Anal. Calcd for $C_{25}H_{34}O_5$: C, 64.95; H, 7.41. Found: 65.51; H, 7.50.

Acid Hydrolysis of the Anhydride 7a in the Pregnane Series.—A solution of 190 mg (0.45 mmol) of the anhydride **7a** in 40 ml of methanol containing 25 drops of concentrated hydrochloric acid was boiled under reflux for 1 hr, allowed to cool, and poured into 200 ml of water. The resulting solution was saturated with salt, and the white precipitate which formed was collected and recrystallized from methanol to give 42 mg, (25%) of **7c**: mp 180–182°; ir (KBr) 2.80, 2.90, 5.54, 5.84, and 5.90 μ; nmr δ 0.69 (18-CH_3), 1.12 (19-CH_3), 2.12 (21-CH_3), 3.42 (s, 3, 5-OCH_3), and 3.63 (m, 3α-**H**).

Anal. Calcd for $C_{22}H_{32}O_6$: C, 67.32; H, 8.22. Found: C, 67.54; H, 8.31.

Jones Oxidation of the Ketotriol 3c in the Cholestane Series.—To a solution of 408 mg (0.855 mmol) of the ketotriol in 35 ml of dry acetone was added dropwise with stirring 1.2 ml of Jones' reagent. The reaction mixture was stirred for 8 min and then 50 ml of methanol was added and the reaction mixture was worked up as above to give 315 mg of an oily solid. The solid was chromatographed on 30 g of silica and elution with 10:1 benzene–ether gave 160 mg (39%) of anhydride **7d**: mp (after recrystallization from benzene–petroleum ether) 185.5–187°; ir (KBr) 3.01–3.03, 5.54, 5.62, 5.73, 5.87, and 8.11–8.18 μ; nmr δ 0.73 (18-CH_3), 1.12 (19-CH_3), 2.04 (3β-$OCOCH_3$), and 3.89 (5-O**H**, disappears on the addition of D_2O).

Anal. Calcd for $C_{29}H_{46}O_6$: C, 70.82; H, 9.45. Found: C, 70.58; H, 9.23.

Acetylation of the Anhydride 7d in the Cholestane Series.—A solution of 58 mg (0.012 mmol) of **7d** in 2 ml of acetic anhydride and 2 ml of pyridine was heated on a steam bath for 3.5 hr and poured onto ice. The resulting precipitate was collected and chromatographed on silica. Elution with benzene gave 41 mg of **7e** which was recrystallized from aqueous methanol and then had mp 147–148°: ir (KBr) 5.52, 5.63, 5.71, 8.04, and 8.07 μ; nmr δ 0.74 (18-CH_3), 1.12 (19-CH_3), 2.05 and 2.12 (3- and 5-$OCOCH_3$'s), and 5.00 (m, 1, 3α-**H**).

Anal. Calcd for $C_{31}H_{48}O_7$: C, 69.90; H, 9.08. Found: C, 70.26; H, 9.14.

Jones Oxidation of the Ketotriol 3e in the Androstane Series.—To a solution of 243 mg (0.575 mmol) of the ketotriol in 25 ml of dry acetone was added dropwise with stirring over a period of 5 min 1 ml of Jones reagent. After an additional 15 min of stirring 10 ml of methanol was added and the solution was allowed to stand for 2 hr more and worked up as above to give 232 mg of oily solid. Earlier experiments indicated that partial deacetylation had occurred, so the material was dissolved in 5 ml of pyridine and 5 ml of acetic anhydride and heated on a steam bath for 14.5 hr. The solution was then poured into water and the resulting solid was collected to give 144 mg, mp 209–210.5°, homogeneous to tlc. The solid was chromatographed on 20 g of silica. Nothing was eluted with twelve 50-ml fractions of benzene and two 50-ml fractions of 20:1 benzene–ether. Elution with four more fractions of the latter solvent gave 107 mg which was recrystallized from methanol to give 61 mg (22%) of **7f**: mp 215–215.5°; ir (KBr) 5.53, 5.62, 5.75, 7.95, and 8.03 μ; nmr δ 0.85 (18-CH_3), 1.13 (19-CH_3), 2.03 (nine protons, 3-, 5-, and 17-$OCOCH_3$'s), 4.48 (t, 1 17α-**H**), and 5.08 (m, 3α-**H**).

Anal. Calcd for $C_{25}H_{34}O_9$: C, 62.77; H, 7.18. Found: C, 63.22; H, 7.18.

Registry No.—Potassium permanganate, 7722-64-7; **3a**, 26145-85-7; **3b**, 26145-86-8; **3c**, 26145-87-9; **3d**, 26145-88-0; **3e**, 26145-89-1; **3f**, 26145-90-4; **5a**, 26145-91-5; **5b**, 26210-96-8; **5c**, 26145-92-6; **5e**, 26145-93-7; **5f**, 26210-97-9; **7a**, 26145-94-8; **7b**, 26145-95-9; **7c**, 26145-96-0; **7d**, 26145-97-1; **7e**, 26145-98-2; **7f**, 26145-99-3.

Synthesis and Photocycloadditions of Compounds Related to 3-Carboxycyclohexenone[1]

WILLIAM C. AGOSTA[2] AND WILLIAM W. LOWRANCE, JR.

Laboratories of The Rockefeller University, New York, New York 10021

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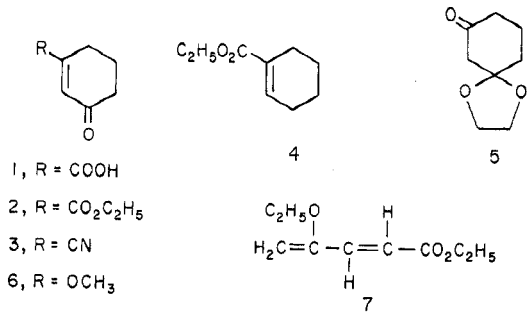
Irradiation of **1**, **2**, and **3** in the presence of ethylene, acetylene, and 2-butyne leads to formation of cycloaddition products **22–26**. Bromination–dehydrobromination of **23** yields the cyclooctadienone **27**. The 3-carbethoxycyclohexenones **16** and **17** are prepared from the Diels–Alder adduct **13** of maleic anhydride with the new diene **7**. Reaction of 3-methoxycyclohexenone (**6**) with diethylaluminum cyanide gives the corresponding nitrile **3** in a single step.

We have explored the chemistry of derivatives of 3-carboxycyclohex-2-enone (**1**) as synthetic intermediates and as models for more highly substituted compounds. Some of our observations appear to be of general interest, and we record these below. They include the smooth photochemical cycloaddition of ethylene, acetylene, and 2-butyne to three of the simplest examples of this system, **1**, **2**, and **3**; a one-step preparation of nitrile **3** which may be broadly applicable; and a new route to ring-substituted derivatives of **1** employing the Diels–Alder reaction. Previous preparations of simple derivatives of **1** have involved either chromic acid oxidation of the unsaturated ester **4** to give **2**,[3] or addition of hydrogen cyanide to the ketal (**5**) of dihydroresorcinol, followed by hydrolysis and dehydration to **3**.[4] The exact conditions in the former reaction are critical and the method is inherently limited in applicability. The cyanide addition gives only moderate overall yields but presumably could be applied to substituted cyclohexane-1,3-diones. In our hands the published procedures for both these reactions were not wholly satisfactory, and in the Experimental Section we report details of improved conditions.



(1) A portion of this work has been published in preliminary form: W. C. Agosta and W. W. Lowrance, Jr., *Tetrahedron Lett.*, 3053 (1969).

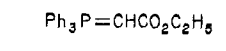
(2) Fellow of the Alfred P. Sloan Foundation. Author to whom correspondence should be addressed.

(3) M. Mousseron, R. Jacquier, A. Fontaine, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, 1246 (1954).

(4) M. W. Cronyn and J. E. Goodrich, *J. Amer. Chem. Soc.*, **74**, 3331 (1952).

We have found a simple alternative preparation of **3** from the readily available enol ether **6**.[5] This compound reacts with diethylaluminum cyanide[6] in benzene at room temperature to yield **3** directly in a Michael-type addition–elimination reaction. Hydrolysis of **3**, protected as the ethylene ketal, or of **2** gives the previously unknown parent acid **1**.

As an approach to ring-substituted derivatives of **1**, we have prepared diene **7** and investigated its Diels–Alder addition to suitable dienophiles. Wittig reaction of carbethoxymethylenetriphenylphosphorane (**8**) with α-ethoxyacrolein (**9**)[7] gives exclusively the trans isomer of **7**, as expected.[8] The nuclear magnetic resonance (nmr) spectrum of the reaction product showed that a single isomer is formed, and a vicinal coupling constant of 15 Hz indicated[9] this to be the trans compound. Derivatization of **7** gave the known[10] 2,4-dinitrophenylhydrazone of ethyl β-acetoacrylate. With the pyrrolidine enamine of cyclopentanone, **7** formed an adduct which on treatment with acid underwent loss of pyrrolidine and oxidative aromatization to the indan **11**.[11]



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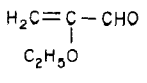

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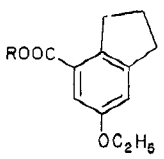
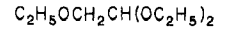


11, R = C_2H_5

12, R = H



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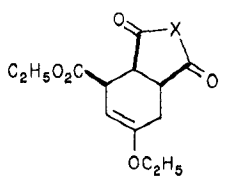
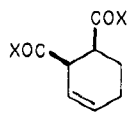


13, X = O

14, X = N–Ph



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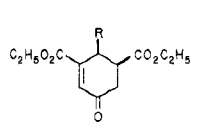
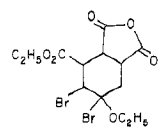
The conditions used lead to ester hydrolysis, and the product was isolated as the parent acid **12**. Reaction of diene **7** with the active dienophiles maleic anhydride and N-phenylmaleimide at 110° yielded the nicely crystalline cyclohexenes **13** and **14**. The related condensation of vinylacrylic acid with acrylic acid and that of vinylacrylyl chloride with acrylyl chloride have been examined[12] with care, and it is known that the cis adducts **15** are preferentially formed. Similarly, reaction of vinylacrylic acid or ester with quinone leads only to cis,cis addition.[13] These experimental observations are completely in accord with theoretical prediction,[14] and we assume then that the single isomers (**13** and **14**) obtained from **7** in greater than 60% yield have the cis,cis stereochemistry indicated.

The maleic anhydride adduct **13** was employed for further transformation and could be converted into triester **16** and diester **17**, examples of ring-substituted 3-carbethoxycyclohexenones. Compound **13** absorbed 1 equiv of bromine quite readily; the crude product (**18**) was treated first with hot ethanol containing hydrogen chloride and then briefly with aqueous sulfuric acid at room temperature. Exposure to acidic alcohol presumably serves three functions, esterification of the succinic anhydride, conversion of the α-bromo ether of **18** into a ketal, and dehydrobromination of the intermediate β-bromo ester. Final treatment with mild aqueous acid allows hydrolysis of the ketal and formation of the isolated cyclohexenone **16**. Although there is opportunity for epimerization to the trans isomer in this sequence, this apparently does not occur. In the nmr spectrum of **16** at 220 MHz the geminal protons adjacent to the ketone carbonyl group are separated cleanly from all other signals and are seen as the AB portion of a typical ABX system with $J_{AB} = 17$, $J_{AX} = 5.0$, and $J_{BX} = 3.5$ Hz. Examination of molecular models of **16** and its trans diastereomer, and application of the Karplus relation[15] show that the observed coupling constants are reasonable only for the cis isomer shown. An alternative preparation of **16** was possible through ketotriester **19**, formed on esterification[16] of **13** with ethanol containing *p*-toluenesulfonic acid and subsequent mild hydrolysis of the intermediate ketal. Bromination of **19** in acetic acid, followed by dehydrobromination using lithium bromide and lithium carbonate in dimethylformamide,[17] gave **16**, identical with the material described above. Successful reaction conditions were considerably less critical in this case than in direct bromination of **13**; the sequence is less interesting, however, since its application to a ketone lacking the symmetry



16, R = $CO_2C_2H_5$

17, R = H



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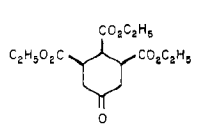

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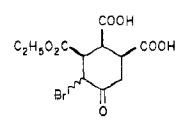

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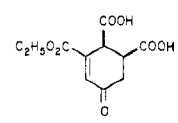

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(5) H. Born, R. Pappo, and J. Szmuszkovicz, *J. Chem. Soc.*, 1779 (1953).

(6) W. Nagata and M. Yoshioka, *Tetrahedron Lett.*, 1913 (1966).

(7) M. F. Shostakovskii and N. A. Keiko, *Dokl. Akad. Nauk SSSR*, **162**, 362 (1965). α-Ethoxyacrolein (**9**) is prepared by condensation of formaldehyde with ethoxyacetaldehyde; in the course of this work we observed that readily available ethoxyacetal (**10**) may be hydrolyzed and used *in situ* for this reaction without intermediate isolation of the unstable aldehyde. This simple modification should make **9**, which has been little studied, a much more conveniently available compound.

(8) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957); S. S. Novikov and G. A. Shvekhgeĭmer, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 673 (1960); V. F. Kuckerov, B. G. Kovalev, G. A. Kogan, and L. A. Yanovskaya, *Dokl. Akad. Nauk SSSR*, **138**, 1115 (1961).

(9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 301–302, and references cited therein.

(10) S.-O. Lawesson, M. Dahlén, and C. Frisell, *Acta Chem. Scand.*, **16**, 1191 (1962).

(11) For similar reactions of vinylacrylic ester with enamines, see S. Danishefsky and R. Cunningham, *J. Org. Chem.*, **30**, 3676 (1965), and G. A. Berchtolb, J. Ciabattoni, and A. A. Tunick, *ibid.*, **30**, 3679 (1965).

(12) K. Alder, M. Schumacher, and O. Wolff, *Justus Liebigs Ann. Chem.*, **564**, 79 (1949).

(13) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

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

(15) Reference 9, pp 281–298, and references cited therein.

(16) A. C. Cope and E. C. Herrick, *J. Amer. Chem. Soc.*, **72**, 983 (1950).

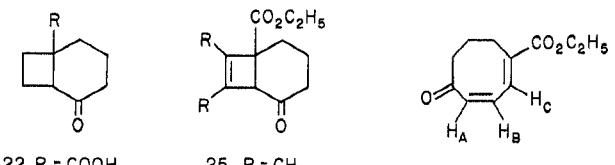
(17) R. P. Holysz, *ibid.*, **75**, 4432 (1953); R. Joly, J. Warnant, G. Nominé, and D. Bertin, *Bull. Soc. Chim. Fr.*, 366 (1958).

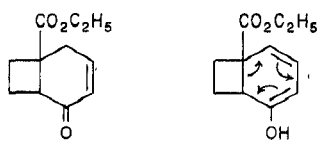
of **19** would undoubtedly lead to a mixture. The path from **13** first outlined, on the other hand, may be of some general use in preparing 3-carboxycyclohexenones.

The bromination–dehydrobromination conditions just described for **13** involved direct ethanolysis after bromination. If instead the crude bromide **18** was treated with water, a different sequence of reactions ensued. Water apparently opens the anhydride and converts the α-bromo ether to the corresponding ketone. The resulting bromoketo acid **20** was heated directly at 80° in hexamethylphosphoramide[18] and underwent dehydrobromination to give intermediate **21**, followed by thermal decarboxylation of this vinylogous β-keto acid.[19] Subsequent esterification gave the diester **17**.

We now turn attention to photochemical cycloadditions of the simple unsaturated systems **1**, **2**, and **3**. These are the first examples of addition of an alkene or alkyne to cyclohexenones having strongly electron-withdrawing groups in the β position; the reaction is clearly quite favorable in comparison with additions involving other cyclohexenones.[20-22] Ethylene, an olefin generally unreactive in cycloadditions, condenses with compounds **1**, **2**, and **3** on irradiation through Pyrex[23] in benzene solution to give the expected bicyclic products **22**, **23**, and **24**, respectively. Hydrolysis of ester **23** and nitrile **24** yielded **22**, and the structures of all three adducts are secure from spectroscopic properties. For carboxylic acid **1** and ester **2** the addition of ethylene is rapid and very clean; the yield of ester **23** is 98%. Nmr spectra indicate that **22** and **23** are unchanged by treatment with mild aqueous base or contact with alumina, and we conclude that only cis-fused bicyclic systems are isolated in these additions.[20-22] In similar fashion irradiation of **2** in the presence of 2-butyne or acetylene itself leads to the unsaturated adducts, **25** and **26**. Previous attempts[24] to form cyclobutenes by photoaddition of acetylene to activated olefins have met with quite limited success, and the 30% yield of **26** observed here is unusually high.

Reaction of **23** with bromine in chloroform–acetic acid followed by treatment[17] with lithium bromide and lithium carbonate in hot dimethylformamide gave carbethoxycyclooctadienone **27** as the only isolated product. We suggest that α-bromination followed by loss of hydrogen bromide leads to the expected unsaturated ketone **28**, which undergoes enolization, rearrangement (**29**),[25] and ketonization. The structure of **27** follows from spectroscopic measurements; ultraviolet [λ_{max} = 282 mμ (ϵ 9700)[26]] and infrared (1710, 1662 cm^{-1}) absorptions are consistent with the assignment, and the nmr spectrum is particularly informative. At 220 MHz signals for the three olefinic protons are well separated and interpretable upon inspection (H_A 5.95 ppm, d, J_{AB} = 12.5 Hz; H_B 6.50 ppm, dd, J_{AB} = 12.5, J_{BC} = 5.5 Hz; H_C 7.30 ppm, d, J_{BC} = 5.5 Hz). Using this observed J_{BC} in the modified Karplus equation appropriate[27] to such systems in medium rings, we estimate the dihedral angle between H_B and H_C to be about 45°, a value that appears reasonable in molecular models of **27**. This sequence of cycloaddition followed by bromination–dehydrobromination provides rather convenient access to this substituted cyclooctadienone.





Experimental Section

Materials and Equipment.—Irradiations were 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 filter sleeve. In reactions involving ethylene or acetylene the hydrocarbon was bubbled through the reaction mixture before and during the irradiation. Saturated solutions of ethylene and acetylene in benzene at 15° are 0.16 and 0.24 *M*, respectively.[28]

Vapor phase chromatography (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% SE-30 on Chromosorb W support. Spectra were recorded using a Perkin-Elmer 237B grating ir spectrophotometer, a Cary 14 PM uv spectrophotometer, and Varian A-60 (60 MHz) and HR-220 (220 MHz) nmr spectrometers. Measurement of pH was performed with a Radiometer TTT1 pH meter equipped with a type GK2021-B glass membrane–calomel electrode. All reactions and distillations were conducted with care to exclude air and moisture, under a blanketing stream of prepurified nitrogen.

3-Oxo-1-cyclohexene-1-carboxylic Acid Ethyl Ester (2).—In a modification of the method of Mousseron,[3] chromic anhydride (15.0 g) was added over 30 min to a mechanically stirred solution of 1-carboethoxycyclohexene (15.0 g) in 100 ml of acetic acid and 2 ml of water while the reaction temperature was maintained at 40° by external cooling. After another 60 min at 40–50°, the mixture was cooled by addition of ice, neutralized cautiously with a concentrated solution of KOH, and extracted with ether. The ether extract was washed with saturated $NaHCO_3$, water, and brine, and dried over Na_2SO_4. Distillation provided 7.9 g (48%) of slightly yellow oil: bp 143° (20 mm); ir ($CHCl_3$) 1720, 1685, 1615 (w) cm^{-1}; uv (95% ethanol) λ_{max} 240 mμ (ϵ 12,000), 345 (28); nmr (CCl_4) δ 1.33 (t, J = 7 Hz, 3 H), 1.7–2.7 (m, 6 H), 4.24 (q, J = 7 Hz, 2 H), 6.60 (t, J = 2 Hz, 1 H).

The melting behavior and uv spectrum of the 2,4-dinitrophenylhydrazone were as reported:[3] mp 201° (ethanol); uv (95% ethanol) λ_{max} 260 mμ (ϵ 33,100).

3-Oxo-1-cyclohexene-1-carbonitrile (3). A. From the Monoethylene Ketal of Cyclohexane-1,3-dione (5).—Reaction of the

(18) H. Normant, *Bull. Soc. Chim. Fr.*, 791 (1968).

(19) P. Rabe and E. Pollock, *Ber.*, **45**, 2924 (1912); E. C. Horning, M. O. Denekas, and R. E. Field, *J. Org. Chem.*, **9**, 547 (1944).

(20) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

(21) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966).

(22) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969). This paper contains a more complete list of references and also a brief review of the reaction.

(23) Similar conditions using unfiltered light are described in ref 21.

(24) G. Koltzenburg, P. G. Fuss, and J. Leitich, *Tetrahedron Lett.*, 3409 (1966); S. Farid, W. Kothe, and G. Pfundt, *ibid.*, 4147 (1968); I. W. J. Still, M-H. Kwan, and G. E. Palmer, *Can. J. Chem.*, **46**, 3731 (1968).

(25) Equilibration of the parent bicyclo[4.2.0]octa-2,4-diene with cycloocta-1,3,5-triene at 80–100° was described by A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952).

(26) The parent cycloocta-2,4-dienone shows λ_{max} 278 mμ (ϵ 5770): N. Heap, G. E. Green, and G. H. Whitham, *J. Chem. Soc., C*, 160 (1969); see also J. K. Crandall and L-H. Chang, *J. Org. Chem.*, **32**, 532 (1967).

(27) G. V. Smith and H. Kriloff, *J. Amer. Chem. Soc.*, **85**, 2016 (1963).

(28) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, **17**, 125 (1931).

monoethylene ketal of cyclohexane-1,3-dione[29] (20 g) with aqueous NaCN as described by Cronyn[4] gave the cyanohydrin ketal, which was extracted into ether, concentrated, and then stirred vigorously at 25° for 72 hr with 10 ml of 6.0 *M* HCl. The product was extracted with ether, washed with 5% Na_2CO_3, water, and brine, and dried over Na_2SO_4. Distillation provided 7.2 g (46%) of 3-cyanocyclohexenone: bp 80° (0.5 mm); ir (CCl_4) 2225 (w), 1700, 1605 cm^{-1}; nmr (CCl_4) δ 1.9–2.8 (m, 6 H), 6.58 (t, J = 2 Hz, 1 H).

B. From 3-Methoxycyclohexenone (6).—3-Methoxycyclohexenone[5] (vpc purified, 38 mg, 0.30 mmol) in 2 ml of benzene and 1.5 ml of toluene was added dropwise over 15 min to a magnetically stirred benzene solution of diethylaluminum cyanide[6] (CAUTION: toxic and possibly pyrophoric) (approximately 1.5 mmol) at 0°. The solution was allowed to warm to 25° over 1 hr, poured into 40 ml of 0.0125 *M* MaOH at 0°, then extracted with ether. The ether extract was washed with 5% Na_2CO_3, water, and brine and dried over Na_2SO_4. The heavy oil left after removal of solvent was chromatographed on a column of Woelm grade II neutral alumina to give 20 mg (55%) of 3-cyclocyclohexenone.

The 2,4-dinitrophenylhydrazones of the ketones made by methods A and B melted at the same temperature (204–205°, ethanol) singly and in mixture (lit.[4] 204–204.5°), and had identical ir spectra (KBr disk).

3-Oxocyclohexene-1-carboxylic Acid (1). A. From 3-Cyanocyclohexenone (3).—Removing water with a Dean–Stark trap from a refluxing solution of 3-cyanocyclohexenone (726 mg, 6.0 mmol) and ethylene glycol (372 mg, 6.0 mmol) in 30 ml of benzene containing a trace of *p*-toluenesulfonic acid gave the ethylene ketal.[4] The nitrile function was then hydrolyzed by heating at reflux with 3 ml of 2.5 *M* NaOH for 12 hr; the ketone was then regenerated from the ketal by stirring with 3 ml of 1.0 *M* HCl at 0° for 1 hr. The resulting keto acid was extracted into ether, washed with brine, and dried over Na_2SO_4. Crystallization from hot benzene gave 270 mg (45%) white needles: melting behavior, sinters 100–129°, melts 129°; ir ($CHCl_3$) 3500–2600, 1700, 1680, 1620 (w) cm^{-1}; nmr ($CDCl_3$) δ 1.9–2.8 (m, 6 H), 6.87 (t, J = 2 Hz, 1 H), 10.80 (s, 1 H).

Anal. Calcd for $C_7H_8O_3$: C, 59.99; H, 5.75. Found: C, 60.03; H, 5.70.

B. From 3-Carbethoxycyclohexenone (2).—3-Carbethoxycyclohexenone (60 mg, 0.39 mmol) in 2 ml of methanol was stirred with a solution of K_2CO_3 (215 mg, 1.60 mmol) in 2 ml of water for 12 hr at 25°. The mixture was acidified and extracted with ether. The ether extract was washed with brine and dried over Na_2SO_4. The 30 mg (80%) of white needles left after evaporation of solvent and recrystallization from hot benzene was identical with the carboxylic acid prepared by method A.

2-Ethoxyacrolein (9).—1,1,2-Triethoxyethane[30] (22.0 g) was stirred with 3.0 *M* HCl at 25° for 45 min, then neutralized at 0° with 6.0 *M* NaOH. This solution was added in one portion to 37% formalin (11.6 ml), diethylamine hydrochloride (14.9 g), and hydroquinone (100 mg) in a flask maintained at 60° equipped with a mechanical stirrer, condenser, and pH electrode. The apparent pH, which fluctuated over the first 10 min, was adjusted to 7.6 by addition of 6.0 *M* NaOH; the reaction was stirred for 2.5 hr at 60°. It was then cooled to 0° and extracted with pentane. The pentane extract was washed with water and brine and dried over Na_2SO_4. Evaporation of solvent through a Vigreux column and subsequent distillation provided 5.90 g (44%) of the lacrymatory 2-ethoxyacrolein:[7] bp 41° (18 mm); ir (CCl_4) 1712, 1614 cm^{-1}; nmr (CCl_4) δ 1.39 (t, J = 7 Hz, 3 H), 3.87 (q, J = 7 Hz, 2 H), 5.02 (s, 2 H), 9.16 (s, 1 H).

***trans*-4-Ethoxy-2,4-pentadienoic Acid Ethyl Ester (7).**—2-Ethoxyacrolein (9) (4.65 g) was heated at reflux with carbethoxymethylenetriphenylphosphorane (8) (16.20 g) in 35 ml of CH_2Cl_2 for 4.5 hr. The reaction was cooled, freed of solvent using a rotary evaporator, and poured into 300 ml of ligroin; after 12 hr at 0° the liquid was decanted from the triphenylphosphine oxide and concentrated. Rapid distillation from a small amount of hydroquinone gave 3.85 g (48%) of colorless sweet-smelling oil, bp 87° (5 mm), which could not survive vpc at 150°: ir ($CHCl_3$) 1700, 1640, 1590 cm^{-1}; uv (95% ethanol) λ_{max} 218 mμ (ε 8500), 270 (13,500); nmr (CCl_4) δ 1.30 (t, J = 7 Hz, 3 H), 1.38 (t, J = 7 Hz, 3 H), 3.85 (q, J = 7 Hz, 2 H), 4.16 (q, J = 7 Hz, 2 H), 4.41 (s, 2 H), 6.12 (d, J = 15 Hz, 1 H), 6.96 (d, J = 15 Hz, 1 H). A second distillation gave an analytical sample.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.46; H, 8.37.

Treatment of the enol ether with 2,4-dinitrophenylhydrazine in methanol containing a few drops of 6.0 *M* HCl produced the 2,4-dinitrophenylhydrazone of ethyl 3-acetylacrylate, mp 148° (ethanol) (lit.[10] 148°).

Anal. Calcd for $C_{13}H_{14}N_4O_6$: C, 48.45; H, 4.38; N, 17.39. Found: C, 48.36; H, 4.43; N, 17.46.

6-Ethoxy-4-indancarboxylic Acid (12).—The pyrrolidine enamine of cyclopentanone (328 mg, 2.4 mmol), prepared by the method of Stork,[31] was heated at reflux with ethyl 4-ethoxypentadienoate (7) (204 mg, 1.2 mmol) in 2 ml of benzene for 72 hr. The reaction mixture was then extracted with pentane, and the extract was washed with 5% w/v HCl, water, and brine, and dried over Na_2SO_4. In order to eliminate any remaining pyrrolidine,[11] the oil was stirred with 10 ml of 95% ethanol containing 0.05 ml of concentrated HCl at 25° for 4 hr. The product was extracted into ether, washed with brine, and dried over Na_2SO_4. Solvent was evaporated to leave 170 mg (69%) white solid which was recrystallized from aqueous methanol to give white needles: mp 121–122° (sinters 90–100°); ir ($CHCl_3$) 3400–2900, 1685, 1605 cm^{-1}; nmr ($CDCl_3$) δ 1.48 (t, J = 7 Hz, 3 H), 1.9–2.4 (broad m, 2 H), 2.98 (t, J = 8 Hz, 2 H), 3.30 (t, J = 8 Hz, 2 H), 4.1 (q, J = 7, 2 H), 7.0 (m, 1 H), 7.45 (d, J = 2.5 Hz, 1 H), 13.0 (s, 1 H).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.02; H, 6.87.

5-Ethoxy-4-cyclohexene-1,2,3-tricarboxylic Acid 1,2-Anhydride 3-Ethyl Ester (13).—Maleic anhydride (210 mg, 2.1 mmol) and ethyl 4-ethoxypentadienoate (7) (374 mg, 2.1 mmol) were heated at reflux for 4 hr in 7 ml of toluene containing 2,5-di-*tert*-butylhydroquinone (20 mg). The Diels–Alder product was recrystallized from hot ethyl acetate–cyclohexane to yield 340 mg (63%) of colorless square plates: mp 92° dec; ir ($CHCl_3$) 1865 (w), 1787, 1725, 1653 cm^{-1}; nmr ($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 3 H), 2.40–2.55 (m, 2 H), 2.8–3.3 (m, 1 H), 3.80 (broad s, 2 H), 3.87 (q, J = 7 Hz, 2 H), 4.25 (q, J = 7 Hz, 2 H), 4.72 (broad s, 1 H).

Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.32; H, 6.05.

***N*-Phenyl-5-ethoxy-4-cyclohexene-1,2-dicarboximide-3-carboxylic Acid Ethyl Ester (14).**—*N*-Phenylmaleimide (173 mg, 1.0 mmol) and ethyl 4-ethoxypentadienoate (7) (170 mg, 1.0 mmol) were heated at reflux for 4.5 hr in 5 ml of toluene containing 2,5-di-*tert*-butylhydroquinone (5 mg). Evaporation of solvent left gummy material which was crystallized from hot ethyl acetate–cyclohexane to 227 mg (66%) white needles: mp 94–95° dec; ir ($CHCl_3$) 1780, 1710, 1647, 1595 cm^{-1}; nmr ($CDCl_3$) δ 1.28 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 2.5–2.8 (m, 2 H), 3.2–3.7 (m, 3 H), 3.75 (q, J = 7 Hz, 2 H), 4.18 (q, J = 7 Hz, 2 H), 4.8–5.1 (m, 1 H), 7.1–7.6 (m, 5 H).

Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.45; H, 6.08; N, 3.98.

5-Oxocyclohexane-1,2,3-tricarboxylic Acid Triethyl Ester (19).—The Diels–Adler adduct **13** (500 mg) was heated at reflux for 12 hr with 2 ml of ethanol containing *p*-toluenesulfonic acid (20 mg). Toluene (0.5 ml) was then added and the ethanol–water–toluene azeotrope distilled away until the vapor temperature fell to 65°. Another 2-ml portion of ethanol was added and the esterification cycle repeated.[16] In order to hydrolyze the ketal formed under these conditions, the oil was stirred with 2.7 *M* H_2SO_4 (2 ml) in 15 ml of tetrahydrofuran at 25° for 4 hr. The ketone was extracted into ether, washed with $NaHCO_3$, water, and brine, and dried over Na_2SO_4. Evaporation of the solvent left 580 mg (100%) of heavy oil, ir ($CHCl_3$) 1730 (broad). Short path distillation gave an analytical sample.

Anal. Calcd for $C_{15}H_{22}O_7$: C, 57.31; H, 7.06. Found: C, 57.18; H, 7.43.

5-Oxo-3-cyclohexene-1,2,3-tricarboxylic Acid Triethyl Ester (16). A. From the Enol Ether 13.—Bromine (0.082 ml, 1.5 mmol) was added to the enol ether (400 mg, 1.5 mmol) in 50 ml of dry ether at 25°; the solution blanched immediately. After the solvent had been evaporated using a rotary evaporator,

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ethanol (40 ml) and acetyl chloride (4 ml) were added to the residue; the solution was heated at reflux for 36 hr, cooled to 25°, and stirred with 4 ml of 0.4 *M* H_2SO_4 for 20 min. The ketone was extracted into ether, washed with $NaHCO_3$, water, and brine, and dried over Na_2SO_4. The product recovered from the solvent was purified for analysis by vpc at 215° to a slightly yellow oil (40%): ir ($CHCl_3$) 1730 (broad), 1695 cm^{-1}; 220 MHz nmr (CCl_4) δ 1.15–1.50 (m, 9 H), 2.45 (dd, J = 7 Hz, J = 5.0 Hz, 1 H), 2.76 (dd, J = 17 Hz, J = 3.5 Hz, 1 H), 3.43–3.50 (broad s, 1 H), 4.05–4.40 (m, 7 H), 6.64 (s, 1 H).

Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46. Found: C, 57.79; H, 6.41.

B. From the Ketone 19.—The keto triester (300 mg, 0.96 mmol) in 10 ml of acetic acid was treated with bromine (0.060 ml, 1.10 mmol) for 15 min at 25°. After neutralization with saturated $NaHCO_3$ the reaction mixture was extracted with ether. The extract was washed with water and brine, dried over Na_2SO_4, and concentrated to give 372 mg (98%) oily bromo ketone. The crude bromo ketone was dissolved in 20 ml of dimethylformamide previously flushed with nitrogen. After addition of anhydrous LiBr (500 mg) and Li_2CO_3 (500 mg), the reaction was stirred at 120° for 1 hr.[17] The mixture was diluted with cold water and extracted repeatedly with ether. The ether extracts were washed with water and brine and dried over Na_2SO_4. The ketone was purified for analysis by vpc at 215° (55%). Its ir and 220 MHz nmr spectra as well as vpc retention time were identical with those of the ketone prepared by method A.

Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46. Found: C, 57.95; H, 6.44.

5-Oxo-3-cyclohexene-1,3-dicarboxylic Acid Diethyl Ester (17).—To the enol ether **13** (400 mg, 1.50 mmol) in 20 ml of $CHCl_3$ at 0° was added bromine (0.084 ml., 1.54 mmol) in 3 ml of $CHCl_3$ over 15 min; the product was stirred with water (0.5 ml) at 25° for 4 hr. The solvents were evaporated *in vacuo* for 12 hr. The yellow glassy residue was dissolved in 2 ml of hexamethylphosphoramide and heated at 80° for 15 min. The cooled reaction was added to water and extracted with ether; the extract was washed with brine, dried over Na_2SO_4, and concentrated.

The oil dissolved in 20 ml of ethanol containing *p*-toluenesulfonic acid hydrate (50 mg) was heated for 24 hr in a Soxhlet apparatus whose extraction thimble was charged with Linde type 3A molecular sieves.[32] The solution was then concentrated, stirred for 1 hr with 0.6 *M* HCl to hydrolyze the ketal, and extracted with ether. The extracts were washed with $NaHCO_3$, water, and brine and dried over Na_2SO_4. From the concentrated product mixture the major volatile component was isolated by vpc at 220° (approximately 20%, analytically pure): ir (CCl_4) 1740, 1725, 1690 cm^{-1}; 220 MHz nmr (CCl_4) δ 1.30 (t, J = 7 Hz, 3 H), 1.37 (t, J = 7 Hz, 3 H), 2.4–2.9 (m, 5 H), 4.12 (q, J = 7 Hz, 2 H), 4.22 (q, J = 7 Hz, 2 H), 6.68 (s, 1 H).

Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.08; H, 6.68.

5-Oxobicyclo[4.2.0]octane-1-carboxylic Acid (22).—Irradiation of 3-carboxycyclohexenone (1) (200 mg) in 200 ml of benzene saturated with ethylene for 2 hr gave, after evaporation of benzene, a 90% yield of distillable oil: ir ($CHCl_3$) 3500–2500, 1700 cm^{-1}; nmr ($CDCl_3$) δ 1.8–2.8 (m, 10 H), 3.0–3.3 (m, 1 H), 10.0 (broad s, 1 H). Short path distillation gave an analytical sample.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.12; H, 7.20.

There was no change in the nmr spectrum on treatment of the adduct with 5% w/v K_2CO_3.

5-Oxobicyclo[4.2.0]octane-1-carboxylic Acid Ethyl Ester (23).—A solution of 3-carbethoxycyclohexenone (2) (2.0 g) in 200 ml of benzene was saturated with ethylene and irradiated for 3.5 hr. Evaporation of the benzene left 2.3 g (98%) of the ethylene adduct which was purified for analysis by vpc at 175°: ir (CCl_4) 1726, 1712 cm^{-1}; uv (95% ethanol) λ_{max} 290 mμ (ε 7); mass spectrum parent peak (calcd, 196.10994; found, 196.10916); nmr (CCl_4) δ 1.30 (t, J = 7 Hz, 3 H), 1.6–2.6 (m, 10 H), 3.18 (broad m, 1 H), 4.15 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.11; H, 8.25.

Exposure of the adduct to Woelm grade I neutral alumina for 30 min and to ethanolic sodium ethoxide at 25° for 12 hr left the nmr spectrum unaffected.

The ester (59 mg, 0.32 mmol) was saponified for 26 hr in 2 ml of refluxing methanol containing 1.0 *M* NaOH (0.65 ml, 0.65 mmol). The solution was acidified and extracted with ether; the extract was washed with water and brine, and dried over Na_2SO_4. Evaporation of the solvent provided 49 mg (98%) of carboxylic acid **22** as evidenced by identity of ir and nmr spectra.

5-Oxobicyclo[4.2.0]octane-1-carbonitrile (24).—A solution of 3-cyanocyclohexenone (**3**) (200 mg) in 200 ml of benzene was saturated with ethylene and irradiated for 2.5 hr; polymer formation was evident. The crude product was distilled bulb-to-bulb at 0.2 mm, and then purified by vpc at 180° to give 149 mg (62%) analytically pure oil: ir (CCl_4) 2220, 1712 cm^{-1}; mass spectrum parent peak (calcd, 149.08406; found, 149.08420); nmr (CCl_4) δ 1.8–2.8 (m, 10 H), 3.0–3.3 (m, 1 H).

Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.44; H, 7.50; N, 9.33.

The nmr spectrum of the ketone was not altered by treatment with refluxing 5% w/v K_2CO_3 for 3 hr.

The nitrile (47 mg) was heated at reflux with 1.0 *M* NaOH (2 ml) and 0.5 ml of methanol for 36 hr. The reaction mixture was acidified and extracted with ether; the extract was washed with water and brine, and dried over Na_2SO_4. Removal of solvent left 40 mg (76%) 22 as evidenced by identity of ir and nmr spectra.

7,8-Dimethyl-5-oxobicyclo[4.2.0]oct-7-ene-1-carboxylic Acid Ethyl Ester (25).—Irradiation of a solution of 3-carbethoxycyclohexenone (2) (200 mg) and 2-butyne (5.0 g) in 200 ml of benzene for 2.5 hr resulted in formation of one volatile product, which was purified by vpc at 180° to give 132 mg (50%) of analytically pure adduct: ir (CCl_4) 1727, 1702 cm^{-1}; uv (95% ethanol) end absorption, shoulder 284 mμ (ε 122); nmr (CCl_4) δ 1.29 (t, J = 7 Hz, 3 H), 1.65 (s, 6 H), 1.7–2.5 (m, 6 H), 3.3 (broad s, 1 H), 4.16 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.16; H, 8.13.

5-Oxobicyclo[4.2.0]oct-7-ene-1-carboxylic Acid Ethyl Ester (26).—Acetylene (Matheson) was freed of acetone by being passed through a Dry Ice–acetone cold trap, a mercury safety valve, an empty bottle, a large bottle of H_2SO_4, NaOH pellets, then another empty bottle;[33] it was then bubbled through a solution of 3-carbethoxycyclohexenone (2) (200 mg) in 180 ml of benzene. Irradiation for 14 hr resulted in optimum formation of volatile product; amorphous, insoluble material was also formed. The solution was filtered, concentrated, distilled bulb to bulb at 110° (0.2 mm), and purified by vpc at 180° to give 70 mg (30%) of the cyclobutene. This was further purified by vpc to give an analytical sample: ir (CCl_4) 1730, 1705 cm^{-1}; uv (95% ethanol) end absorption, shoulder 287 mμ (ε 121); nmr (CCl_4) δ 1.28 (t, J = 7, 3 H), 1.7–2.6 (m, 6 H), 3.50 (s, 1 H), 4.15 (q, J = 7 Hz, 2 H), 6.18 (s, 2 H).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.03; H, 7.45.

In a parallel experiment the crude product remaining after removal of benzene was dissolved in 40 ml of ethanol containing 5% palladium on carbon (20 mg) and hydrogenated at room temperature and 1 atm pressure. The reaction consumed 0.3 equiv of H_2 based on starting **2**. After removal of catalyst and solvent the product was distilled bulb to bulb and then purified by vpc to give cyclobutane **23** in 30% yield. Nmr and ir spectra and vpc retention time of the product were identical with those of **23** prepared above.

5-Oxo-1,3-cyclooctadiene-1-carboxylic Acid Ethyl Ester (27).—Bromine (0.112 ml, 2.05 mmol) in 5 ml of $CHCl_3$ was added at −15° over 15 min to the ketone **23** (400 mg, 2.0 mmol) in 25 ml of $CHCl_3$ containing 1 ml of acetic acid. The solution was then washed with $NaHCO_3$, water, and brine and dried over Na_2SO_4. The concentrated product was dissolved in 10 ml of dimethylformamide containing anhydrous LiBr (800 mg) and Li_2CO_4 (800 mg) and then stirred at 160° for 1.5 hr.[17] The organic material was extracted into ether, washed with water and brine, dried over Na_2SO_4, and freed of solvent. Following bulb-to-bulb distillation at 1.0 mm, the mixture was subjected to vpc at 190°. The product, isolated in approximately 20% yield as a colorless oil was analytically pure: ir (CCl_4) 1710, 1662, 1620 (weak),

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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.

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

WILLIAM C. AGOSTA[1] AND AMOS B. SMITH, III

Laboratories of The Rockefeller University, New York, New York 10021

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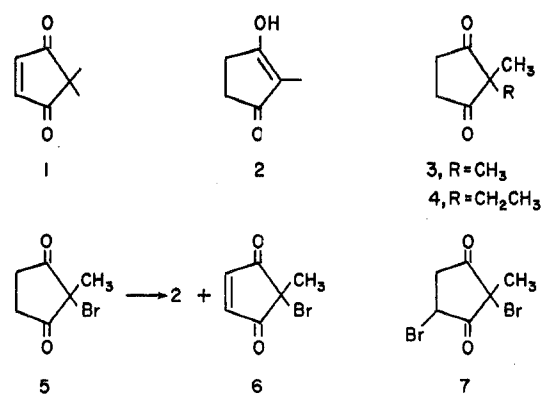
Treatment of **3** with *N*-bromosuccinimide yields **1**. Simple addition–elimination reactions of **1** and the related ketone **6** give **9**, **10**, **11**, and **14**. Enedione **1** is a sluggish dienophile relative to the parent compound **18**, but it behaves as a normal dipolarophile. The 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.

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