc.*, **77**, 2315 (1955).

(25) For detailed evidence relative to the structures of **29b** and **32–34**, see Experimental Section. Reaction of **29b** with hydroxylamine yields an oxime (see Experimental Section) isomeric with **33**. It is likely that the oxime is 1-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione.

(26) (a) E. Dane, J. Schmitt, and C. Rautenstrauch, *Justus Liebigs Ann. Chem.*, **532**, 29 (1937); (b) G. Singh, *J. Amer. Chem. Soc.*, **78**, 6109 (1956).

(27) Prepared by the method of ref 6.

hydroxide 1a has λ_max 261 mμ (ε 52,500); however, the chemistry of this system has not been elaborated. Solutions of 1a in dimethylformamide react sluggishly with sodium hydride with evolution of 1 equivalent of hydrogen and formation of an insoluble monosodium salt which resists further reaction with sodium hydride. Benzoyl chloride (2 equiv) and 1a in excess triethylamine give intractable products. Excess bromine in dioxane reacts with 1a at 0° to yield, after sublimation at 100° (0.3 mm), 2-bromo-1,3,4-cyclopentanetrione as white crystals: yield 0.40 g (44%); mp 152–153°; ir 3120 (enol), 1760, and 1700 cm⁻¹ (C=O); pmr τ 6.83 (CH₂) and 0.00 (enol H). Efforts to dibrominate 1a with bromine or N-bromosuccinimide were unsuccessful.

Anal. Calcd for C₅H₃BrO₃: C, 31.35; H, 1.67; Br, 41.75. Found: C, 31.19; H, 1.87; Br, 41.62.

Reaction of the Dilithium Salt of 1b with Benzoyl Chloride.—A solution of 1b (1.00 g, 0.0076 mol), enol absorption at 3220 cm⁻¹, in tetrahydrofuran (25 ml) was treated under nitrogen with butyllithium (9 ml, 15% by weight in hexane, 0.015 mol). A solution of benzoyl chloride (2.2 g, 0.0157 mol) in tetrahydrofuran was added rapidly with stirring. The blue color was quickly discharged and a yellow solution resulted. The reaction mixture was refluxed for 4 hr, cooled, and poured over ice. The aqueous mixture was extracted with ether. A crystalline material began separating from the ether and was collected. The solvent was removed and the residue was combined with the precipitate. The product was recrystallized from benzene–hexane to give 6 as yellow needles: yield 1.2 g (43%); mp 161–161.5°; ir 1750, 1690, 1340, 1230, 1080 (split peak), 725, and 705 cm⁻¹; uv max (CHCl₃) 310 (ε 27,000) and 235 mμ (ε 34,5000).

Anal. Calcd for C₂₄H₁₆O₄: C, 78.30; H, 4.35. Found: C, 78.44; H, 4.19.

Reaction of 1b with Benzoyl Chloride.—A stirred suspension of 1b (6.35 g, 0.026 mol) in dry benzene (150 ml) upon addition of triethylamine (15 ml, 0.107 mol) gave a violet solution. Benzoyl chloride (10 g, 0.076 mol) in benzene (30 ml) was added (10 min), and a dark purple solution formed. The solution was stirred at room temperature for 12 hr and filtered free of amine salts. The filter cake was washed with benzene and the filtrates were combined. The solvent was removed to give a pasty red solid which was recrystallized from ethyl acetate–hexane to give 10a as large, purple needles: yield 5.75 g (47%); mp 182–184°; uv max (tetrahydrofuran) 245 (ε 60,000) and 485 mμ (ε 43,000).

Anal. Calcd for C₃₁H₂₀O₅: C, 78.80; H, 4.27. Found: C, 79.14; H, 4.27.

Reaction of 6 with Benzoyl Chloride.—A solution of 6 (0.39 g, 0.00106 mol), benzoyl chloride (0.23 g, 0.00165 mol), and triethylamine (2.5 ml, 0.0175 mol) in tetrahydrofuran (15 ml) was refluxed for 8 hr. The solution was filtered and the solvent was removed to give a dark red residue. Recrystallization from ethyl acetate–hexane resulted in dark needles of 10a, yield 0.25 g (50%), mp 180–182°, identical with that described previously.

Reaction of 10a and N-Phenylmaleimide.—A solution of 10a (2.01 g, 0.0043 mol) and N-phenylmaleimide (1.50 g, 0.0087 mol) in dry benzene (100 ml) was refluxed for 14 hr. At the end of this time, the intense purple color of 10a had disappeared and a clear, yellow solution resulted. Filtration and removal of solvent yielded a fluffy, amorphous product, mp 175–197°. Chromatography on silica gel (120 g, British Drug House) and elution with benzene (120 ml) led to recovery of N-phenylmaleimide (0.638 g). Elution of the column with methylene chloride (150 ml) and removal of solvent gave 12a as white needles: yield 2.19 g (67%); mp 208–208.5° from ethyl acetate–hexane.

Anal. Calcd for C₄₁H₂₇NO₇: C, 76.27; H, 4.20; N, 2.18. Found: C, 76.37; H, 4.28; N, 2.28.

Reaction of Tetracyclone and N-Phenylmaleimide.—Tetracyclone (3.00 g, 0.0072 mol) and N-phenylmaleimide (2.70 g, 0.0157 mol) was refluxed in dry benzene (100 ml) for 10 hr. The yellow solution was filtered and the solvent was removed. Recrystallization of the yellow glass from ethyl acetate–hexane gave 12b as white needles: yield 2.6 g (64%); mp 215–216.5°; ir 1760, 1710, 1480, 1360, 1180, 770, and 690 cm⁻¹; pmr multiplet (aromatic) and τ 5.3 (s, N-phenylsuccinimide moiety protons).

Anal. Calcd for C₃₉H₂₇O₃N: N, 2.51. Found: N, 2.46.

Reaction of 1,4-Diphenylcyclopentadiene and N-Phenylmaleimide.—1,4-Diphenylcyclopentadiene[28] (2.00 g, 0.0092 mol) and

N-phenylmaleimide (1.85 g, 0.011 mol) were refluxed in dry benzene (20 ml) for 14 hr. Removal of the solvent resulted in yellow oil which crystallized. Recrystallization from ethyl acetate–hexane gave 13 as white needles: yield 2.2 g (60%); mp 165.5–166.2°; ir 1712 (C=O) and 1770 cm⁻¹ (imide); pmr τ 7.7 (s, apical CH₂), 6.25 (s, N-phenylsuccinimide protons), and 3.45 (s, vinyl).

Anal. Calcd for C₂₇H₂₁O₂N: C, 82.92; H, 5.38; N, 3.58. Found: C, 83.09; H, 5.49; N, 3.55.

A solution of 13 (0.61 g, 0.00156 mol) in ethyl acetate (25 ml) was shaken with Pd–C catalyst (ca. 10 mg) and hydrogen (40 psi) for 2 hr. Filtration of the hot solution and removal of solvent left off-white crystals. Recrystallization (charcoal) from ethyl acetate–hexane gave the 5,6-dihydro adduct of 13: yield 0.52 g (85%); mp 210.8–212.0°; ir 1735, 1510, 1395, 1200 (split peak), 770 (split peak), 740, and 700 cm⁻¹; pmr τ 7.85 (s, apical CH₂), 7.58 (q, *J* = 10 cps, apparently the 5,6 CH₂), 6.55 (s, succinimide moiety protons), and 2.8 and 2.3 (m, phenyl protons). Comparison with the pmr spectrum of 13 shows a shift of 17 cps (from τ 6.25) of the succinimide moiety protons, indicating their probable *exo* configuration.[13]

Reaction of 1,4-Diphenylcyclopentadiene and Tetracyanoethylene.—Tetracyanoethylene (0.62 g, 0.0004 mol) and 1,4-diphenylcyclopentadiene were refluxed in benzene (25 ml) for 20 min. The precipitate from the cooled reaction mixture was washed with cold 50% benzene in hexane. Recrystallization from ethyl acetate–hexane gave 14 as white needles, yield 0.90 g (59%), mp 164.5–165.4° dec. Adduct 14 gives deep blue solutions in hot ethyl acetate. The color quickly fades as the crystals deposit during cooling. Identical behavior results during recrystallization of 14 from ethanol, with the exception that the supernatant liquid retains its blue color.

Anal. Calcd for C₂₃H₁₄N₄: C, 79.83; H, 3.95; N, 16.20. Found: C, 79.95; H, 4.00; N, 15.96.

Reaction of 1b with *p*-Anisoyl Chloride.—A solution of 1b (4.0 g, 0.0157 mol) and triethylamine (7.15 g, 0.071 mol) in benzene (100 ml) was stirred with *p*-anisoyl chloride (10.0 g 0.059 mol) for 24 hr and filtered, and the solvent was removed. Recrystallizations of the product from ethyl acetate yielded 10b as red needles: yield 5.6 g (65%); mp 169–171°; ir 1715 cm⁻¹ (C=O); uv max (tetrahydrofuran) 482 (ε 4000) and 265 mμ (ε 61,000).

Anal. Calcd for C₃₃H₂₄O₇: C, 74.60; H, 4.45. Found: C, 74.77; H, 4.68.

Reaction of 1b with Acetyl Chloride.—To 1b (2.0 g, 0.079 mol) and triethylamine (4.0 g, 0.028 mol) in dry benzene (100 ml) was added acetyl chloride (2.5 g, 0.032 mol) in benzene (20 ml) during 20 min. The solution was stirred for 2 hr and filtered, and the solvent was evaporated. Recrystallization of the solid from absolute ethanol resulted in 10c as dark red needles: yield 0.79 g (30%); mp 165–168° dec; ir 1770 (acetate C=O) and 1712 cm⁻¹ (cyclopentadienone C=O); uv max 485 (ε 1570) and 254 mμ (ε 40,000).

Anal. Calcd for C₂₁H₁₆O₅: C, 70.52; H, 4.47. Found: C, 70.65; H, 4.70.

Reaction of 10b and N-Phenylmaleimide.—A mixture of 10b (1.61 g, 0.003 mol) and N-phenylmaleimide (0.911 g, 0.0053 mol) in benzene (40 ml) was refluxed for 22 hr. Removal of solvent gave a tacky solid which was extracted with boiling ethyl acetate to yield 12d as white needles, yield 1.60 g (75%), mp 225–227.50°, recrystallized from benzene–hexane, mp 226–227.5°.

Anal. Calcd for C₄₁H₃₁O₉N: C, 69.00; H, 4.35; N, 1.96. Found: C, 69.17; H, 4.21; N, 2.10.

Reaction of 10c and N-Phenylmaleimide.—A mixture of 10c (0.600 g, 0.00168 mol) and N-phenylmaleimide (0.4 g, 0.0023 mol) in benzene (20 ml) was refluxed for 25 hr. The yellow solution was filtered and the solvent was removed. Recrystallization of the light tan product from ethyl acetate–hexane gave 12e as white crystals, yield 0.60 g (68%), mp 225–226°.

Anal. Calcd for C₃₁H₂₃O₇N: C, 71.21; H, 4.41; N, 2.68. Found: C, 71.41; H, 4.49; N, 2.57.

Reaction of 10b with Benzyne.—A mixture of 10b (4.0 g, 0.0075 mol) and isoamyl nitrite (2.3 g, 0.0196 mol) in dry tetrahydrofuran (100 ml) was brought to reflux. Anthranilic acid (2.6 g, 0.0190 mol) in tetrahydrofuran (15 ml) was added during 1 hr. Filtration and removal of solvent gave a brown oil which crystallized overnight. Extraction with hot ethanol gave tan crystals, mp 217–276°. Recrystallizations from benzene–hexane (charcoal) gave 18 as white needles: yield 3.96 g (91%); mp 283–

(28) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

285°; ir 1735–1740 cm^{-1} (ester C=O) but no bridge C=O); pmr τ 6.28 (s, 6, OCH$_3$) and 3.40–2.16 (m, 22, aromatic protons).

Anal. Calcd for C$_{38}$H$_{28}$O$_6$: C, 78.60; H, 4.86. Found: C, 78.75; H, 4.89.

Saponification of 18.—A solution of 18 (0.318 g, 0.00055 mol) in 5% ethanolic potassium hydroxide (10 ml) was refluxed for 7 hr. The cooled mixture was poured into cold 10% hydrochloric acid (25 ml). The yellow precipitate was filtered, washed free of acid, stirred for 2 hr with 5% potassium carbonate (5 ml), filtered, washed, and dried. Recrystallization from benzene (charcoal) gave 19, yield 0.12 g (70%), mp 239–240° (lit.[17] mp 241–242°). A mixture of 19 with authentic 2,3-dihydroxy-1,4-diphenylnaphthalene has a melting point of 238–239°. The infrared spectra of the two materials are superimposable.

Reaction of 1b and Diazomethane.—A suspension of 1b (3.0 g, 0.0113 mol) in ether (70 ml) was stirred with an ether solution of diazomethane until evolution of nitrogen ceased. Excess diazomethane was removed by evaporation of half the ether; addition of an equal volume of petroleum ether (bp 30–60°) and chilling at 0° gave yellow crystals, mp 90–92°. Recrystallization from cyclohexane resulted in 2.3 g (73%) of 19: mp 94.0–94.8° (lit.[7] mp 94–95°); ir 1750, 1690 (split peak), 1590, 1450, 1350, 1320, 950, 782, and 735 cm^{-1}; uv max 320 (ϵ 11,500) and 238 mμ (ϵ 14,000).

Reaction of 19 with *p*-Anisoyl Chloride.—A solution of 19 (2.00 g, 0.0072 mol) and triethylamine (5 ml, 0.035 mol) in benzene (80 ml) was added to *p*-anisoyl chloride (2.0 g, 0.0117 mol) in benzene (20 ml) in 20 min. The mixture was stirred for 12 hr and filtered, and the solvent was removed. Attempts to recrystallize a small portion of the red oil from absolute ethanol resulted in decomposition of the product. The material showed similar instability to steam. Recrystallization from ether–pentane at −10° gave silky, scarlet needles of 10d: yield 0.95 g (32%); mp 130–130.8°; uv max (tetrahydrofuran) 482 (ϵ 6700) and 260 mμ (ϵ 30,000).

Anal. Calcd for C$_{26}$H$_{20}$O$_5$: C, 75.71; H, 4.88. Found: C, 76.00; H, 5.01.

Reaction of 1c and Diazomethane.—A suspension of 1c (2.1 g, 0.0114 mol) in ether (70 ml) was stirred with excess diazomethane in ether at 0°. Concentration of the mixture and sublimation (60°, 0.3 mm) of the product yielded 21 as yellow needles: yield 0.80 g (35%); mp 56.0–56.8° (lit.[19] mp 54–55°); ir 1750 and 1690 (conjugated C=O), 1605 (C=CC$_6$H$_5$), and 1200 cm^{-1} (vinyl ether); uv max (tetrahydrofuran) 235 (ϵ 13,000) and 305 mμ (ϵ 11,000).

Reaction of 1d and Diazomethane.—A suspension of 1d[20] (2.22 g, 0.0716 mol) in ether (30 ml) was stirred with excess diazomethane in ether at 0°. Removal of the solvent gave a clear residue which solidified on cooling. Sublimation at 50° (0.3 mm) gave 24 as white needles: ir 1050 and 1170 (vinyl ether) and 1710 and 1760 cm^{-1} (C=O); uv max (tetrahydrofuran) 270 mμ (ϵ 24,200).

Anal. Calcd for C$_7$H$_8$O$_3$: C, 60.00; H, 5.71. Found: C, 60.11; H, 5.80.

Reaction of 1a and Diazomethane.—A suspension of 1a (2.25 g, 0.02 mol) in ether was stirred with excess diazomethane in ether at 0° until evolution of nitrogen ceased. Removal of the solvent and sublimation at 75° (0.3 mm) of the residue gave 25: yield 2.05 g (81%); mp 84.5–86.0°; uv max 262 mμ (ϵ 25,000).

Anal. Calcd for C$_6$H$_6$O$_3$: C, 57.14; H, 4.80. Found: C, 57.24; H, 4.77.

Hydrogen Evolution in Reactions of Sodium Hydride with 1b, 6, and 19.—Solutions of 1b, 6, and 19 in tetrahydrofuran were treated with sodium hydride in wax dispersions and the hydrogen evolved was measured.

In a typical determination, a weighed quantity of reactant in tetrahydrofuran (10 ml) was added, *via* a pressure-equalizing funnel, to a stirred, heterogeneous mixture of excess sodium hydride in dry tetrahydrofuran (10 ml). The hydrogen evolved was collected over water in a gas burette separated by a Drierite tube; corrections were made for the vapor pressure of water and for the pressure of the measurement. Three experiments were conducted with each of the ketones studied. The number of moles of hydrogen evolved per mole in reaction of 1b, 6, and 19 was 1.93–2.01, 1.04–1.07, and 1.07–1.1, respectively. In independent experiments, 1b, 6, and 19 were each recovered in acidification of solutions of their anions.

Structure of 32.—Ketone 32 was prepared from anhydroacetone benzil, red phosphorus, and hydriodic acid in refluxing acetic acid as yellow crystals: mp 108.5–111.0° [lit. mp 108–110°

(procedure of ref 25a)]; ir 1680 (conjugated C=O), and 890 and 860, and 700 and 690 cm^{-1} (*two* monosubstituted phenyls); pmr τ (ABX) pattern) 7.10 (d), 7.75 (J = 7.0 cps, nonequivalent CN$_2$), 5.4 (d, J = 7.0 cps), and 3.3 (d, J = 1.5 cps, vinyl protons).

Nitrosation of 32 to 33.—A solution of 32 (15.0 g, 0.055 mol), butyl nitrite (12.3 g, 0.12 mol), and concentrated hydrochloric acid (4 ml) in absolute ethanol (70 ml) was warmed to 65°. The mixture was stored for 3 hr and filtered to give 33, yield 13.2 g (88%), mp 214.5–215.5° (lit.[24] mp 215–216°).

Hydrolysis of 33 to 34.—A solution of 33 (13 g, 0.048 mol), 37% formaldehyde (75 ml), and concentrated hydrochloric acid (12 ml) in glacial acetic acid (75 ml) was warmed to 30° and stirred overnight at room temperature. The orange-yellow product was washed with water, dried, and recrystallized from benzene–hexane to give 34 as deep orange crystals: yield 5.0 g (44%); mp 152–155°; ir 1750 (C=O) and 1700 cm^{-1} (conjugated C=O); uv max (tetrahydrofuran) 298 (ϵ 27,500) and 215 mμ (ϵ 20,000); pmr τ 5.2 (d), 2.8 (s), and 2.75–2.50 (m), no distinct vinyl proton is observed, ratio of aromatic to aliphatic protons is 11.1:1.0.

Anal. Calcd for C$_{17}$H$_{12}$O$_2$: C, 82.26; H, 4.84. Found: C, 82.32; H, 4.75.

Hydrolysis of 34 to 29b.—A solution of 34 (0.320 g, 0.0013 mol), concentrated hydrochloric acid (1.0 ml), and glacial acetic acid (4.0 ml) was refluxed for 2 hr. Removal of solvent under vacuum and crystallization of the residue from benzene–hexane resulted in 29b: yield 0.21 g (66%); mp 182–183° (lit.[24] mp 185–187°); ir 1760 and 1700 (C=O) and 1570 cm^{-1} (split peak, conjugation); pmr τ 6.55 (s, CH$_2$), and 2.7 and 2.67 (pair of s, phenyl protons), ratio of aliphatic to aromatic protons is 1:5.

Hydrolysis of 33 to 29b.—A solution of 33 (5.0 g, 0.02 mol), 37% formaldehyde (30 ml), and concentrated hydrochloric acid (5 ml) in glacial acetic acid (30 ml) was refluxed for 45 min. After 15 hr, the precipitate formed was washed with water, dried, and recrystallized from benzene to give 29b as yellow needles, yield 1.7 g (35%), mp 186–188°, identical with previous 29b.

Reaction of 29b and Hydroxylamine.—Diketone 29b (0.40 g, 0.0016 mol) in ethanol was warmed with a neutralized solution of hydroxylamine hydrochloride in water (5 ml). The derivative formed was crystallized from ethyl acetate–acetic acid to give the oxime of 29b, possibly 1-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione, yield 0.31 g (73%), mp 241–242° dec. This oxime depresses the melting point of 33.

Anal. Calcd for C$_{17}$H$_{13}$NO$_2$: C, 77.72; H, 4.94; N, 5.32. Found: C, 77.86; H, 5.11; N, 5.51.

Deuterium Exchange Experiments.—The various ketones were stirred with deuterium oxide in the presence of acids or bases. After a stated period of time, solvent was removed and the ketone were recovered by crystallization or sublimation. Identity with original, nondeuterated compounds was established by comparison of infrared spectra and by mixture melting point. The pmr spectra of recovered compounds were compared with the original spectra to determine the extent of deuterium exchange.

A. 19, D$_2$O, and Et$_3$N.—To a solution of 19 (0.26 g, 0.0097 mol) and deuterium oxide (1.0 ml) in dry tetrahydrofuran (12 ml) was added triethylamine (*ca.* 0.01 ml). The mixture was stirred for 1 hr and the solvent was removed to yield a dark purple solid which recrystallized as yellow needles identical with original 31. The pmr spectrum at 4.2 ppm showed 80% disappearance of benzylic protons.

B. 19, D$_2$O, and HCl.—A solution of 19 (0.26 g, *ca.* 0.001 mol), deuterium oxide (1.0 ml), and concentrated hydrochloric acid (0.01 ml) in tetrahydrofuran (10 ml) was stirred for 4 hr. Removal of solvent and crystallization of the residue from cyclohexane gave 19, whose melting point (93–95°) is identical with that of initial material. The pmr spectrum indicated complete disappearance of the benzylic proton at 4.2 ppm.

C. 21, D$_2$O, and Et$_3$N.—A mixture of 21 (0.23 g, 0.00114 mol), deuterium oxide (0.80 ml), and triethylamine (*ca.* 0.01 ml) in dry tetrahydrofuran (8 ml) was stirred for 6 hr and concentrated. The residue was sublimed at 60° (0.3 mm) to give 21, yield 0.18 g, whose pmr spectrum at τ 7.05 revealed complete exchange of methylene protium for deuterium.

D. 21, D$_2$O, and HCl.—Stirring of 21 (0.20 g, 0.001 mol), deuterium oxide (0.80 ml), concentrated hydrochloric acid (*ca.* 0.02 ml), and tetrahydrofuran (8 ml) for 14 hr, removal of solvent, and sublimation of the residue at 60° (0.3 mm) resulted in 21

whose pmr spectrum showed 85–87% exchange of methylene protium for deuterium.

E. 24, D₂O, and Et₃N.—A mixture of **24** (0.20 g, 0.00141 mol), deuterium oxide (0.80 ml), dry tetrahydrofuran (10 ml), and triethylamine (*ca.* 0.01 ml) resulted in some decomposition of **24** in 6 hr. Sublimation led to **24**, yield 0.12 g, whose pmr spectrum revealed complete disappearance of the 2.95-ppm signal for methylene protium.

F. 24, D₂O, and HCl.—Sublimed **24** (0.19 g), obtained from a mixture of **24** (0.22 g, 0.00157 mol), deuterium oxide (0.80 ml), and hydrochloric acid (*ca.* 0.01 ml) in tetrahydrofuran (10 ml) for 10 hr, contained only 10% methylene protium.

G. 25, D₂O, and Et₃N.—Diketone **25** is extensively decomposed in less than 15 min in deuterium oxide–tetrahydrofuran containing small amounts of triethylamine.

H. 25, D₂O, and HCl.—In neat deuterium oxide containing a trace of hydrochloric acid, **25** undergoes 90% exchange of its methylene protium for deuterium in 20 hr.

I. 29a, D₂O, and Sodium Acetate.—A suspension of **29a** (0.30 g, 0.00175 mol) in deuterium oxide (1.2 ml) containing sodium acetate (10 mg) was stirred for 12 hr. Examination of

29a after removal of solvent showed no decomposition to have occurred. The infrared spectrum and melting point of the **29a** recovered were the same as of initial **29a**. The pmr spectrum of the recovered **29a** showed that 40% of its methylene protium, τ 6.6, has been exchanged.

J. 29a, D₂O, and HCl.—A solution of **29a** (0.25 g, 0.0145 mol), deuterium oxide (1.0 ml), and concentrated hydrochloric acid (0.01 ml) in deuterioacetic acid (4.0 ml) was refluxed for 2 hr and then kept at 50° for 9 hr.

Registry No.—**6**, 22837-57-6; **10a**, 22837-58-7; **10b**, 22837-59-8; **10c**, 22837-60-1; **10d**, 22837-61-2; **12a**, 22837-62-3; **12b**, 20142-93-2; **12d**, 22837-64-5; **12e**, 22837-65-6; **13**, 22837-66-7; 5,6-dihydro adduct of **13**, 22837-67-8; **14**, 22837-68-9; **18**, 22837-69-0; **24**, 7180-62-3; **25**, 22837-71-4; **34**, 22837-73-6; 1-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione, 22837-72-5; 2-bromo-1,3,4-cyclopentanetrione, 22922-42-5.

A New Synthesis of 2-Hydroxy-3-methylcyclopent-2-en-1-one. II[1]

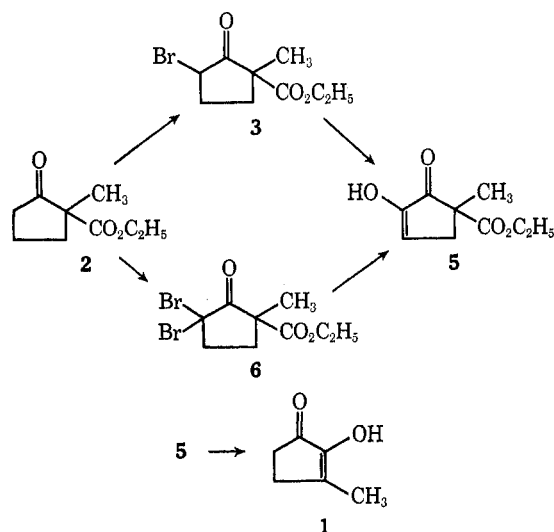KIKUMASA SATO, YASUHIKO KOJIMA, AND HARUHITO SATO

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The synthesis of 2-hydroxy-3-methylcyclopent-2-en-1-one (**1**) was accomplished by the DMSO oxidation of 5-bromo-2-carbethoxy-2-methylcyclopentanone (**3**), the side reaction of which was prevented by the addition of epichlorohydrin (**7**). The two-step hydrolysis of 5,5-dibromo-2-carbethoxy-2-methylcyclopentanone (**6**) using morpholine gave **1** in a pure state. On the other hand, the reaction of 2,5-dibromocyclopentanone (**9**) with morpholine gave 2-morpholino-2-cyclopentenone (**10**), while 2,6-dibromocyclohexanone (**11**), when subjected to similar conditions, was converted into 1-cyclopentene-1-carboxymorpholide (**12**).

An earlier paper in this series[1] described a synthesis of 2-hydroxy-3-methylcyclopent-2-en-1-one (**1**) following two synthetic routes from 2-carbethoxy-2-methylcyclopentanone (**2**). Both procedures involved the oxidation of **2** with selenium dioxide and the nitrosation of **2** with *n*-butyl nitrite, respectively. In addition, it has been found[1] that the dimethyl sulfoxide (DMSO) oxidation of 5-bromo-2-carbethoxy-2-methylcyclopentanone (**3**) gave 3-bromo-5-carbethoxy-2-hydroxy-5-methylcyclopent-2-en-1-one (**4**).

In this paper, we aim to elucidate such an abnormal oxidation of cyclic α-bromo ketones as described above,

3

2

HO ... **5**

Br Br ... **6**

5 → ... **1**

and accomplish the preparation of **1** from the intermediate **2**, *via* two routes containing 5-carbethoxy-2-hydroxy-5-methylcyclopent-2-en-1-one (**5**) as the key precursor: the DMSO oxidation of **3** and the hydrolysis of 5,5-dibromo-2-carbethoxy-2-methylcyclopentanone (**6**).

The DMSO oxidation of 2-bromocyclopentanone and 2-bromocyclohexanone gave 3-bromo-2-hydroxycyclopent-2-en-1-one and 3-bromo-2-hydroxycyclohex-2-en-1-one, respectively. Accordingly, this series of reactions was confirmed to be a characteristic one of cyclic α-bromo ketones. Since Hunsberger and Tien[2] have reported that dimethyl sulfoxide oxidizes hydrogen bromide to bromine, it appeared that a normal reaction could occur when hydrogen bromide liberated in the reaction was captured by such a neutral base as an epoxide. The DMSO oxidation of **3** in the presence of epichlorohydrin (**7**) gave a normal product **5** (58.5%) along with 1-bromo-3-chloro-2-propanol (**8**). Expected α diketone was also obtained by the DMSO oxidation of 2-bromocyclohexanone using phenyl glycidyl ether as the epoxide. From these results, the extraordinary reaction mentioned above is interpreted as follows. The existence of **7** prevents the produced α-diketone from subsequent bromination, because epoxides react with hydrogen bromide formed in the reaction. This process of the DMSO oxidation gave **1** in an overall yield of 29% based upon the diethyl adipate. This is a satisfactory result, compared with the two procedures[1] already described.

The bromination of ketone **2** gave **6** in 85% yield. Compound **1** could be prepared merely by the hydrolysis

(1) For previous paper, see K. Sato, S. Suzuki, and Y. Kojima, *J. Org. Chem.*, **32**, 339 (1967).

(2) I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), 88 (1967).