(7.7 mL, 100 mmol) in 1,2-dichloroethane (50 mL). A rapid evolution of methane occurs. After the reaction mixture is stirred for 12 h at room temperature, it is treated with iodine[6] (30.45 g, 120 mmol) in THF (100 mL) at −30 °C and then with saturated aqueous K_2CO_3 (10 mL) at 0 °C. The heterogeneous mixture is thoroughly extracted with hexane (4 × 50 mL) and ether (2 × 50 mL), and the extract is dried over $MgSO_4$. After evaporation of the solvents, a one-fifth aliquot of the crude 4-iodo-3-methyl-3-buten-1-ol is treated at room temperature with *tert*-butyldimethylsilyl chloride (3.93 g, 26 mmol), triethylamine (4.23 mL, 28 mmol), and 4-(dimethylamino)pyridine (0.20 g, 1.6 mmol) in methylene chloride (40 mL.)[16] After being stirred overnight, the reaction mixture is diluted with ether (50 mL), washed with water and aqueous NH_4Cl, and dried over Na_2SO_4. After evaporation of solvents, the crude product is purified by flash chromatography (3% EtOAc/hexane) to give **12** in 87% yield (5.68 g, 98% GLC purity): $n^{23}{}_D$ 1.4850; IR (neat) ν 1614 (w), 1310 (m), 1219 (s), 1052 (s), 756 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.3 (s, 6 H), 0.86 (s, 9 H), 1.83 (s, 3 H), 2.41 (t, J = 7 Hz, 2 H), 3.68 (t, J = 7 Hz, 2 H), 5.96 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 2.51, 18.17, 24.22, 25.85, 42.59, 61.28, 76.47, 144.55. High-resolution mass spectrum m/e calcd for $C_{11}H_{23}OSiI$ ($-C_4H_9$): 268.986. Found: 268.986.

Acknowledgment is made to the National Institutes of Health, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. (*E*)-**5**, 78592-73-1; (*E*)-**6**, 78592-74-2; (*E*)-**8**, 78592-75-3; (*E*)-**11**, 78592-76-4; (*E*)-**12**, 78592-77-5; (*E*)-**13**, 78592-78-6; (*E*)-**14**, 78592-79-7; (*E*)-**17**, 78592-80-0; 1-octyn-3-ol, 818-72-4; 2-methyl-1-octen-3-ol, 37156-89-1; (*E*)-(3-methyl-3-octenoxy)-*tert*-butyldimethylsilane, 78592-81-1; 3-butyn-1-ol, 927-74-2; 3-butynoxy-*tert*-butyldimethylsilane, 78592-82-2; 4-iodo-1-butyne, 43001-25-8; 3-butynyl phenyl sulfide, 10575-06-1; 2-propyn-1-ol, 107-19-7; 2-propynyl phenyl sulfide, 5651-88-7; methyl (*E*)-5-hydroxy-3-methyl-2-pentenoate, 35066-36-5; ethyl (*E*)-5-iodo-3-methyl-2-pentenoate, 78592-83-3; (*E*)-3-methyl-5-(thiophenoxy)-2-pentenoic acid, 78592-84-4; (*E*)-3-methyl-5-(thiophenoxy)-2-penten-1-ol, 78592-85-5; (*E*)-1-iodo-2-methyl-3-(thiophenoxy)-1-propene, 71570-22-4; (*E*)-3-methyl-4-(thiophenoxy)-2-buten-1-ol, 78592-86-6; zirconocene diiodide, 1298-41-5; Cl_2ZrCp_2, 1291-32-3.

Supplementary Material Available: Spectral and analytical data (2 pages). Ordering information is given on any current masthead page.

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(16) S. K. Chaudhary and O. Hernandez, *Tetrahedron Lett.*, 99 (1979).

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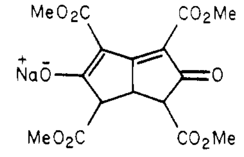
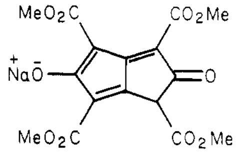
Bicyclo[3.3.0]octa-1,5-diene-3,7-dione

Summary: Bicyclo[3.3.0]octa-1,5-diene-3,7-dione (**5**) has been prepared by the hydrolysis–decarboxylation of tetramethyl 3-hydroxy-7-oxobicyclo[3.3.0]octa-1,3,5-triene-2,4,6,8-tetracarboxylate sodium salt (**2**), which was obtained in one step from "Vossen's Red Salt" (**1**).

Sir: The "Red Salt" (**1**), first isolated by Schroeter and Vossen,[1] has been investigated by several workers as a possible precursor of compounds in the bicyclo[3.3.0]octane and pentalene series.[2]



1



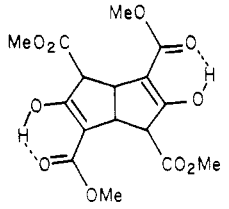
2

Attempts to introduce additional unsaturation into **1** with bromine have been unsuccessful.[2d] We now report that the use of dimethyl bromomalonate as a bromine carrier in methanol–sodium methoxide solution has produced the sodium salt of tetramethyl 3-hydroxy-7-oxobicyclo[3.3.0]octa-1,3,5-triene-2,4,6,8-tetracarboxylate (**2**) in 75–80% yield from **1**.

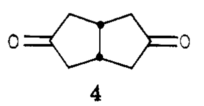
Compound **2** crystallizes readily from aqueous methanol as deep red needles:[3,4] ^1H NMR (Me_2SO-d_6) δ 3.52 (s, 3 H), 3.67 (s, 6 H), 3.73 (s, 3 H), 4.45 (s, 1 H); UV-vis (CH_3CN) λ_{max} 210 nm (ϵ 15 000), 283 (29 000), 310sh (12,000), 467 (6000).[5]

Addition of sodium methoxide solution to a methanol solution of **2** produces a light blue precipitate of the disodium salt; similarly, **1** produces a yellow precipitate. Both processes are reversible. Addition of aqueous base to a water solution of **2** gives a blue solution; analogously, **1** gives a yellow solution. Computer-assisted analysis of potentiometric and spectrophotometric data[6] showed that the parent acid of **2** is notably strong: $pK_1 = 1.4$; $pK_2 = 8.4$.

Sodium amalgam reduction of **2** gives the same product **3** that is obtained similarly from **1**. Hydrolysis–decarboxylation of **3** obtained from either **1** or **2** produces **4** in 94% yield. By using a two-phase system (ether/water) the yield in the reduction of **1** has been improved from 35%[2d] to 80%.[7] Even with the improvement of this step, however, the overall yield of **4** from **1** is not as high as the yield from the Bertz modification[8a] of the Weiss reaction of glyoxal with 3-ketoglutarate.[9]



3



4

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(1) G. Vossen, Doctoral Dissertation, University of Bonn, 1910; G. Schroeter, *Justus Liebigs Ann. Chem.*, **426**, 1 (1922).

(2) (a) H. W. Wanzlick, *Chem. Ber.*, **86**, 269 (1953); (b) H. Paul and I. Wendel, *Chem. Tech. (Berlin)*, **8**, 189 (1956); (c) S. Tanaka, *J. Am. Chem. Soc.*, **80**, 5264 (1958); (d) P. Yates, E. S. Hand, and G. B. French, *ibid.*, **82**, 6347 (1960); (e) E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

(3) A satisfactory elementary analysis was obtained.

(4) Recrystallized **1** is a pale pink solid when freed of methanol and/or water of solvation.

(5) The corresponding spectrum for **1**: λ_{max} 342 nm (ϵ 53 000), 257 (10 000), 450 (10).

(6) G. E. Knudson and J. Bickel, *Proc. Iowa Acad. Sci.*, **83**(3), 116–7 (1976).

(7) A procedure developed in this laboratory with J. A. Duncan and later used by J. E. Baldwin and M. S. Kaplan, *J. Am. Chem. Soc.*, **93**, 3969 (1971).

(8) (a) S. H. Bertz, Doctoral Dissertation, Harvard University, 1978; (b) S. H. Bertz, G. Rihs, and R. B. Woodward, *Tetrahedron*, in press.

(9) U. Weiss and J. M. Edwards, *Tetrahedron Lett.*, 4885 (1968).

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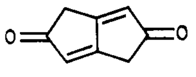
When 2 is subjected to hydrolysis–decarboxylation in boiling, dilute HCl, a 35–40% yield of the title compound **5** is obtained after separation of polymeric material.



5

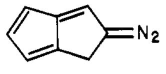
Compound **5** is a very pale yellow crystalline substance:[3] mp 240–242 °C;[10] ^{1}H NMR δ 3.28 (s, 4 H), 6.36 (s, 2 H); ^{13}C NMR 36.4, 128.1, 172.2, 202.9; mass spectrum, m/e (relative intensity) 134 (M^+, 100), 106 (23), 78 (73), 67 (M^{2+}, 14); UV–vis λ_{max} 270 nm (ϵ 27 000), 310 sh (170).

The chemistry of **5** so far investigated parallels in many respects that of 4-cyclopentene-1,3-dione:[11] it is essentially nonenolic, unstable in contact with base, and reactive toward diazonium ion. The methylene hydrogens exchange readily with deuterium as shown by the disappearance of the δ 3.28 peak in the NMR. Under rigorously dry and oxygen-free conditions, a solution of potassium *tert*-butoxide in *tert*-butyl alcohol was added to a solution of **5** in *tert*-butyl alcohol. An immediate deep purple solution was formed, which rapidly changed to brown. No clearly defined NMR absorption was observed.[12]

Attempts to form an enol derivative by using isopropenyl acetate did not yield an identifiable product. The bis(tosylhydrazone) **6** of **5** forms readily in nearly quantitative yield in acidified methanol solution, precipitating analytically pure as bright yellow, feathery crystals.[3] Compound **6** is highly insoluble in organic solvents but dissolves readily in aqueous NaOH solution.

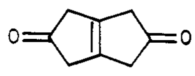
Attempts to obtain pentalene by vacuum pyrolysis or photolysis of the dilithium salt of **6** failed. Treatment of a suspension of **6** in ether with methyllithium[13,14] under nitrogen was also unsuccessful with nearly quantitative recovery of **6**.

Photolysis of a solution of **6** in aqueous NaOH with Sylvania "Daylight" fluorescent lamps produced 3-diazabicyclo[3.3.0]octa-1,5,7-triene (**7**). To avoid photolysis of **7** it was necessary to remove it as it formed by a vacuum steam distillation at 40–45 °C. Compound **7** was extracted from the distillate with pentane. Removal of the pentane under reduced pressure left a photolabile, orange red semisolid:[15] IR (argon matrix) 2090, 2080 cm^{-1}; mass spectrum, m/e (relative intensity) 130 (96), 102 (100), 76 (39); ^{1}H NMR (at −20 °C, CDCl$_3$) δ 3.26–3.28 (m, 2 H), 6.55–6.74 (m, 4 H).



7

Treatment of **5** with zinc dust in tetrahydrofuran–acetic acid (100:1, v/v) yields bicyclo[3.3.0]octa-1(5)-ene-3,7-dione (**8**) as white needles: mp 208–215 dec;[3] ^{1}H NMR δ 3.0 (s); ^{13}C NMR 42.3, 138.5, 214.5; mass spectrum, m/e 136 (M^+, 47), 108 (61), 80 (37), 79 (100).



8

Compound **8** is stable in crystalline form and in dry aprotic solvents. However, its solutions, in methanol for example, quickly become yellow, presumably due to a shift of the double bond to the conjugated position.[16]

Other aspects of the chemistry and photochemistry of the title compound and its derivatives are being investigated.

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Registry No. 1, 78698-09-6; 2, 78698-10-9; 3, 68703-09-3; 4, 74513-16-9; 5, 78698-11-0; 6, 78698-12-1; 7, 78698-13-2; 8, 78698-14-3; dimethyl bromomalonate, 868-26-8.

Supplementary Material Available: Detailed experimental directions for the preparation of compounds 2 and 5; more complete IR and UV spectra for compounds 2, 5, 7, and 8 (2 pages). Ordering information is given on any current masthead page.

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[10] This compound has also been isolated by Dr. S. H. Bertz from the hydrolysis–decarboxylation (and adventitious oxidation) of 1 (ref 8a).

[11] C. H. DePuy and P. R. Wells, *J. Am. Chem. Soc.* **82**, 2909 (1960), and earlier papers.

[12] We are indebted to Dean Kahl and J. I. Brauman, Stanford University, for the *tert*-butoxide experiments.

[13] R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967).

[14] G. Kaufman, F. Cook, J. Schechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

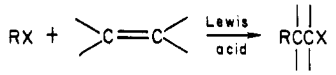
[15] We are indebted to O. L. Chapman and his associates at Iowa State University and the University of California at Los Angeles for these spectral analyses.

[16] The conjugated isomer has been prepared by Dr. S. H. Bertz (ref 8a); it turns yellow immediately upon exposure to oxygen.

Zinc Chloride Catalyzed Addition Reactions of Propargyl Chlorides with Acyclic 1,3-Dienes

Summary: Zinc chloride catalyzed reactions of propargyl chlorides with acyclic 1,3-dienes (at −78 °C) give linear addition products, which cyclize to 4-(chloroalkylidene)-cyclohexenes at elevated temperature.

Sir: In a theoretical analysis of Lewis acid catalyzed additions of alkyl halides RX to olefins (eq 1), we came to



$$\mathrm{RX} + \mathrm{>C{=}C<} \xrightarrow[\text{acid}]{\text{Lewis}} \mathrm{RCCX} \qquad (1)$$

the conclusion that the formation of 1:1 products is only possible when the initial carbenium ions R^+ are better stabilized than the carbenium ions RCC^+ formed in the addition step.[1] Solvolysis rates of alkyl chlorides were employed to predict whether a certain addition reaction is feasible or not.

In this communication we report Lewis acid catalyzed additions of propargyl chlorides to acyclic 1,3-dienes as an example for the application of these rules in planning syntheses.

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[1] Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 184.

0022-3263/81/1946-4097$01.25/0