leaving 620 mg of a slightly yellow oil, containing **11** and **12** (ratio 27:73, yield 70%, based on NMR integration with benzene as internal reference).

Separation of the mixture of **11** and **12** was accomplished by preparative TLC (silica gel, pentane) affording 105 mg (0.3 mmol, 10% yield based on intake of **2**) of **11** as a colorless oil. In the pure state at room temperature **11** proved to be quite unstable, decomposing completely within 2 h to unidentified products, in tetrachloromethane solution at 0 °C, **11** could be kept for weeks without decomposition.

Crude **12** was obtained as a colorless, very viscous oil after preparative TLC (silica gel, dichloromethane) in about 50% yield (determined by NMR integration, with benzene as internal reference). Although stable at room temperature a complete purification could not be achieved, due to decomposition during chromatography. All efforts to crystallize **12** at lower temperatures were in vain.

Spectroscopic data of **11**: ^{1}H NMR, see Table I; ^{13}C NMR, see Table II; IR (CCl_4 solution) 1625 (C=C) cm^{-1}; mass spectrum *m/e* 356 $C_{13}H_{16}{}^{35}Cl_3{}^{79}Br$ (M^+),[41] 277 ($M^+ - {}^{79}Br$), 241 ($M^+ - {}^{79}Br - H^{35}Cl$).

12: ^{1}H NMR (C_6D_6, 35 °C) δ 4.78 (s, 2 H, CH_2Br), 4.20 (s, 2 H, CH_2CCl_3), 2.10 (s, 3 H), 2.03 (s, 3 H), 1.87 (s, 6 H); ^{13}C NMR ($CDCl_3$, 35 °C) δ 137.3, 136.6, 135.2, 134.2, 133.5, 128.0, 100.1 (CCl_3), 52.3 (t, J_{CH} = 130 Hz, CH_2CCl_3), 32.5 (t, J_{CH} = 150 Hz, CH_2Br), 19.8, 17.4, 17.1, 16.4; mass spectrum *m/e* 355.947 (calcd 355.950) $C_{13}H_{16}{}^{35}Cl_3{}^{79}Br$ (M^+), 277 ($M^+ - {}^{79}Br$), 241 ($M^+ - {}^{79}Br - H^{35}Cl$).

Kinetic Measurements of the Conversion of 7 into 9. To 30 mg (0.1 mmol) of a mixture of **7** and **8** was added 1 mL of hexadeuteriobenzene. The solution, kept at 21 °C, was measured every 6 h by ^{1}H NMR spectroscopy. When the logarithm of the concentration of **7** was plotted vs. time, a straight line (to 85% conversion) was obtained from which the rate constant was calculated to be 6.9×10^{-6} s^{-1}. No decomposition of **8** was observed.

Behavior of 7 and 8 in Nitromethane and Methanol Solution. When a mixture of **7** and **8** was dissolved in perdeuterionitromethane, the ^{1}H NMR spectrum taken after mixing displayed only peaks due to **8** and **9**, showing that the conversion of **7** into **9** was complete within 10 min, whereas **8** was unaffected.

A mixture of **7** and **8**, left overnight in methanol solution, afforded, after removal of the solvent in vacuo, a (1:1) mixture of **28** and **9** (90% yield, determined by ^{1}H NMR with benzene as internal reference); **8** had remained unchanged.

Synthesis of 1-(2,2,2-Trichloroethyl)-2-methoxymethyl-3,4,5,6-tetramethylbenzene (28). A total of 160 mg (0.5 mmol) of **9** was treated with 200 mg (1 mmol) of silver perchlorate in 20 mL of methanol overnight. Soon a white precipitate (silver chloride) was formed. After filtration and evaporation of the solvent, the residue was extracted with pentane and the pentane solution was filtered and dried over sodium sulfate. Removal of the solvent gave a colorless oil, containing **28** in 70% yield (based on NMR integration, with benzene as internal reference). Further purification was achieved by preparative TLC (silica gel, dichloromethane), affording 80 mg of **28** as a colorless oil (50% yield, based on intake of **9**). Compound **28** was prepared in the same way from **12**, also in 50% yield (silver bromide being precipitated).

Spectroscopic data of **28**: ^{1}H NMR (CCl_4, 35 °C) δ 4.59 (s, 2 H, CH_2OCH_3), 4.31 (s, 2 H, CH_2CCl_3), 3.28 (s, 3 H, OCH_3), 2.40 (s, 3 H), 2.24 (s, 6 H), 2.22 (s, 3 H); IR 1610 (C=C) cm^{-1}; mass spectrum *m/e* 308.051 (calcd 308.050) $C_{14}H_{19}{}^{35}Cl_3O$ (M^+), 276 ($M^+ - CH_3OH$), 272 ($M^+ - H^{35}Cl$).

Treatment of a Mixture of 5 and 6 with Sodium Perchlorate. A mixture of **5** and **6** was stirred overnight in tetrahydrofuran in the presence of a small excess (1.2 equiv) of silver perchlorate at room temperature, silver bromide being precipitated. Excess silver perchlorate was then removed by adding an aqueous solution of sodium chloride, followed by filtration of the precipitate. The resulting solution was extracted with pentane, and the latter was dried over sodium sulfate. Evaporation of the solvent afforded, according to NMR, a mixture of **6** and unidentified products, no **5** being present anymore.

Registry No. **1**, 56745-77-8; **2**, 50590-86-8; **3**, 70130-71-1; **4**, 70190-91-9; **5**, 70130-72-2; **6**, 70190-92-0; **7**, 70130-73-3; **8**, 70190-93-1; **9**, 70130-74-4; **11**, 70130-75-5; **12**, 70130-76-6; **28**, 70130-77-7; tetrachloromethane, 56-23-5; bromotrichloromethane, 75-62-7.

(41) The intensity of the parent peak was too low to be used for an exact mass determination.

Bicyclo[4.2.0]oct-3-ene-7,8-dione and Its Monoenol Silyl Ether

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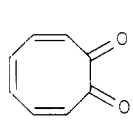
Received January 16, 1979

The readily available enediol bis(trimethylsilyl) ether **7** has been demonstrated to be a useful intermediate in the synthesis of free bicyclo[4.2.0]oct-3-ene-7,8-dione (**3**) as well as a protected form, the monoenol silyl ether **6**. Bromination of **7** gave small amounts of both **3** and **6**. If bromination was followed by addition of triethyl amine, **6** could be obtained in 41% yield. Other products isolated from the bromination of **7**, depending on the conditions, were the cyclobutene-1,2-dione **13**, the benzocyclobutene-1,2-dione **15**, and the benzocyclobutenol silyl ether **16**. The best route to **3** involved the oxidative desilylation of **7** by means of DDQ in dioxane.

Rather unexpectedly, the theoretically interesting molecule 3,5,7-cyclooctatriene-1,2-dione **1** proved to be an



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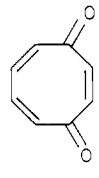


2

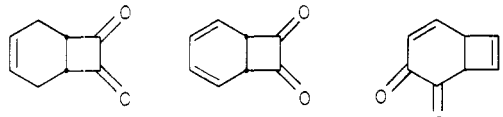
elusive synthetic target. Much effort has been expended on this problem, by a number of groups,[1] which only saw fruition in early 1977 with the successful generation of **1** in solution by Oda, Oda, Miyakoshi, and Kitahara.[1e] The corresponding 1,4-isomer **2** had been prepared earlier by

(1) Complete surveys of the early work on the attempted syntheses of **1** are found in the following: (a) P. Gund, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1967; *Diss. Abstr. B*, **28**, 3642 (1968); *Chem. Abstr.*, **69**, 35531 (1968); (b) J.-H. Tsao, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1974; *Diss. Abstr. B*, **35**, 4401 (1975); *Chem. Abstr.*, **83**, 42891 (1975). For collected references to the more recent work, see: (c) P. A. Chaloner and A. B. Holmes, *J. Chem. Soc., Perkin Trans. 1*, 1838 (1976); (d) T. R. Kowar and E. LeGoff, *J. Org. Chem.*, **41**, 3760 (1976); (e) M. Oda, M. Oda, S. Miyakoshi, and Y. Kitahara, *Chem. Lett.*, 293 (1977).

0022-3263/79/1944-2387$01.00/0

the same group.[2] Neither compound gave any evidence of special character which could be attributed to aromaticity, and in fact 1 proved to be so unstable that it could not be isolated in the free state but only observed spectroscopically and on the basis of its reactivity in solution.

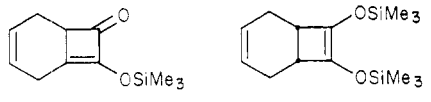
In view of the successful generation of 1 by Oda and co-workers, we wish now to report our own studies in this area by describing convenient syntheses of bicyclo[4.2.0]oct-3-ene-7,8-dione (3), a potential precursor of 4,



3 4 5

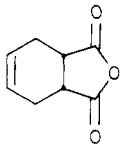
which, as a valence isomer of 1, was expected to open readily to the eight-membered diketone. Previously, the isomeric 5 was prepared and shown not to open to 1 on thermolysis.[3] Compound 3 and its monoprotected enol silyl ether 6, also described in the present paper, are of interest in themselves and as precursors of other compounds in the bicyclo[4.2.0] series in addition to 4.

As a convenient intermediate in the synthesis of 3 and 6, we prepared the known bis(trimethylsilyl) ether 7 by



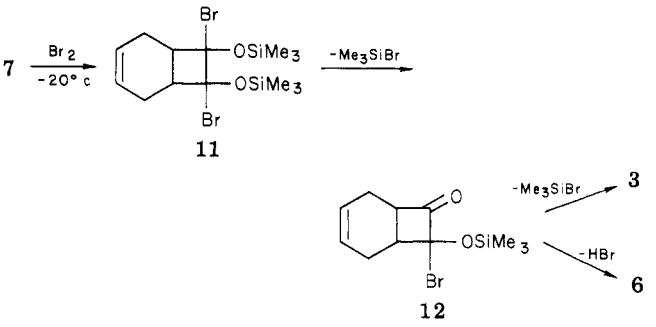
6 7

the method of Bloomfield.[4] Conversion of monocyclic bis(trimethylsilyloxy)cyclobutenes to 1,2-diones had been carried out previously by treatment with bromine[5] or by hydrolysis to the acyloin followed by oxidation.[6] Addition of a solution of 1 equiv of bromine in carbon tetrachloride to a solution of 7 at −20 °C gave a low yield (about 7%) of diketone 3 along with the monoenol ether 6 in 41% yield. The diketone proved to be difficult to handle. If insufficient care attended its purification, the crude substance underwent rapid conversion to a polymer-like material which showed infrared carbonyl absorption at 1710 cm^{-1}, indicative of ring opening. The structure of 3 was confirmed by elemental and spectroscopic analysis. The infrared spectrum showed carbonyl absorption at 1795 and 1774 cm^{-1}, typical of a four-ring α-diketone.[7] Also present was a very weak absorption at 3545 cm^{-1}, indicating the presence of a small amount of enol tautomer. The NMR spectrum showed the symmetrical features expected for this structure, resembling closely that of the model anhydride 8.[8]



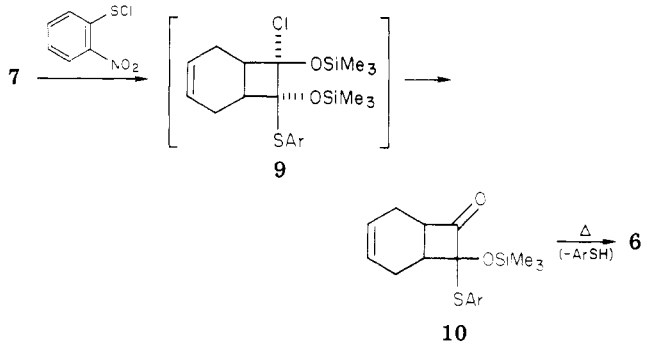
8

Scheme I



11 12

The second compound 6 obtained as the major product in the bromine reaction with 7 also underwent rapid decomposition in the impure state. Repeated distillation gave a homogeneous product whose structure was established on the basis of the NMR spectrum which exhibited a sharp 2-proton multiplet at δ 5.47 (olefinic protons), a 3-proton multiplet at 2.7–2.95 (bis(allylic) and bridgehead protons), a 2-proton multiplet at 2.0 (allylic protons), and a singlet of area 9 at 0.12 for the trimethylsilyl group. The infrared spectrum showed strong bands at 1768 and 1658 cm^{-1} due to the carbonyl and olefinic enol ether functions, respectively. An alternate synthetic route to 6 is also consistent with this formulation. Addition of sulfenyl chlorides to olefins is a well-known reaction which proceeds via episulfonium ion intermediates to yield β-halosulfides. With trimethylsilyl enol ethers, β-keto sulfides are formed via loss of trimethylsilyl chloride from the initial chlorosulfide adduct.[9] Treatment of 7 with



9 10

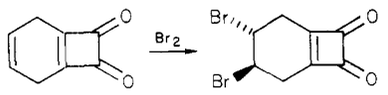
o-nitrophenylsulfenyl chloride gave in 20% yield the adduct 10. Distillation of 10 was accompanied by the elimination of o-nitrobenzenethiol. The stereochemistry of 10 was not established but is believed to represent the exo-arylthio isomer.[10]

The addition of bromine to the more nucleophilic double bond of the enediol bis(trimethylsilyl) ether 7 is probably followed by a two-stage elimination of trimethylsilyl bromide to give the α-diketone (Scheme I). Unfortunately, the reaction was not easily reproducible aside from the fact that the yields were very poor. This complication may have been due to the fact that hydrogen bromide, liberated in the reaction, can cause decomposition of the starting material and both of the reaction products. When excess triethylamine was added to the reaction mixture during workup, only 6 was obtained. In this case, 3 was either destroyed or converted to 6 by reaction with the

(2) M. Oda, Y. Kayama, H. Miyazaki, and Y. Kitahara, *Angew. Chem.*, 87, 414 (1975).
(3) M. Oda, M. Oda, and Y. Kitahara, *Tetrahedron Lett.*, 839 (1976); *Chem. Commun.*, 446 (1976).
(4) J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968).
(5) H. Wynberg, S. Reiffers, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 89, 982 (1970); *Synthesis*, 209, 211 (1971).
(6) (a) J. J. Bloomfield, J. R. S. Irelan, and A. P. Marchand, *Tetrahedron Lett.*, 5647 (1968); (b) A. DeGroot, D. Oudman, and H. Wynberg, *ibid.*, 1529 (1969); (c) J. M. Conia and J. M. Denis, *ibid.*, 3545 (1969).
(7) J. J. Bloomfield and R. E. Moser, *J. Am. Chem. Soc.*, 90, 5625 (1968).
(8) A. C. Cope and E. C. Herrick, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 890.
(9) S. Murai, Y. Kuroki, K. Hasegawa, and S. Tsutsumi, *Chem. Commun.*, 946 (1972).
(10) Compare: (a) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, 90, 2075 (1968); 88, 2866 (1966); (b) H. C. Brown, J. H. Kawakami, and K. T. Liu, *ibid.*, 95, 2209 (1973); (c) H. C. Brown and K. T. Liu, *ibid.*, 92, 3502 (1970).

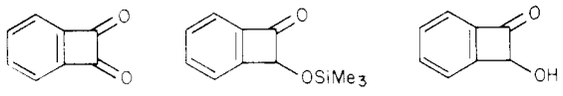
liberated trimethylsilyl bromide under the basic conditions.

Under these basic conditions, there was also isolated in about 5% yield the new cyclobutene-1,2-dione derivative **13**. Assignment **13** was made on the basis of spectral data



13 **14**

and confirmed by treatment with bromine which the known dibromide **14**.[11] Formation of **13** can be rationalized as arising from the monodesilylated product **12** by bromination α to the keto function followed by loss of trimethylsilyl bromide and dehydrobromination or from **6** by bromine addition followed by the same sequence of reactions. Treatment of **6** with bromine in a separate experiment gave the same diketone **13**. However, when the reaction with **7** was repeated by treatment with a fourfold excess of triethylamine following addition of 2 equiv of bromine, **13** was not formed. Instead, two aromatic compounds, **15** and **16**, were isolated in yields of 1.7

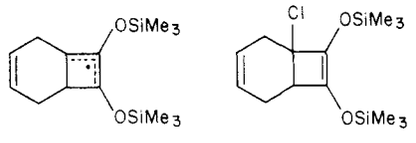


15 **16** **17**

and 22%, respectively. The former has been described previously by Cava.[12] Assignment of structure **16** was based on its rapid hydrolysis to the corresponding acyloin **17** followed by reduction of the latter by means of lithium aluminum hydride to the known cis 1,2-diol.[12]

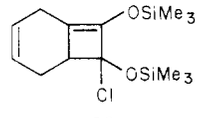
Although the course of the reaction leading to the formation of **15** and **16** is obscure, it is possible to rationalize the results readily by a series of steps involving loss of trimethylsilyl bromide or hydrogen bromide with aromatization as a potent driving force.

Treatment of **7** with sulfuryl chloride gave **3** in very low yield. With *tert*-butyl hypochlorite at −45 to −30 °C under irradiation by means of a sunlamp, the α,β-unsaturated monoketone **6** was obtained in 45% yield. This suggests involvement of the free radical **18** in the formation of the



18 **19**

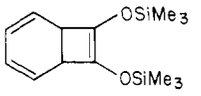
presumed intermediate chlorides **19** and/or **20**. *tert*-Butyl



20

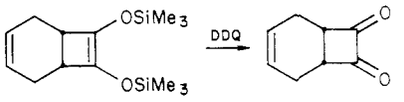
hypochlorite is reported to be highly selective in free-radical halogenation (tertiary > secondary > primary)[13] and does not normally add to olefins.[14] Facile loss of trimethylsilyl chloride from either **19** or **20** would lead to **6**.

Finally, an excellent method for the synthesis of **3** was developed by accident during an attempt to prepare triene **21** from **7** by dehydrogenation by means of DDQ. Instead



21

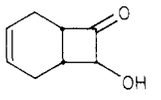
of yielding the expected product, this reaction gave after a 2-h period of reflux in dioxane a 37% yield of **3**. In



7 **3**

benzene with DDQ or in dioxane by substitution of DDQ by chloranil no reaction took place. No mechanistic studies of this interesting desilylative oxidation were carried out although it may be related to the oxidative desilylation of monoenol trimethylsilyl ethers described recently by Murai and co-workers.[15] Following initial conversion to **6**, the byproduct hydroquinone would be expected to cause deblocking of the trimethylsilyloxy group to give **3**.

Prior to the development of this convenient route to **3**, we examined the possible oxidation of acyloin **22**. De-



22

blocking of **7** was previously effected by means of methanol or ethanol.[4] In our hands, this method failed although hydrolysis proceeded well (45%) upon refluxing for 5–6 h in 20% aqueous acetone.[16] On the basis of the NMR spectrum and comparison with the spectrum of 7-*endo*-chlorobicyclo[3.2.0]hept-2-en-6-one, we have assigned the endo configuration to **22**.[17] Thus protonation of the ene diol intermediate or its equivalent mono trimethylsilyl ether occurs from the less hindered side of the molecule. Preliminary attempts to oxidize the acyloin **22** were abandoned after development of the oxidative desilylation route to **3**.

Experimental Section[18]

Bicyclo[4.2.0]oct-3-ene-7,8-dione (3). A solution of 11.3 g of **7** and 10.2 g of DDQ in 55 mL of pure dioxane was refluxed under N_2 for 2 h. The mixture was cooled and filtered, and the residue was washed with dry CCl_4. The combined filtrate and washings were concentrated by rotary evaporation under reduced pressure on a water bath (45 °C), and 200 mL of dry CCl_4 was added. The CCl_4 solution was again filtered and the filtrate was evaporated again in the same manner. The resulting red-colored residue was distilled in a short path apparatus. After a small forerun, an orange oil was distilled at 45–50 °C (0.5 mm) and solidified in the condenser (air cooling). The tacky solid (3.5 g) was pressed between filter paper to remove most of the oily material, washed with a small amount of dry hexane, and quickly

(11) T. R. Kowar and E. LeGoff, *Synthesis*, 212 (1973).
(12) M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Am. Chem. Soc.*, **85**, 2076 (1963).
(13) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).
(14) E. S. Huyser, *Synthesis*, 7 (1970).
(15) I. Ryu, S. Murai, Y. Hatayama, and N. Sonoda, *Tetrahedron Lett.*, 3455 (1978).
(16) For previous success with the aqueous acetone method, see ref 6c and H. M. Fischler, H.-G. Heine, and W. Hartmann, *Tetrahedron Lett.*, 857 (1972).
(17) The same conclusion was reached independently by E. Casadevall and Y. Pouet [*Tetrahedron*, **31**, 757 (1975)]. These workers obtained **22** only as a viscous yellow oil whereas we obtained it in crystalline form. For similar reactions carried out on the analogous trans-fused [4.2.0] system, see E. Casadevall and Y. Pouet, *Tetrahedron*, **34**, 1921 (1978).
(18) Melting points and boiling points are uncorrected. Infrared spectra were obtained on Beckmann IR-10, Perkin-Elmer 237B, and Perkin-Elmer 727 instruments, and NMR spectra were obtained on Varian A-60 and Perkin-Elmer R-12 instruments with Me_4Si as internal standard unless otherwise noted. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory under the direction of Charles Meade and Gregory Dabkowski and associates.

transferred to a sublimation apparatus. Two consecutive sublimations at 40–50 °C (0.1 mm) gave 2.00 g (36.8%) of the diketone **3** as orange prisms: mp 73–74 °C; IR (CCl_4) 1795, 1774 cm^{-1} (C=O); NMR (CCl_4) δ 2.55 (m, 4, allylic), 3.4 (m, 2, bridgehead), 5.8 (m, 2, vinylic). Attempted recrystallization from dry ether resulted in polymerization within a few minutes to give a yellow powder: mp ca. 145 °C; IR ($CHCl_3$) 1710 cm^{-1}.

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92; Found: C, 70.22; H, 6.25.

8-(Trimethylsilyloxy)bicyclo[4.2.0]octa-3,8-diene-7-one (6). A magnetically stirred solution of 28.25 g of **7** in 190 mL of dry CCl_4 was cooled to −25 to −20 °C by means of dry ice–acetone. To the solution was added dropwise under N_2 a solution of 16 g of Br_2 in 120 mL of dry CCl_4. The addition was completed as rapidly as the Br_2 disappeared (1.5 h). After removal of the cooling bath, the solution was allowed to warm to −5 °C, and 22 g of triethylamine in 45 mL of dry CCl_4 was added over a period of 20 min during which time a white solid separated. The mixture was stirred for 4–5 h and filtered to remove Et_3N·HBr (25 g). The filtrate, from which additional amounts of white solid kept separating, was filtered several times until a clear solution was obtained. Evaporation of the solvent and distillation of the residue gave 12.1 g of orange liquid, bp 68–70 °C (0.1 mm), which was redistilled twice, the second time using a 10-in. Vigreaux column, to give 8.60 g (41.3%) of the pure ketone as an orange oil: bp 61–62 °C (0.1 mm); IR (neat) 1768 cm^{-1} (C=O), 1658 cm^{-1} (C=C); NMR (CCl_4, Me_4Si external reference) δ 0.12 (s, 9, $SiMe_3$), 2.0 (m, 2, allylic), 2.7–2.95 (m, 3, bis(allylic) and bridgehead protons), and 5.47 (m, 2, vinylic). Because of the instability of the material, a perfectly satisfactory analytical sample could not be obtained.

Anal. Calcd for $C_{11}H_{16}O_2Si$: C, 63.42; H, 7.74; Si, 13.48. Found: C, 62.17; H, 7.66; Si, 13.25.

3,6-Dihydrobenzocyclobutadienoquinone (13). The method described above for compound **6** was repeated using 35.3 g of **7**, 20 g of Br_2, and 25.6 g of NEt_3 except that stirring was continued after addition of the base for 1.5 days. The mixture was diluted with 150 mL of CH_2Cl_2 and washed quickly with two 150-mL portions of cold $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with three 100-mL portions of CH_2Cl_2. The combined extracts were washed quickly with 100 mL of cold 1.5 N HCl, 100 mL of cold saturated $NaHCO_3$, 100 mL of cold H_2O, and 50 mL of saturated NaCl solution. The dried ($MgSO_4$) solution was concentrated to give a red-brown oil from which yellow crystals began to separate on cooling (−5 °C). A small amount of CCl_4 was added, and the mixture was stored overnight in a refrigerator (−5 °C) and filtered to give 0.85 g of the crude diketone which after crystallization from CH_2Cl_2–Et_2O (1:3; v/v) gave 0.80 g (4.8%) of the pure material as yellow crystals: mp 139–140 °C; IR ($CHCl_3$) 1792, 1755 cm^{-1} (C=O), 1588 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.4 (s, 4, bis(allylic)) and 5.85 (s, 2, vinylic). An analytical sample was obtained by sublimation at 100 °C (0.15 mm), mp 139–140 °C.

Anal. Calcd for $C_8H_6O_2$: C, 71.63; H, 4.51. Found: C, 71.84; H, 4.59.

From the CCl_4 filtrate there was obtained 7.2 g (27.8%) of **6** in the manner described above.

3,4-Dibromobicyclo[4.2.0]-1(6)-ene-7,8-dione (14). To a solution of 134 mg of **13** in 15 mL of dry CH_2Cl_2 maintained at −78 °C was added with stirring and protection from moisture 160 mg of Br_2 in 18 mL of dry CH_2Cl_2 over a period of 15 min. The resulting solution was allowed to warm to room temperature over a period of 1 h. After removal of the solvent under reduced pressure at room temperature, there was obtained a solid which upon extracting with a small amount of $CHCl_3$ to remove the starting material gave 150 mg of **14**, mp 151 °C. Recrystallization from CH_2Cl_2–cyclohexane (1:4 v/v) gave 140 mg (47.6%) of the pure diketone as milk-white crystals: mp 155–156 °C (lit.[11] mp 161–164 °C); IR ($CHCl_3$) 1795 (C=O), 1615 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.7 (m, 4, CH_2), 4.7 (m, 2, CHBr). The infrared and NMR spectra were identical with those reported for an authentic sample.[11]

Benzocyclobutadienoquinone (15) and α-(Trimethylsilyloxy)benzocyclobutenone (16). A solution containing 21.2 g of **7** in 200 mL of dry CH_2Cl_2 was cooled to −75 to −65 °C by means of a dry ice–acetone bath. Under an atmosphere of N_2, there was added with stirring 24 g of Br_2 in 150 mL of dry CH_2Cl_2 over a period of 105 min. The red-orange solution was allowed to warm slowly to room temperature and was stirred for an additional 1.5 h. After the solution was cooled to 5 °C, 45 mL of NEt_3 in 40 mL of dry CH_2Cl_2 was added with vigorous stirring over a period of 10 min. The mixture was refluxed for 1.5 days, cooled, and filtered to remove Et_3N·HBr (14 g). The filtrate was washed with 100 mL of H_2O, 100 mL of saturated $NaHCO_3$, three 100-mL portions of 1 N HCl, 50 mL of saturated $NaHCO_3$, three 100-mL portions of H_2O, and 100 mL of saturated NaCl solution. The dried ($MgSO_4$) solution was rotary evaporated at 25 °C to give 9.5 g of brown oil which was distilled in a short-path apparatus to remove tarry materials. There was obtained 4.10 g of yellow oil, bp 72–76 °C (0.15–0.2 mm), admixed with some yellow crystals. The mixture was dissolved in a small amount of CH_2Cl_2, and the solution was treated dropwise with Skelly B (bp 60–70 °C) until yellow crystals separated. After being cooled in a refrigerator (−10 °C) overnight, the mixture was filtered to give 0.34 g of crude **15**, mp 112–120 °C. Chromatography on silica gel (grade 1, Fisher Scientific) in a 2 × 45 cm column using benzene–Et_2O (4:1; v/v) as eluant gave 0.165 g (1.7%) of the pure diketone, mp 129–130 °C (lit.[12] mp 130–131 °C). The IR and NMR spectra were identical with those reported for an authentic sample.[12,19]

The original Skelly B–CH_2Cl_2 filtrate from which the crude sample of **15** had separated was evaporated, and the residue was distilled to give 3.42 g (22.0%) of **16** as a yellow oil: bp 70–71.5 °C (0.08 mm); IR (CCl_4) 1774 cm^{-1} (C=O); NMR (CCl_4) δ 0.2 (s, 9, $SiMe_3$), 5.66 (s, 1, CH), 7.55 (AA′, BB′, 4, Ar). The silyl ether was very sensitive to moisture which converted it to the corresponding acyloin. Its identity was established by conversion to the hydrolysis product (see below).

α-Hydroxybenzocyclobutenone (17). A solution of 0.83 g of **16** in 5 mL of CCl_4 was allowed to evaporate slowly to dryness in an open beaker. Sublimation of the waxlike residue (0.54 g) at 54 °C (0.2–0.3 mm) gave 0.50 g (92%) of the α-hydroxy ketone as white crystals: mp 56.5–58.5 °C; IR ($CHCl_3$) 3598, 3404 (OH), 1763 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.45 (broad s, 1, OH), 5.75 (s, 1, CH), 7.55 (AA′BB′, 4, Ar). The analytical sample, mp 57–58.5 °C, was obtained by an additional sublimation.

Anal. Calcd for $C_8H_6O_2$: C, 71.63; H, 4.51. Found: C, 71.51; H, 4.15.

Reduction of α-Hydroxybenzocyclobutenone (17) to *cis*-1,2-Dihydroxybenzocyclobutene. To a rapidly stirred slurry of 35 mg of $LiAlH_4$ in 10 mL of dry ether was added dropwise a solution of 150 mg of **17** in 17 mL of the same solvent at 0 °C under N_2. The mixture was stirred for 20 min at room temperature, cooled, and treated with 0.5 mL of saturated aqueous Na_2SO_4. When the mixture had turned completely white, it was filtered. The solid was washed with benzene–Et_2O (1:3; v/v), and the dried ($CaSO_4$) filtrate was rotary evaporated at room temperature to give a solid which was crystallized from CH_2Cl_2–pentane (1:3; v/v) to give 10 mg (6.7%) of the diol as fine white needles, mp 129–130 °C (lit.[12] mp 129–130 °C). The infrared spectrum was identical with that of an authentic sample.

8-(Trimethylsilyloxy)-8-(*o*-nitrophenylthio)bicyclo[4.2.0]oct-3-en-7-one (10). A solution of 14.13 g of **7** in 70 mL of dry CH_2Cl_2 was treated dropwise (40 min) under N_2 with a solution of 9.48 g of (*o*-nitrophenyl)sulfenyl chloride[20] in 50 mL of dry CH_2Cl_2 while maintaining the temperature between −35 and −30 °C with a dry ice–acetone bath. The mixture was allowed to warm to room temperature over a period of 15 min and rotary evaporated from a water bath at 25 °C. Addition of ether to the brown residue gave a yellow powder (1 g, mp 193–5 °C) identified as *o*-nitrophenyl disulfide.[20] The ether filtrate was rotary evaporated at room temperature, and the residue was covered with hexane and treated with small amounts of ether until it solidified to give 8 g of yellow solid, mp 82–92 °C.[21] Two recrystallizations from absolute EtOH (50–60 °C) gave 3.53 g (19.4%) of the ketone as yellow needles: mp 102–103 °C; IR

(19) M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, **92**, 1605 (1970).

(20) (a) M. T. Bogert and A. Sull, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 220; (b) M. H. Hubacher, *ibid.*, Collect. Vol. II, 1943, p 455.

(21) In one run an attempt was made at this point to purify the crude solid by distillation. The only materials obtained were *o*-nitrobenzenethiol along with **6** (30%), bp 60–62 °C (0.15 mm).

($CHCl_3$) 1780 (C=O), 1515, 1335 cm^{-1} (NO_2); NMR ($CDCl_3$; Me_4Si external reference) δ 0.25 (s, 9, $SiMe_3$), 2.4 (m, 4, CH_2), 2.6–3.0 (m, 1, CHC(OSiMe$_3$)), 3.6–4.1 (m, 1, CHC=O), 5.85 (m, 2, vinylic), 7.2–8.4 (m, 4, Ar). The material decomposed within a few hours on standing in air. An analytical sample was obtained by recrystallization from Et_2O–pentane (1:8; v/v) at −5 °C, mp 102–3 °C.

Anal. Calcd for $C_{17}H_{21}NO_4SSi$: C, 56.17; H, 5.82; S, 8.82. Found: C, 56.07; H, 5.72; S, 8.78.

Treatment of 7,8-Bis(trimethylsilyloxy)-*cis*-bicyclo[4.2.0]octa-3,7-diene with *tert*-Butyl Hypochlorite. A solution of 5.65 g of **7** and 2.17 g of *t*-BuOCl[22] in 60 mL of spectral grade CCl_4 was irradiated at −45 to −30 °C by means of a GE 275-W sunlamp. After 100 min, the sunlamp was removed, and the solution was warmed to room temperature. Rotary evaporation of the solvent (40 °C) followed by distillation of the residue gave 2.0 g (45%) of **6** as an orange oil, bp 83–85 °C (0.4–0.45 mm), identified by infrared and NMR spectral comparison with an authentic sample prepared as described above.

8-Hydroxybicyclo[4.2.0]oct-3-en-7-one (22). A solution of 14.2 g of **7** in 50 mL of 20% aqueous acetone (v/v) was refluxed under N_2 for 5–6 h, cooled, and extracted with several 30-mL portions of ether. The ether extracts were dried (Na_2SO_4) overnight in a refrigerator, filtered, and rotary evaporated at room temperature to give an oily solid. A solution of the crude solid in 12 mL of ether was cooled in dry ice–acetone for several hours, and the supernatant liquid was decanted. The resulting solid was purified by solution in Et_2O and addition of hexane to the cloud point. Cooling at −20 °C for several hours gave 3.15–3.25 g (43–47%) of **22** as white crystals: mp 59–60 °C; IR ($CHCl_3$) 3595, 3450 (OH), 1775 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.21 (m, 4, CH_2), 2.5–3.3 (m, 2, bridgehead), 3.7 (broad s, shifting with concentration, 1, OH), 4.95 (dd, J = 9.5, 3 Hz, 1, CHOH), 5.7 (m, 2, vinylic). These spectral data agree with those reported by Casadevall and Pouet.[17]

(22) M. T. Mintz and C. Walling, *Org. Synth.*, **49**, 9 (1969).

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Registry No. **3**, 70355-61-2; **6**, 70355-62-3; **7**, 18014-24-9; **10**, 70355-63-4; **13**, 70355-64-5; **14**, 70355-65-6; **15**, 6383-11-5; **16**, 70355-66-7; **17**, 70355-67-8; **22**, 56402-15-4; *cis*-1,2-dihydroxybenzocyclobutene, 70355-68-9; (*o*-nitrophenyl)sulfenyl chloride, 7669-54-7.

Cycloaddition of Alkynes with *o*-Chloranil: A Route to Halogenated Naphthalenes and Biphenyls

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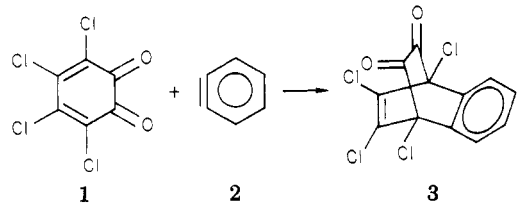
A synthetic route to chlorinated aromatic glyoxylic acids and analogues has been developed via nucleophilic scission of the α-diketone bridge of the Diels–Alder cycloadducts of *o*-chloranil and alkynes. The adduct of *o*-chloranil and benzyne produced 2,3,4-trichloronaphthalene-1-glyoxylic acid on treatment with aqueous sodium hydroxide. X-ray diffraction confirmed the product structure. The adduct of *o*-chloranil and phenylacetylene produced two glyoxylic acid isomers upon treatment with hydroxide. The major "meta" isomer, 2,3,4-trichlorobiphenyl-5-glyoxylic acid, was separated by fractional recrystallization from the minor "ortho" isomer, 3,4,5-trichlorobiphenyl-2-glyoxylic acid. The latter acid was converted to a trichlorofluorenone upon heating. Both biphenylglyoxylic acids were converted to methyl esters and to known biphenyltrichlorocarboxylates. Applicability of the route to variously substituted halogenated aromatics appears likely.

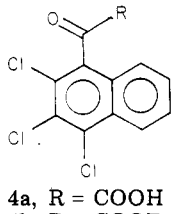
Adducts formed from the Diels–Alder cycloaddition of *o*-chloranil, **1**, and a number of alkynes have been observed



1 **2** **3**

to occur principally across the homodiene. In contrast, cycloaddition with many alkenes occurs across the dicarbonyl.[1] Applications of this reaction in synthesis indicate that the reaction has potential for the formation of chlorinated aromatic systems, including specific isomers of the polychloro- and polybromobiphenyls, although this potential has not been demonstrated. Aromatization and loss of the dicarbonyl bridge by thermal or photolytic action upon adducts such as **3** is the most direct route. A second possibility is nucleophilic attack upon a carbonyl with concomitant ring opening. This course is demonstrated here for the cycloadducts of *o*-chloranil with benzyne and phenylacetylene.

Hydrolysis of the adduct **3**, formed between *o*-chloranil and benzyne, with 5% aqueous sodium hydroxide, produced an aromatic, yellow, crystalline carboxylic acid. The mass spectrum revealed an isotopic pattern for a trichloro derivative, with the largest mass observed at m/e 257. The assignment of the structure **4a** to the product was consistent with the appearance of an acidic ^1H NMR signal and with the formation of the corresponding acylium ion



4a, R = COOH
4b, R = COOEt
4c, R = COOMe
5, R = OMe

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