Table I. Decomposition Data for Bicyclic Azoalkanes

compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}[a]
1	33.7 ± 0.2	10.0 ± 0.3	1.0
2	36.2[b]	6.1[b]	0.0057
3	44.3[b]	9.5[b]	10^{-6}
9	32.9 ± 0.5[c]	4.1 ± 1.4[c]	0.14

[a] Relative rates (s^{-1}) at 120 °C calculated from data of the previous two columns. [b] Average of values in ref 1a. [c] Reference 10.

of bicyclo[2.1.0]pentane in acetone to give an adduct analogous to **7** in quantitative yield.[3] Electron-deficient olefins react with **6** to give bicyclo[2.1.1]hexane derivatives and cyclobutenes ("ene" products).[4] A stepwise, biradical mechanism is implicated.[4] We have found that reaction of **5a** or **5b** with **6** in CH_2Cl_2, $CHCl_3$, THF, or acetone is rapid at room temperature (as monitored by the disappearance of the color of **5**) but gives a complex mixture of products which contains <5% of the desired adduct **7** (vide infra). However, addition of **5** in a small amount of ether to a solution of **6** in a large volume of *n*-hexane at 63 °C results in a much slower reaction, and the ^1H NMR of the crude product shows **7** as the only adduct. Flash chromatography[5] on silica gel (3:1 CH_2Cl_2/Et_2O) gives a 40% isolated yield of **7**.[6] The decreased polarity of the reaction medium is the major factor responsible for the improved yield. We have not characterized the remaining material, but we suspect that some form of polymerization has occurred. The total absence of "ene" adduct **8** in the crude product mixture, and the marked solvent effect on the rate and product composition could signal a change in mechanism from that discussed above.

Hydrolysis–oxidation of **7b** by a slight modification of Gassman's procedure[7] produced **1** as an extremely volatile white solid in 65% yield.[8] The UV spectrum of **1** (*n*-hexane) is highly structured, relative to related compounds,[2] with an intense 0,0 band [λ_{max} 331 nm (ϵ 1360), $w_{1/2}$ = 2.4 nm] and three smaller peaks (325 (143), 320 (186), 316 (124)]. This result is consistent with the rigid structure of **1**.[2]

Thermal decomposition of **1** in C_6D_6 was studied over four temperatures in the range 85–115 °C, and the kinetics proved to be cleanly first order.[9] The sole detectable product (≥99.8% by 500-MHz ^1H NMR) was bicyclobutane (**6**). Table I lists activation parameters and relative rates for **1**–**3** and 2,3-diazabicyclo[2.2.0]hex-2-ene (**9**), an isomer of **1** prepared recently by Carpenter.[10] Although the strain energy of **1** is calculated to be 31 kcal/mol greater than that of **2**,[11] the two structures show only a modest difference in $\Delta H^{\ddagger}$. This is no doubt due to the fact that much of the strain in **1** is retained in the transition state in the form of a four-membered ring. Empirical force field calculations[12] indicate that **9** is approximately 7 kcal/mol more strained than **1**, but this difference is not reflected in the activation parameters or relative rates for decomposition (Table I). If the force field method can be considered reliable for such highly strained structures, then this result is consistent with an orbital symmetry factor[10] which raises the barrier to decomposition in **9** or leads to different mechanisms for **9** and **1**.

Further studies concerning the mechanisms of the reactions described herein and the photochemical decomposition of **1** are underway.

Note Added in Proof. We have learned that Dr. Amey from Du Pont has also been studying the reactions of triazolinediones with bicyclobutanes with some very interesting results. See accompanying Note in this issue.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the Camille and Henry Dreyfus Foundation for support of this work, and the use of the Southern California Regional NMR Facility located at Caltech and supported by the National Science Foundation.

Registry No. **1**, 72192-13-3; **5b**, 13274-43-6; **6**, 157-33-5; **7b**, 78715-55-6.

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[3] Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695–8.

[4] Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128–36.

[5] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–5.

[6] We have found it to be more convenient to work with **7b**: ^1H NMR ($CDCl_3$) δ 1.75 (dd, 2 H, H_a), 2.30 (m, 2 H, H_b), 3.08 (s, 3 H), 4.70 (t, 2 H, H_c); complete spectral simulation gives: $J_{aa'}$ = 6.5, J_{ab} = 8.4, J_{bc} = 2.0 Hz; ^{13}C NMR ($CDCl_3$) δ 25.74 (CH_3), 40.55 (CH_2), 62.32 (CH), 161.30 (C=O); IR ($CHCl_3$) 1720 cm^{-1}; mp 134–134.5 °C. Anal. Calcd for ($C_7H_9N_3O_2$) C, H, N.

[7] Gassman, P. G.; Mansfield, K. T. *Org. Synth.* **1969**, *49*, 1–6. We have obtained better yields using cupric bromide instead of cupric chloride.

[8] ^1H NMR (C_6D_6) δ 1.22 (m, 2 H), 1.60 (dd, 2 H) 4.40 (t, 2 H); preliminary spectral simulation gives coupling constants essentially identical with those for **7b**; ^{13}C NMR (CCl_4) δ 59.01 (CH_2), 76.36 (CH); mp (sealed tube) 63–4 °C; IR (CCl_4): 3020, 2960, 2870, 1475, 1430, 1260, 1210, 1100, 1015, 960 cm^{-1}; mass spectrum (degassed sample, 15 eV), *m/e* 54 (98), 39 (100), 28 (55).

[9] Thermolyses were performed in C_6D_6 in sealed NMR tubes and were monitored by multiple ^1H NMR integrations. All rate plots and the Arrhenius and Eyring plots gave linear correlation coefficients of 0.9998 or better. Rate constant × 10^5 s^{-1} (T, °C): 0.321 ± 0.006 (84.98), 1.20 ± 0.03 (95.04), 4.20 ± 0.08 (104.97), 13.5 ± 0.4 (115.06), E_a = 34.4 ± 0.2 kcal/mol, log A = 15.50 ± 0.09.

[10] Wildi, E. A.; Van Engen, D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, 102, 7994–6.

[11] Kao, J.; Huang, T-N. *J. Am. Chem. Soc.* **1979**, *101*, 5546–57.

[12] Calculations performed in the present work using the force field of ref 11.

A Versatile and Selective Route to Difunctional Trisubstituted (*E*)-Alkene Synthons via Zirconium-Catalyzed Carboalumination of Alkynes[1]

Summary: The Zr-catalyzed carboalumination of propargyl and homopropargyl derivatives containing OH, $OSiMe_2Bu$-*t*, SPh, or I provides, in a highly stereo- and regioselective manner, the corresponding (*E*)-(2-methylalkenyl)dimethylalkanes, which are convertible to various difunctional trisubstituted (*E*)-alkene synthons.

Sir: Trisubstituted olefins with two proximal functional groups such as **1**–**4** are potentially useful synthons for the synthesis of a variety of natural products of terpenoid origin. In principle, the syn methylmetalation of propargyl or homopropargyl derivatives followed by replacement of the carbon–metal bond with heterofunctional groups Z or CH_2Z would provide a versatile route to **1**–**4**. In practice, however, all previously reported controlled carbometalation reactions of propargyl and homopropargyl derivatives,[2]

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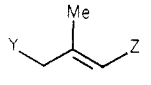
[1] Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis, 19. Controlled Carbometalation 9. Part 8. T. Yoshida and E. Negishi, *J. Am. Chem. Soc.*, **103**, 1276 (1981).



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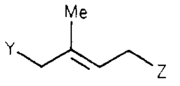

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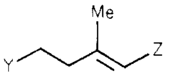

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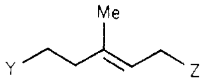
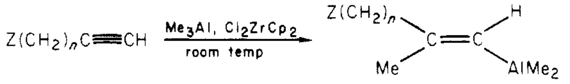


4

Y and Z = heterofunctional groups

which are of synthetic value, either are nonregio- and/or nonstereoselective or display regioselectivity opposite to that which is observed with simple alkynes, presumably due to marked directive effects of the proximal hetero atoms.

We now report that, in marked contrast with the other known carbometalation reactions, the Zr-catalyzed carboalumination of acetylenes we recently discovered[3] displays a uniformly high regioselectivity with propargyl and homopropargyl derivatives containing OH, $OSiMe_2Bu$-*t*, SPh, or iodine groups (eq 1). The experimental results

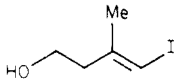


$$Z(CH_2)_nC{\equiv}CH \xrightarrow[\text{room temp}]{Me_3Al,\ Cl_2ZrCp_2} \overset{Z(CH_2)_n}{\underset{Me}{}}C{=}C\overset{H}{\underset{AlMe_2}{}} \quad (1)$$

Z = OH, OSiMeBu-*t*, SPh, or I; *n* = 1 or 2

are summarized in Table I. These results are quite unexpected in light of the known inability of hydroalumination[4] to cope with donor-type substituents as well as of the "reverse" regioselectivity observed in the carbometalation of alkynols with Al–Ti reagent systems.[2b] More significantly, the Zr-catalyzed carboalumination of heterofunctional terminal alkynes coupled with a variety of carbon–carbon[5] and carbon–heteroatom[6] bond-forming reactions now provides a versatile and selective route to difunctional trisubstituted olefin synthons.

Although we have previously established that the Zr-catalyzed carboalumination of simple acetylenes involves an exclusive syn addition, it seemed desirable to establish the stereochemistry of each of the reactions herein reported to rule out any unexpected heteroatom effects, such as that reported in the Ni-catalyzed carbomagnesation.[2c] The ^{13}C and/or ^{1}H NMR spectra of all isolated trisubstituted olefins, crude or pure, clearly indicate that these compounds are single stereoisomers of ≥98% stereoisomeric purity. The homoallylic alcohol **5** is converted into the



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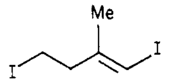

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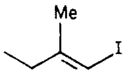

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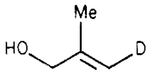

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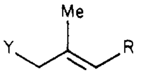

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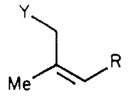

10

Y = carbon or heteroatom group, R = carbon group

iodide **6** via tosylation and treatment with NaI in acetone. The spectral properties of **6** thus obtained are identical with those of **6** obtained by the Zr-catalyzed carboalumination of homopropargyl iodide. The iodide was cleanly converted into **7** by selective reduction of the alkyl carbon–iodine bond with $LiBEt_3H$, leaving the alkenyl carbon–iodine bond intact. Treatment of **7** with *n*-BuLi at −60 °C gives a single isomer of 3-methyl-3-octene. Its ^{1}H NMR singlet at 1.59 ppm coupled with the complete absence of a peak at ca. 1.67 ppm clearly establishes its *E* geometry.[7] Since alkylation of alkenyl iodides with alkyllithiums is known to proceed with retention, the *E* geometry of **5** and **6** is now firmly established. Deuterolysis of the product of carbometalation of the propargyl alcohol produces **8**, the identity and stereochemistry of which are established by comparing its ^{1}H NMR spectrum with the completely peak-assigned spectrum of 2-methylpropenol.[8] In the other cases, the stereochemical assignments are based on a tentative but seemingly reliable generalization[9] that the ^{13}C NMR signals for the allylic methyl carbon atoms of **9** and **10** appear at ca. 16 ± 3 and >19 ppm, respectively. On the basis of the chemical shift data shown in Table I as well as the above-described experiments, we conclude that all carbometalation reactions herein reported involve an exclusive or nearly exclusive syn addition of the Me–Al bond.

Although the regioselectivity of the reaction is high, it is somewhat dependent on the proximal heteroatoms. As Table I indicates, the regioselectivity of the carbometalation of homopropargyl derivatives is in the range of 92–100% except for the case of homopropargyl phenyl sulfide which displays a regioselectivity of 83% with Me_3Al–Cl_2ZrCp_2. Fortunately, we soon found that it could be raised to >98% by using Me_3Al–Me_2ZrCp_2 (6 h, 50 °C). The origin of this serendipitous finding is unknown at the present time. The regioselectivity observed with propargyl derivatives is ≥98%, although it is possible that the minor regioisomers which would contain a heteroatom β to aluminum might be destroyed via elimination under the reaction conditions.

One of the specific goals of the present study is to develop difunctional isoprene dimer synthons suitable for convergent syntheses of polyenic isopenoids. To this end, **11** was chosen, and its synthesis has been achieved by the Pd-catalyzed cross-coupling of **12** with the trimethylsilyl derivative of homopropargylzinc chloride[5c] to form **13** in 90% yield,[10] followed by selective protonolysis of the Si–O

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(2) (a) Cu: The carbocupration reaction of J. F. Normant, which is practically the only previously reported carbometalation reaction of acetylenes of demonstrated utility, is strongly affected by proximal donor-type groups and tends not to be regioselective. For a review, see J. F. Normant, *J. Organometal. Chem. Library*, 1, 219 (1976). (b) Ti: The carbometalation reaction of alkynols with Ti–Al reagent systems, whose synthetic scope appears very limited, have been shown to be nonregioselective: D. C. Brown, S. A. Nichols, A. B. Gilpin, and D. W. Thompson, *J. Org. Chem.*, **44**, 3457 (1979), and references therein. (c) Ni: The carbometalation reaction of O- or N-substituted butyne and pentyne derivatives with MeMgBr in the presence of a Ni catalyst is nonstereoselective: B. B. Snider, R. S. E. Conn, and M. Karras, *Tetrahedron Lett.*, 1679 (1979), and references therein.

(3) D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, **100**, 2252 (1978).

(4) For a review of hydroalumination, see T. Mole and E. A. Jeffery, "Organoaluminum Compounds", Elsevier, Amsterdam, 1972.

(5) (a) E. Negishi, N. Okukado, A. O. King, D. E. Van Horn, and B. I. Spiegel, *J. Am. Chem. Soc.*, **100**, 2254 (1978); (b) N. Okukado and E. Negishi, *Tetrahedron Lett.*, 2357 (1978); (c) E. Negishi, L. F. Valente, and M. Kobayashi, *J. Am. Chem. Soc.*, **102**, 3298 (1980); (d) M. Kobayashi and E. Negishi, *J. Org. Chem.*, **45**, 5223 (1980); (e) M. Kobayashi, L. F. Valente, E. Negishi, W. Patterson, and A. Silveira, Jr., *Synthesis*, (1980); (f) H. Matsushita and E. Negishi, *J. Am. Chem. Soc.*, **103**, 2882 (1981).

(6) E. Negishi, D. E. Van Horn, A. O. King, and N. Okukado, *Synthesis*, 501 (1979).

(7) (a) D. J. Faulkner, *Synthesis*, 175 (1971); (b) R. B. Bates, D. M. Gale, and B. J. Gruner, *J. Org. Chem.*, **28**, 1086 (1963); (c) J. W. K. Burrell, R. F. Garwood, L. M. Jackman, E. Oskay, and B. C. L. Weedon, *J. Chem. Soc.*, 2144 (1966).

(8) Sadtler ^{1}H NMR Spectra No. 18762M. The multiplets at 4.79 and 4.93 ppm are assigned to the alkenyl protons that are cis and trans to the Me group, respectively.

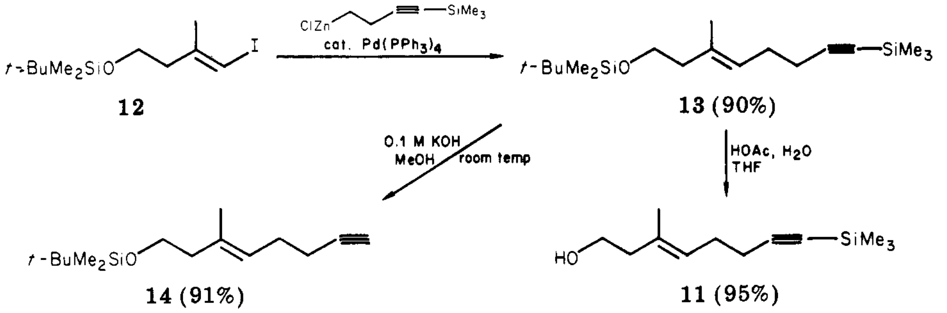
(9) ^{13}C NMR spectral data supporting this generalization may be found in the following: (a) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, 1972; (b) Sadtler Standard Carbon-13 N.M.R. Spectra.

Table I. Preparation of Heterofunctional Trisubstituted (*E*)-Alkenes via Zirconium-Catalyzed Carboalumination of Alkynes[a]

alkyne	product	method[b]	% yield, isolated (GLC)	regioselectivity of carbometalation, %	^{13}C NMR chemical shift of the allylic methyl carbon, ppm
3-butyn-1-ol	5	A	62 (85)	92	
	12	A	87	94	
	methyl (*E*)-5-hydroxy-3-methyl-2-pentenoate	B	(63)	94	18.83
3-butynoxy-*tert*-butyldimethylsilane	12	A	52	94	
4-iodo-1-butyne	ethyl (*E*)-iodo-3-methyl-2-pentenoate	B	74 (89)	>98	16.65
	6	A	60	>98	
3-butynyl phenyl sulfide	(*E*)-3-methyl-5-(thiophenoxy)-2-pentenoic acid	C	62	83 (>98)[c]	16.26
	(*E*)-3-methyl-5-(thiophenoxy)-2-penten-1-ol	D	78	83 (>98)[c]	
2-propyn-1-ol	8	E	41	94	
1-octyn-3-ol[d]	17	A	60 (77)	>98	10.94[e]
2-propynyl phenyl sulfide	(*E*)-1-iodo-2-methyl-3-(thiophenoxy)-1-propene	A	75	>98	
	(*E*)-3-methyl-4-(thiophenoxy)-2-buten-1-ol	D	78	>98	15.42

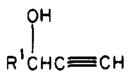
[a] Unless otherwise stated, the carbometalation is carried out in CH_2Cl_2 or $(CH_2Cl)_2$ at room temperature, using Me_3Al (3 equiv) and Cl_2ZrCp_2 (1 equiv). [b] $A^6 = I_2$ in THF. B^{5b} = ClCOOMe or ClCOOEt. C^{5b} = evaporation of Me_3Al, precipitation of Cl_2ZrCp_2, ate complexation with 1 equiv of *n*-BuLi, and treatment with CO_2. D^{5b} = ate complex formation as in C followed by paraformaldehyde. $E^3 = D_2O$. [c] The reaction of 3-butynyl phenyl sulfide with Me_3Al–Me_2ZrCp_2 (3:1) for 6 h at 50 °C gives, after hydrolysis, 3-methyl-3-butenyl phenyl sulfide in 90% yield, the amount of the regioisomer, i.e., 3-pentenyl phenyl sulfide, being ≤1%, as judged by GLC (Carbowax 20 M and SE-30) examination. [d] Zirconocene diiodide (1 equiv) is used in place of Cl_2ZrCp_2. [e] The branching in the α position shifts the allylic methyl signal above 13 ppm. The corresponding ^{1}H chemical shift is 1.54 ppm.

Scheme I



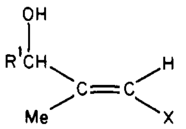
bond with aqueous acetic acid[11] (95%). Treatment of **13** with methanolic KOH,[12] on the other hand, selectively removes the Me_3Si group to give **14** in 91% yield (Scheme I).

Propargylic alcohols **15** are particularly attractive substrates in the present study, as their carboalumination will provide an efficient and selective route to allylic alcohols **16**, which can be further converted into chiral compounds containing two or more contiguous asymmetric carbon atoms.[13] Furthermore, **15** can now be readily available as optically pure compounds via asymmetric reduction of alkynones.[14] It is therefore gratifying that the reaction of 1-octyn-3-ol with Me_3Al (3 equiv) and I_2ZrCp_2[15] (1 equiv) at room temperature gives 2-methyl-1-octen-3-ol in 77% yield, on protonolysis, and (*E*)-1-iodo-2-methyl-1-octen-3-ol (**17**) in 60% yield, on iodinolysis. The synthetic utility of allylic alcohols represented by **16** as well as of various other trisubstituted olefin synthons now readily available by the Zr-catalyzed carboalumination is being explored in our laboratories.



$$\mathrm{R^1}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HC{\equiv}CH}$$

15



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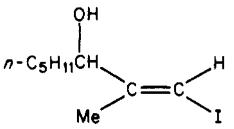

17

X = H, I, or carbon group

The following preparation of (*E*)-(4-iodo-3-methyl-3-buten-1-oxy)-*tert*-butyldimethylsilane is representative. To a solution of Me_3Al (pyrophoric!) (21.6 g, 28.8 mL, 300 mmol) and Cl_2ZrCp_2 (7.30 g, 25 mmol) in 1,2-dichloroethane (200 mL) is added dropwise at 0 °C 3-butyn-1-ol

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(10) We have also found that **12** can be converted to (*E*)-(3-methyl-3-octenoxy-*tert*-butyl)dimethylsilane by treatment with either *n*-BuLi in THF at −60 °C or with *n*-butylzinc chloride in THF in the presence of $Pd(PPh_3)_4$ at room temperature in 60 and 68% yields, respectively.

(11) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

(12) C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc. C*, 1364 (1967).

(13) For recent reviews of this subject, see (a) P. A. Bartlett, *Tetrahedron*, **36**, 3 (1980); (b) Y. Kishi, *Aldrichim. Acta*, **13**, 23 (1980).

(14) M. M. Midland, D. C. McDowell, R. L. Hatch, and A. Tramontano, *J. Am. Chem. Soc.*, **102**, 867 (1980).

(15) The use of Me_3Al–Cl_2ZrCp_2 instead of Me_3Al–I_2ZrCp_2 results in reduction of the product yield by 10–20%.

(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.

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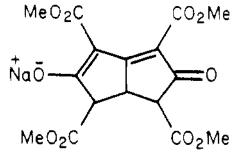
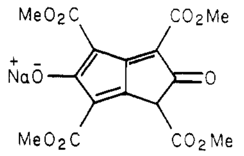
Bicyclo[3.3.0]octa-1,5-diene-3,7-dione

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



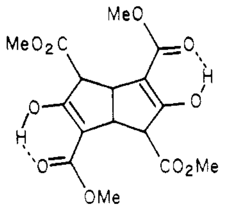
2

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 15000), 283 (29000), 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]



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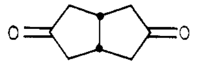

4

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[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 53000), 257 (10000), 450 (10).

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[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).

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