

process occurs via a nucleophilic mechanism, most likely a two-step process where the overall rate constant may result from the balance of the equilibrium constant of the formation of the intermediate and the rate constant of its cleavage to products, the electronic features of the substrates playing an opposite role.

Conclusions

It appears that the only nucleophilic oxidation observed in this study is the oxidation of sulfoxides with *m*-chloroperbenzoate anion. Therefore, even the Mo(VI)-peroxo anions formed in basic media oxidize the model sulfoxides via an electrophilic oxygen transfer, though less efficiently than the corresponding neutral species. This behavior has been previously observed in similar systems.⁴ In the light of these results it appears rather unlikely that the structure of the peroxomolybdenum anion could be similar to that of *m*-chloroperbenzoate anion, i.e., involving the Mo-O-O⁻ moiety, as a result of the opening of the peroxo bridge. A possible alternative is the formation of an oxo anion where the negative charge on the oxo oxygen or on the peroxometal complex as a whole reduces, but not eliminates, the electrophilic character of the peroxo oxygens.

Experimental Section

Materials. Di-*n*-butyl sulfoxide, phenyl methyl sulfoxide, and diphenyl sulfoxide and the corresponding sulfones were prepared by oxidation of the commercially available sulfides with hydrogen peroxide in the presence of catalytic amounts of MoO₂(acac)₂ in ethanol, by using 1 or 2 equiv, respectively, of H₂O₂. The products were purified by column chromatography. Commercial bis(acetylacetonato)dioxomolybdenum(VI), MoO₂(acac)₂, was purified by crystallization from acetone-acetylacetone (1:4).

Sodium ethoxide was prepared by dissolving metallic sodium in ethanol and standardized by acid-base titration.

m-Chloroperbenzoic acid (MCPBA) free of *m*-chlorobenzoic acid was obtained from the commercially available material according to the following procedure: 50 g of the product was dissolved in benzene (1 L) and washed with an aqueous solution buffered at pH 7.4 (NaH₂PO₃-NaOH) (5 × 100 mL). The organic layer was dried over MgSO₄ and carefully evaporated, under vacuum. The remaining solid was then purified by two subsequent crystallizations (CH₂Cl₂, Et₂O): active oxygen, 98% (iodometric titer).

Anhydrous ethanol was obtained by standard procedures from highly pure commercial samples.

All other chemicals were used as received.

Procedures. The stoichiometry of the oxidation was determined by mixing a solution of H₂O₂ (0.55 mmol) in EtOH-0.5 M H₂O with a solution of the PhS(O)CH₃ (1.1 mmol) and the catalyst (0.028 mmol) in the same solvent (final volume 55 mL) in the presence of CH₃SO₃H (5.5 × 10⁻³ mmol) or EtONa (5.5 × 10⁻² mmol). After completion of the reaction (absence of iodometric titer) an appropriate internal standard was added and the reaction mixture analyzed by GLC on a FFAP 3% (2.5 m) on Chromosorb WAW DMCS using a Varian 3700 equipped with a Varian CDS 401 integrator: PhSO₂CH₃, 0.54 mmol (98% yield) acidic conditions, 0.45 mmol (82% yield) alkaline conditions.

All kinetic runs were carried out in a thermostatic bath with temperature control to better than ±0.05 °C. Aliquots of the reaction mixture were withdrawn at various times and analyzed for H₂O₂ content by iodometry, as reported in previous papers of this series.

Caution. Care should be exercised in handling peroxides, particularly in the purification of commercial MCPBA.¹⁰

Registry No. MCPBA, 937-14-4; *n*-Bu₂SO, 2168-93-6; PhS(O)CH₃, 1193-82-4; Ph₂SO, 945-51-7; *n*-Bu₂S, 544-40-1; PhSCH₃, 100-68-5; Ph₂S, 139-66-2; H₂O₂, 7722-84-1; MoO₂(acac)₂, 17524-05-9.

(10) *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, Chapter 6.

Search for Ethynylogues of Allenylidene. Zwitterionic Nature of Dimethylpentatetraenylidene¹

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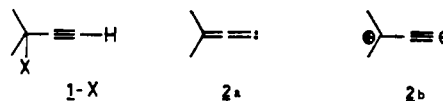
Received April 22, 1987

5-Chloro-5-methylhexa-1,3-diyne (7-Cl) reacts with alkoxide bases to give transient dimethylpentatetraenylidene (8). In methanol, this reaction is strongly accelerated by pressure, permitting the conclusion that this intermediate has a much larger dipole moment than the corresponding allenylidene 2. The products are the unrearranged methyl ether 7-OMe and the rearranged chloroallene 9; the latter compound is the result of return, presumably internal. This return is also manifested by a sharp break in the rate plot of chloride ion formation. In *tert*-butyl alcohol-tetramethylethylene, 8 is trapped to give an adduct that dimerizes to 14, or possibly 15; oxygen sensitivity of this material prevented its complete characterization. The adamantane analogue 16-Cl permitted the isolation of monomeric trapping product 17. Attempts at extension to the next higher ethynylogue were not successful.

Introduction

The work reported herein was inspired by our observation² that the well-known³⁻⁵ generation of allenylidenes from propargyl halides and base responds to the application of hydrostatic pressure in an unusual way; whereas

haloform solvolyses are strongly retarded in their formation of dihalocarbenes under these conditions,⁶ the reaction of 3-chloro-3-methylbut-1-yne (1-Cl) is essentially unaffected.



The volume expansion characterizing these reactions evidently does not occur in this case, although dimethyl-

(1) (a) Preliminary communication: le Noble, W. J.; Basak, S.; Srivastava, S. *J. Am. Chem. Soc.* 1981, 103, 4638. (b) Full details may be found in: Basak, S. Ph.D. Thesis, SUNY at Stony Brook, NY, 1984. (2) le Noble, W. J. *J. Am. Chem. Soc.* 1965, 87, 2434. (3) Hennion, G. F.; Nelson, K. W. *J. Am. Chem. Soc.* 1957, 79, 2142. (4) Hartzler, H. D. *J. Am. Chem. Soc.* 1961, 83, 4990, 4997. (5) Shiner, V. J.; Wilson, J. W. *J. Am. Chem. Soc.* 1962, 84, 2402.

(6) le Noble, W. J.; Duffy, M. *J. Am. Chem. Soc.* 1964, 86, 4512.

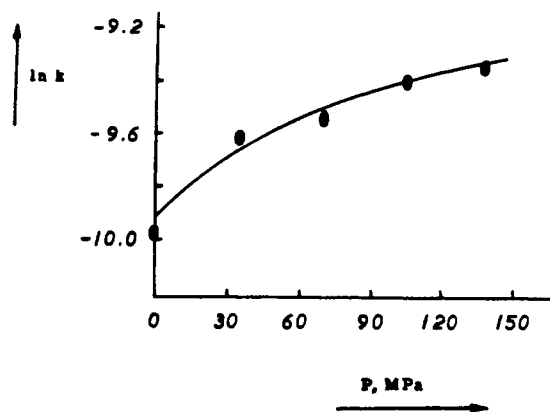
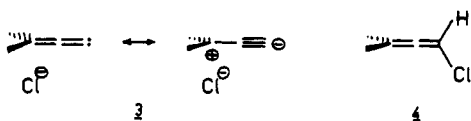


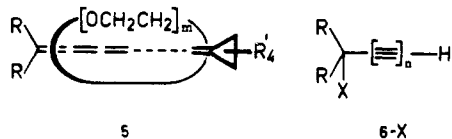
Figure 1. Effect of pressure on the initial rate of solvolysis in aqueous methanol at 30 °C in the presence of excess base.

allenylidene **2** can be trapped. Considerable zwitterionic character (**2b**) should offset the expansion normally exhibited in the formation of carbenes from haloforms as the C-X bond breaks, since ion solvation reduces the volume. Consideration of the volumes of activation encountered in chloroform hydrolysis (+16 cm³/mol) and in the *neutral* (i.e., cationic) hydrolysis of 1-Cl (-15 cm³/mol) led us to estimate that **2a** and **2b** contribute roughly equally.

This picture has since received support from theoretical calculations⁷ leading to a large dipole moment for these carbenes and from our own further experimental work^{8,9} showing that anion-carbene pair **3** precedes the free carbene; this pair, in fact, is the immediate precursor to the isomeric allene product **4** that usually accompanies alcohol 1-OH or ether 1-OR, albeit in minor quantities (1-10%). Insensitivity of the yield of **4** to added chloride ion and retention of configuration in the isomerization of a stereolabeled analogue proved that the return was internal.



It seemed quite possible to us that higher ethynylogues of **2** might have even more pronounced zwitterionic character, and we hoped that their generation in the presence of sufficiently large crown ethers and their subsequent capture by suitable olefins might constitute a template synthesis of rotaxanes such as **5**. These hopes have founded on the instability of the polyacetylenic precursors required (**6-X**); however, partial success was achieved with $n = 2$, as described below.



Results and Discussion

Chloro diyne **7-Cl**, prepared¹⁰ from 1,4-dichlorobut-2-yne via alcohol **7-OH**,¹¹ does indeed behave as we hoped; the

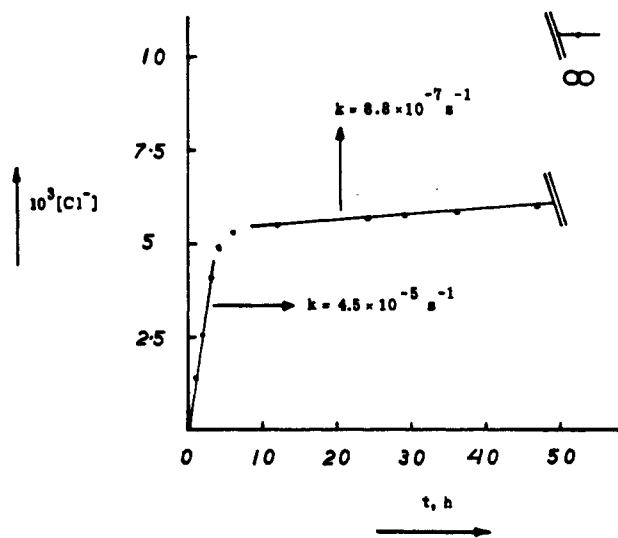
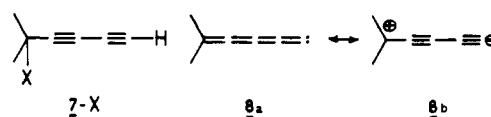


Figure 2. Rate of chloride formation from **7-Cl** in basic methanol at 30 °C.

initial solvolysis rate of this chloride in aqueous methanol at 30 °C in the presence of a 10-fold excess of base is strongly *accelerated* by pressure. The data are shown in Figure 1; the activation volume is -22 cm³/mol. This result is quite comparable with that found in neutral solvolysis of organic chlorides in this medium,¹² and this leads to the conclusion that zwitterionic character is dominant in the intermediate **8a** ↔ **8b**.



Further support for this conclusion is provided by the fact that the basic methanolysis of **7-Cl** is accompanied by much more return than is that of 1-Cl. Thus, if solutions of **7-Cl** in basic methanol are analyzed at atmospheric pressure for chloride release, a sharp break is seen in the pseudo-first-order rate plot after several hours, at which time the slope decreases by a factor of 50; at this point less than half (45%) of the chloride ion has been liberated (see Figure 2). When a sample of this solution is destroyed with lithium aluminum hydride (after replacement of the methanol by tetrahydrofuran), the theoretical titer is found. Another sample was extracted with water and methylene chloride; GC analysis of the organic solution revealed the presence of two materials shown by ¹H NMR to be methyl ether **7-OMe** and rearrangement product **9**. Tetraene **10** was not observed, nor were its possible dimerization products.¹³ Evidently, the chloride anion on its way from C₁ to C₅ encounters the partially charged site at C₃, and collapse occurs then and there.

The carbenic nature of **8a** does assert itself in the presence of a suitable trapping agent. When **7-Cl** was treated with potassium *tert*-butoxide in glyme in the presence of tetramethylethylene, an adduct could be iso-

(7) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.

(8) le Noble, W. J.; Tatsukami, Y.; Morris, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 5681.

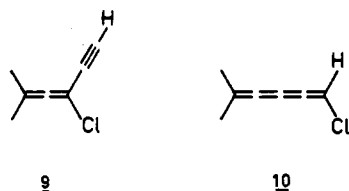
(9) le Noble, W. J.; Chiou, D.-M.; Okaya, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3244.

(10) Gusev, B. P.; Tatarchuk, V. V.; Azerbaev, I. N.; Kucherov, V. F. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1966**, 1163.

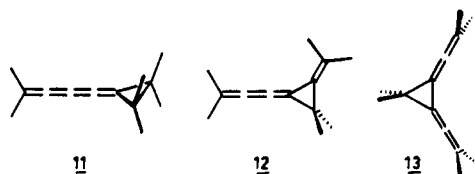
(11) Armitage, J. B.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1952**, 1993.

(12) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. A reviewer commented that the similarity of ΔV^\ddagger for basic hydrolysis of **7-Cl** and neutral hydrolysis of 1-Cl may mean that the former compound heterolyzes in the neutral form, even under basic conditions. However, this is quite unlikely; Shiner⁶ has shown that base-promoted D exchange in 1-Cl is many orders of magnitude faster than hydrolysis, and the same is to be expected to be true of **7-Cl**. The second-order rate law and trapping results would also be unaccounted for.

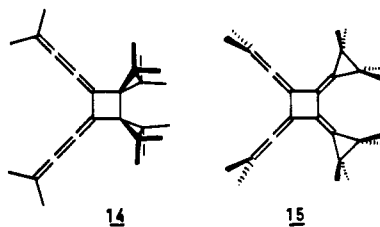
(13) A few monomeric pentatetraenes are known. See, e.g.: Irngartinger, H.; Götzmann, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 340; Nader, F. W.; Brecht, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 93.



lated. However, the structure of this material is clearly not the simple one, 11; thus, the ^1H NMR shows three sharp and equally intense signals at δ 1.06, 1.18, and 1.76.



In view of the well-known propensity of *exo*-methylene-cyclopropanes to rearrange via trimethylenemethanes,¹⁴ 12 and 13 were also considered, but clearly neither satisfies. The dimeric nature of this product became clear from the mass spectrum; the parent peak occurs at m/z 348. Heat-to-tail dimers are ruled out by the proton NMR spectrum. The IR, UV, and ^{13}C NMR spectra leave the two possibilities 14 and 15 open as candidates. A weak

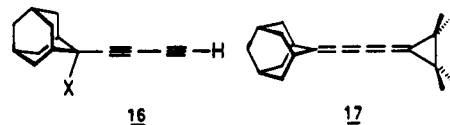


band shows at 1995 cm^{-1} in the IR; the UV spectrum in *n*-hexane shows maxima at 337 nm (ϵ 2000), 318 (3000), 303 (3300), 256 (14000), 243 (15000), 225 (49000), and 214 (52200), in close similarity to Hartzler's D_{4h} dimer of tetra-*tert*-butylhexapentaene.¹⁵ The ^{13}C NMR shows three signals at low and six at high field, in better agreement with 14 than with 15. Strong support for this assignment comes from Stang's recent finding of a similar structure for a head-to-head hexapentaene dimer on the basis of an X-ray diffraction study;¹⁶ our own compound unfortunately proved too unstable to air to permit the growing of a single crystal (the instability of cumulenes to ground-state oxygen is well-known¹⁷).

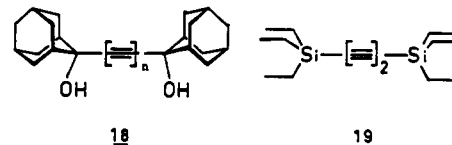
The one missing low-field signal is assumed to be the result of accidental isochronicity, as is the missing ^1H (methyl) signal.

The oxygen sensitivity (all samples gave the correct C/H ratio but contained 5–20% oxygen) led us to try a precursor more likely to give a product resistant to dimerization because of steric bulk. Success was attained with adamantane derivative 16-Cl, which gave 17 under the same conditions we had used before. This product showed no tendency to dimerize (parent m/z 266) or react with oxygen and was easily characterized by its spectra.

The remainder of our effort was directed at extending our knowledge to the next higher member of the odd (number of sp^2 carbons) cumulenylenes; however, syn-



thetic difficulties prevented us from doing so. Since success eluded us, these difficulties are only briefly recounted and more fully described in the Experimental Section. The simple ethynylation procedure, used successfully to produce the alcohols of 1, 7, and 16, when applied to adamantane and hexatriyne (obtained from 1,6-dichlorohexa-2,4-diyne and base) gave only symmetrical diol 18 ($n = 3$). Attempts at oxidative crosscoupling of 16-OH with



(triethylsilyl)ethyne gave only self-coupling products 19 and 18 ($n = 4$). We then tried to apply the Cadiot-Chodkiewicz coupling¹⁸ of cuprous acetylides with bromoacetylenes in three ways (see Scheme I). All three approaches suggested in the scheme led to a solution in which the presence of the product triyne could be demonstrated; in one instance, a solid could be isolated and characterized as 26. However, all attempts to deprotect it met with decomposition.

Experimental Section

Materials. 5-Hydroxy- and 5-chloro-5-methylhexa-1,3-diyne (7-OH¹¹ and 7-Cl,¹⁰ respectively), 1,6-dichloro-2,4-hexadiyne (27),¹⁸ (trimethyl- and (triethylsilyl)acetylene (28 and 29, respectively),¹⁹ 1,4-bis(trimethylsilyl)butadiyne (30),²⁰ 2-ethynyladamant-2-yl trimethylsilyl ether (31),²¹ and (bromoethynyl)trimethylsilane (23)²² were prepared as described in the references given; commercial cuprous bromide was purified according to House and Umen.²⁰

Kinetic Experiments. The high-pressure apparatus used was the same as reported previously;² the solvolysis of 7-Cl was carried out in methanol-water (80:20, v/v) with 10-fold excess NaOH at 30.00 ± 0.02 °C. Acid-quenched samples were analyzed by means of ^1H NMR, the CH_2Br_2 internal standard showing the decay of the methyl signal of 7-Cl at δ 1.86. The activation volume was calculated in the usual way.¹² In atmospheric pressure experiments, the rate of chloride ion formation was followed by conductometric measurements of HNO_3 -quenched samples with standard silver nitrate solution.

Solvolysis Products of 7-Cl. A reaction mixture in which the methanolysis was estimated to be 80% complete was extracted with methylene chloride. GC analysis showed the presence of two components, which were collected and shown to be the methyl ether 7-OMe (^1H NMR δ 3.35 (s, 3 H), 2.16 (s, 1 H), 1.46 (s, 6 H)) and compound 9 (^1H NMR δ 2.19 (s, 1 H), 1.49 (s, 6 H)). Anal. Cl.

Trapping of 8. 7-Cl (20 mmol) dissolved in 10 mL of well-dried glyme was added dropwise (45 min) into a magnetically stirred solution of 21 mmol of freshly sublimed *t*-BuOK in 20 mL of glyme containing a 10-fold excess of tetramethylethylene at -30 °C. The temperature was thereafter allowed to rise slowly (several hours) to ambient temperature; a nitrogen atmosphere was maintained throughout. The volatile components were flash evaporated, and the dark brown residue was extracted several times with 50 mL of hexane; the resulting red solution upon flash evaporation left a dark red wax. Trituration with 50 mL of methanol led to the

(14) Pasto, D. J. *J. Org. Chem.* 1976, 41, 4012.

(15) Hartzler, H. D. *J. Am. Chem. Soc.* 1971, 93, 4527. For a recent example, see: Visser, R. G.; Oostveen, E. A.; Bos, H. J. T. *Tetrahedron Lett.* 1981, 22, 1139.

(16) Kaftory, M.; Agmon, I.; Ladika, M.; Stang, P. J. *J. Am. Chem. Soc.* 1987, 109, 782.

(17) For an example and references, see: Sander, W.; Patyk, A. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 475.

(18) Brandsma, L.; Verkrujsssen, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: New York, NY, 1981; p 221.

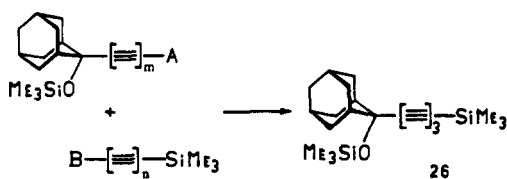
(19) Eastmond, E.; Johnson, T. R.; Walton, D. R. M. *Tetrahedron* 1972, 28, 4601.

(20) House, H. O.; Umen, M. J. *J. Org. Chem.* 1973, 38, 3893.

(21) Chiou, D.-M. Thesis, Dept. of Chemistry, SUNY at Stony Brook, NY, 1978.

(22) Miller, J. A.; Zweifel, G. *Synthesis*, 1983, 128.

Scheme I



- I: A = Br, B = Cu, $m = 1$, $n = 2$ (20 + 21)
 II: A = Cu, B = Br, $m = 2$, $n = 1$ (22 + 23)
 III: A = Cu, B = Br, $m = 1$, $n = 2$ (24 + 25)

appearance of a tan solid in 15% yield; mp 120–124 °C dec. Sublimation at 80 °C (10^{-5} Torr) slowly produced a light yellow solid, mp 129–130 °C dec; most of the product was obtained in somewhat less pure form by column chromatography (silica gel, benzene–dichloromethane–ethyl acetate). The spectra of 14 are discussed in the text above.

2-Butadiynyladamantan-2-ol (16-OH) and Derivatives 16-Cl and 17. A 250-mL three-necked round-bottom flask fitted with a dry ice–acetone condenser and addition funnel was charged with liquid ammonia (100 mL), a pinch of ferric nitrate, and 3.5 g of sodium added in small pieces with efficient magnetic stirring. After 1 h, 6.2 g (0.05 mol) of 1,4-dichloro-2-butyne was added over 0.5 h; 7.5 g (0.05 mol) of adamantanone was added and the mixture stirred overnight. The ammonia was allowed to evaporate, and the residue was treated with 0 °C water (100 mL), acidified with 50% sulfuric acid, and extracted with methylene chloride to yield crude 16-OH as a dark brown solid; after crystallization from benzene, mp 102 °C. Sublimation (190 °C, 1 Torr) gave a white sample, mp 104 °C. Anal. C, H.

A 50-mL round-bottom flask containing a magnetic stirring bar and 4 mL of concentrated hydrochloric acid was maintained at 0–5 °C, while a mixture of 1 g of calcium chloride and 0.01 g of hydroquinone was added. This mixture was warmed to room temperature, and 0.5 g of 16-OH was added in 10 min. A condenser was attached and the mixture heated to 55–60 °C with vigorous stirring for 8 h. Aqueous methylene chloride workup followed by chromatography (silica gel, hexane–benzene, 70:30, v/v) gave light brown 16-Cl, mp 75–80 °C. Sublimation (160 °C, 1 Torr) gave a white sample: mp 79–80 °C; $^1\text{H NMR}$ δ 2.1 (s, 1 H), 2.1–1.5 (br m, 14 H); IR (KBr) 3300 ($\equiv\text{C}-\text{H}$), 2150 ($\text{C}\equiv\text{C}$), 700 cm^{-1} (C–Cl); $^{13}\text{C NMR}$ δ 77.58, 70.73, 70.14, 69.90, 67.34, 40.35, 37.62, 35.85, 31.87, 26.37. Anal. C, H.

In a 100-mL three-necked round-bottom flask fitted with an addition funnel, magnetic stirring bar, and a nitrogen inlet were added 70 mg (0.32 mmol) of 16-Cl, 1.4 g (16 mmol) of tetramethylethylene, and 30 mL of dry glyme. The solution was cooled to 0 °C and purged with nitrogen. A solution of 67 mg (0.6 mmol) of freshly sublimed potassium *tert*-butoxide in 15 mL of dry glyme was added dropwise over a 1-h period, and then the mixture was warmed to room temperature and stirred overnight. After neutralization with ammonium chloride, evaporation, extraction (hexane), filtration, and reevaporation, chromatography (silica gel, hexane) yielded pale solid 17: mp 128–130 °C dec; $^1\text{H NMR}$ δ 2.5 (s, 2 H), 1.9–1.7 (s, 12 H), 1.31 (s, 12 H); IR (CDCl_3) 2040 cm^{-1} ; $^{13}\text{C NMR}$ 161.57, 156.12, 122.68, 118.43, 110.54, 38.85, 36.59, 31.63, 29.62, 27.94, λ_{max} 21.23; MS, m/z 266 (45, M^+), 251 (79), 239 (10); UV (*n*-hexane) [λ_{max} , nm (ϵ)] 234 (139380), 237 (sh) (77240), 256 (sh) (13250), 262 (14740), 290 (10910), 300 (2740).

Bis(2-hydroxy-2-adamantyl)hexatriyne (18; $n = 3$). In a 250-mL three-necked round-bottom flask fitted with a dry ice–acetone condenser and an addition funnel was treated 100 mL of liquid ammonia with small pieces of sodium (1.85 g, 0.08 mol) with efficient magnetic stirring. After 1 h, 3.7 g (0.025 mol) of 28 was added dropwise in 0.5 h, and then 3.7 g (0.025 mol) of adamantanone in 25 mL of cooled ether was added dropwise. The mixture was stirred at –78 °C overnight and quenched with 5 g of solid ammonium chloride, the ammonia was allowed to evaporate, and 100 mL of water and 100 mL of ether were added. After filtration and workup, a brown solid (3 g) resulted; TLC showed only one spot. Crystallization (hexane and ether) gave pale brown crystals: mp 228 °C dec; MS, m/z 374.

Attempted Cross-Coupling of 16-OH and (Triethylsilyl)ethyne. 16-OH (500 mg, 2.5 mmol), ethynyltriethylsilane

(700 mg, 5 mmol), and Hay catalyst²³ [prepared from 1 g of cuprous chloride and 0.5 mL of tetramethylethylenediamine (TMEDA) in 20 mL of acetone] were mixed with acetone (50 mL) in a pressure bottle in a hydrogenation apparatus operated at 25 psi oxygen pressure. After 12 h, the mixture was poured into cold dilute hydrochloric acid and extracted with methylene chloride. The organic solution was dried and reduced to a small volume to give a dark brown oil. $^1\text{H NMR}$ showed multiplets at δ 2.5–1.05 (adamantyl protons) and δ 1.5–0.5 (triethylsilyl protons). TLC (petroleum ether–25% ethyl acetate) showed two spots different from the starting materials. Column chromatography (silica gel) gave a light oil identified as 19: $^1\text{H NMR}$ δ 1.5–0.5 (m, SiEt_3); MS, m/z 278 (M^+). The second component was a light yellow solid identified as 18 ($n = 4$): MS, m/z 398 (M^+); $^1\text{H NMR}$ (C_6D_6) δ 2.5–1.0 (m).

2-(2-Bromoethynyl)-2-adamantyl Trimethylsilyl Ether (20). In a procedure similar to one published,²⁴ a solution of 2-(2-ethynyl)adamantyl trimethylsilyl ether (obtained via ethynylation of adamantanone followed by trimethylsilylation; 5.208 g, 0.021 M) in acetone (140 mL) was treated with *N*-bromosuccinimide (4.361 g, 0.024 M) in the presence of silver nitrate (0.350 g). The solution was stirred for 2 h at room temperature, passed through a short Florisil column, diluted with water (200 mL), and extracted with methylene chloride (three times). After workup and filtration through a short silica gel column, evaporation of solvent afforded 6.7 g (97.5%) of a colorless liquid with a single TLC spot: $^1\text{H NMR}$ δ 1.25–2.25 (m, 14 H), 0.4 (s, 9 H); IR no signal at 3300 cm^{-1} ; MS, m/z 311 (19), 313 (18, $\text{M} - 15$), 247 (100, $\text{M} - \text{Br}$).

Conversion of 20 into 26. A 1.4 M solution of methyl-lithium–lithium bromide complex (3.7 g, 0.005 M) was added dropwise to a solution of 30 (1 g, 0.005 M) in THF (10 mL) at 0 °C. After 1 h of stirring, cuprous bromide was added (0.717 g, 0.005 M). The resulting dark blue solution of 21 was stirred at room temperature for 30 min, the THF was evaporated, and 10 mL of pyridine was added followed by 20 (1.635 g, 0.005 M). After 4 h at room temperature followed by quenching (ammonium chloride solution), extraction (petroleum ether), drying, passage through a short Florisil column, evaporation to small volume, and chromatography (silica gel, petroleum ether), two components were obtained. The first of these was 20 (35%); the other (30%) was a yellow oil, which was reasonably stable in dilute solution at –30 °C but decomposed at higher temperatures; MS (solid probe) m/z 368 (M^+), 353 ($\text{M}^+ - 15$). All attempts to remove solvent resulted in decomposition.

Generation of 22 from 16-OSiMe₃ and Its Reaction with 23. A 1.4 M ether solution (2.1 mL) of MeLi–LiBr was added dropwise to a solution of 16-OSiMe₃ (1 g, 2.9 mM) in THF (5 mL) at 0 °C. After 1 h of stirring, anhydrous (0.417 g, 2.91 mM) cuprous bromide was added, and stirring continued for 1 h at room temperature. Alternatively, this solution could be obtained as follows: A 10-mL THF solution of 16-OSiMe₃ (1.0 g, 3.6 mM) was treated dropwise at –78 °C under nitrogen with a 1.5 M hexane solution of *n*-BuLi (2.44 mL). The mixture was allowed to slowly reach 0 °C; anhydrous cuprous bromide (0.526 g, 3.6 mM) was added, and the mixture was stirred for 1 h at room temperature.

The solvent was removed under reduced pressure and replaced with anhydrous pyridine (10 mL); 23 (0.5 g, 2.9 mM) was introduced via syringe at 0 °C. Further stirring for 4 h and workup afforded only a small amount of 26 at the same yellow liquid encountered before.

(4-Bromobutadiynyl)trimethylsilane (25) and Its Coupling with 24. In a 100-mL round-bottom flask was dissolved 30 (1.94 g, 10 mmol) in 10 mL of dry THF under nitrogen. This was cooled to 0 °C, and a 1.34 M solution of methyl-lithium–lithium bromide (8 mL, 11 mmol) in ether was added dropwise. The mixture was stirred at 0 °C for 30 min, warmed to 25 °C, and stirred for 1 h at that temperature. It was then cooled to –78 °C and treated sequentially with dry pyridine (1.5 mL, 20 mmol) and a solution of bromine (1.76 g, 11 mmol) in 20 mL of methylene chloride. The resulting mixture was stirred at –78 °C for 15 min, gradually warmed to room temperature, and then poured into 25 mL of ice-cold 6 M hydrochloric acid. The layers were separated, and

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the solution was extracted with pentane (2×50 mL). The combined organic extracts were washed with 6 M hydrochloric acid (3×25 mL), 20% aqueous cadmium chloride (20 mL), 10% aqueous sodium sulfite (20 mL), saturated aqueous sodium hydrogen carbonate (20 mL), and saturated aqueous sodium chloride (30 mL) and then dried with magnesium sulfate. The solvent was removed under reduced pressure, the temperature rising by 5–10 °C. The resultant dark brown solution was stirred for 2 at ambient temperature, poured into saturated aqueous sodium chloride solution, and extracted with hexane; the extract was added to 20% aqueous cadmium chloride to precipitate the pyridine. After filtration, the organic layer was washed with bicarbonate and sodium chloride, dried, and reduced in volume to give a viscous dark liquid. It was passed through a silica gel column with hexane as eluant to give a light yellow oil that solidified in a vacuum desiccator. This compound was characterized as **26**: ^1H NMR δ 2.5–1.2 (br s, 14 H), 0.18 and 0.16 (ss, 18 H, two Me_3Si groups); MS, m/z 368 (M^+); ^{13}C NMR δ 88.87, 74.44, 74.35, 74.21, 71.33, 64.03, 61.96, 39.57, 37.54, 35.08, 26.63, 1.78, -0.49. The compound

quickly darkened in solution upon exposure to fluoride ion; no products could be characterized.

Acknowledgment. This work was partially supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society; we acknowledge with thanks the donors of this fund. W.J.L.N. thanks the Humboldt Foundation for the Senior Scientist Award and Dr. R. van Eldik, who graciously served as his host at the University of Frankfurt.

Registry No. 7-Cl, 1000-44-8; 7-OMe, 50398-61-3; **8a**, 79060-03-0; 16-OH, 110391-14-5; 16-Cl, 110372-96-8; 16-OSiMe₃, 110373-03-0; **17**, 110372-97-9; **18** ($n = 3$), 110372-98-0; **18** ($n = 4$), 110372-99-1; **19**, 17047-96-0; **20**, 110373-01-8; **23**, 18243-59-9; **24**, 110391-15-6; **25**, 110373-04-1; **26**, 110373-02-9; **28**, 1066-54-2; **30**, 4526-07-2; 1,4-dichloro-2-butyne, 821-10-3; adamantanone, 700-58-3; tetramethylethylene, 563-79-1; ethynyltriethylsilane, 1777-03-3; 2-ethynyladamant-2-yl trimethylsilyl ether, 110373-00-7.

Solvent Effect in the Reduction of α -Keto Esters by Aqueous Titanium Trichloride

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Received November 14, 1986

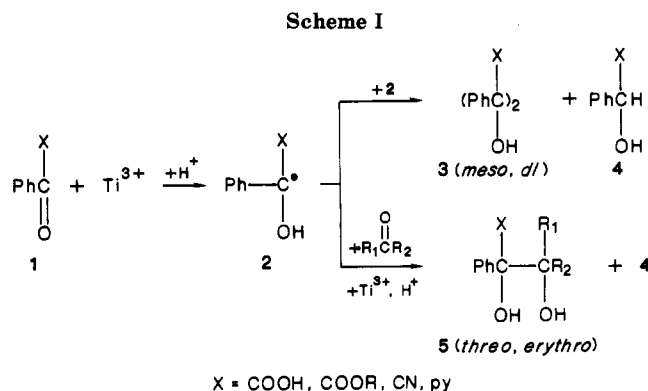
In the reduction of **1** by Ti(III) ion the dimeric **3** or monomeric **4** reduction products could be made to predominate by the choice of the solvent. It is found that (a) dimerization, via coupling of two radicals **2**, increases with increasing simultaneously the dielectric constant and the hydrogen ion concentration of the reaction medium and (b) alcohol formation, which occurs via electron transfer between radical species having different redox potentials, increases with decreasing the hydrogen ion concentration of the medium. Under appropriate reaction conditions, the dimerization process is partially stereoselective. Reaction mechanisms are proposed which account for the ratio of both dimer/alcohol and *meso/dl* under different experimental conditions.

Carbonyl compounds **1**, activated toward reduction by an electron-withdrawing group X, are reduced by aqueous titanium trichloride to the corresponding dimers **3**^{1,2} (Scheme I). If the reaction is carried out in the presence of simple ketones or aldehydes, the formation of symmetrical diols **3** is almost suppressed and radicals **2** selectively add to the carbonyl carbon of $\text{R}_1\text{C}(\text{O})\text{R}_2$ to yield the unsymmetrical diols **5**.^{2,3} The monomeric reduction products **4** are always present. The relative yields of **4** with respect to **3** or **5** are strongly solvent dependent:⁴ higher in alcoholic or ethereal solvents, lower in carboxylic acid solvents.

In this paper we report our investigation of the role played by the solvent on the dimer/alcohol ratio in the reduction of **1** by Ti(III) ion with the aim to better understand the reaction paths and properties of the intermediates involved, in view of their possible use in carbon-to-carbon bond-forming reactions (Scheme I).

Results and Discussion

After preliminary experimentation, we selected methyl phenylglyoxalate (**1**, X = COOCH_3) as a suitable substrate for a detailed study since a precise method of products analysis has been found by using NMR spectroscopy: the



methyl proton shifts of the substrate, *meso* dimer, *dl* dimer, and alcohol are well apart. The effect of the solvent on the ratio dimer/alcohol is shown by some representative reactions collected in Table I, all being performed under identical experimental conditions except for the solvent.

Dimer **3** is the major product in carboxylic acid solvents, whereas alcohol **4** prevails in alcoholic or ethereal ones.

If radical **2** (X = COOCH_3 , Scheme I) were the only reaction intermediate, the possible paths leading to **4** or **3** would be hydrogen atom abstraction of radical **2** from the solvent, further reduction of **2** by Ti(III) ion, and disproportionation or dimerization of **2**. From our experimental results, it comes out that substantially the same dimer/alcohol ratio is obtained in either isopropyl alcohol and *tert*-butyl alcohol, notwithstanding the former is a

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