Figure 1. PE spectra of dithioacetic acid, of 1,2,3-thiadiazole, and of their decomposition products at 730 and 900 K, respectively (hatched: $H_2C=C=S$; reference PE spectra of H_2S and N_2; cf., e.g., ref 10), and correlation with calculated ionization energies[11] for $H_2C=C=S$.

cerns their probably uniform mechanisms, only more general rationalizations are readily at hand: according to bond enthalpy parameters, in dithioacetic acid the $-C$—$S-$ bond should be

the weakest ($\Delta H_b \sim 270$ kJ/mol), and, therefore, the radical chain presumably starts via the ·SH radical.[14] In the 1,2,3-thiadiazole thermolysis no evidence is found for ethynyl mercaptan;[8,15] on the other hand an analogous hydrogen shift accompanies the formation of a C=X double bond, e.g., in the thermal HCl expulsion from ethylene chlorhydrin yielding exclusively acetaldehyde.[16]

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(3) Cf. the Master Thesis of G. Bert, University of Frankfurt, 1977. The liquid educts evaporate at room temperature ($p \sim 10$ Pa) and pass a quarz tube 30 cm long and of ~ 1 cm diameter, heated by an oven of the specified temperature. The distance between oven and spectrometer target chamber amounts to ~ 25 cm, suggesting for thioketene a half-life time of more than 1 s.
(4) The parent molecule thioketene—considerably less stable than its alkyl derivatives—has been reported to be generated by heating *tert*-butyl ethynyl sulfide $R_3CSC\equiv CH$[6] or hexamethyltrithiane $(R_2CS)_3$[7] or photolyzing 1,2,3-thiadiazole,[8] and to be identified in matrix[8] or in the gas phase[7] by infrared[6,8] or microwave spectra.[7]
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(11) The PNO-CEPA (Pseudonatural Orbital—Coupled Electron Pair Approach) calculations[9] started from an ab initio SCF wave function obtained from a GTO basis set (C: 9s/5p/1d, S: 11s/7p/1d, H: 5s/1p) at a geometry adopted from stable thioketenes[12] or from standard structural parameters. An energy threshold 2×10^{-3} eV has been used for selecting configurations; for further details see ref 9.
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(13) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973, pp 124, 125.
(14) The 730 K pyrolysis of dialkyl sulfides

$$R_3CSSCR_3 \xrightarrow{\Delta T} H_2S + \frac{1}{8}S_8 + R_2C=CH_2$$

(R = H, CH_3) is most probably initiated by R_3CS· radicals; cf. Master Thesis of S. Mohmand,[2] University of Frankfurt, 1976.
(15) The methyl derivative $HC\equiv CSCH_3$ exhibits in the lower energy region PE bands at 8.81, 10.34, 11.62, and 12.59 eV; cf. the Master Thesis of U. Stein,[2] University of Frankfurt, 1975.
(16) Master Thesis of H. Zacharias,[2] University of Frankfurt, 1976.

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Synthesis, Trapping, and Dimerization of 9,10-Benzotricyclo[3.3.2.0^{3,7}]deca-3(7),9(10)-diene. X-Ray Crystal Structure of the Dimer

Sir:

The preparation of bridgehead olefins with torsionally strained double bonds has been an area of intense synthetic activity in recent years.[1] A much less studied class of bridgehead olefins consists of those in which the carbons forming the double bonds are pyramidalized,[2] as they are in dehydrobenzene and small cycloalkynes.[3] Several years ago we developed transannular reductive ring closure as a key step in the preparation of a series of such olefins.[4,5] In this communication we
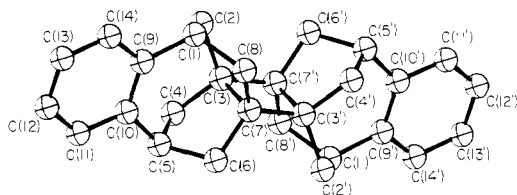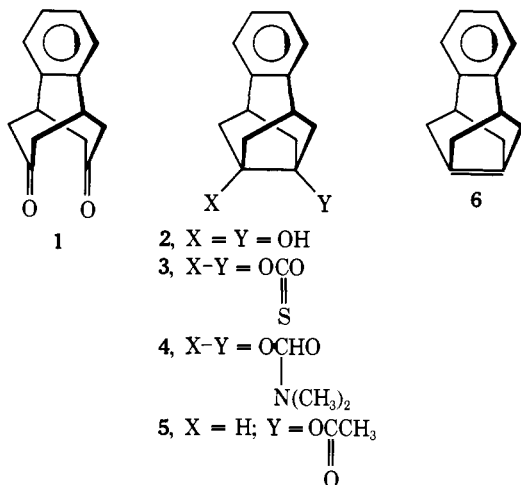
Figure 1. A computer generated drawing of the dimer of **6**. The hydrogens have been omitted for clarity.

report the first successful synthesis of a member of this series and the crystal structure of the dimer formed from it.

1

2, X = Y = OH

3, X–Y = OCO
$\quad\quad\quad\quad \| $
$\quad\quad\quad\quad S$

4, X–Y = OCHO
$\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad N(CH_3)_2$

5, X = H; Y = OCCH_3
$\quad\quad\quad\quad\quad\quad \|$
$\quad\quad\quad\quad\quad\quad O$

6

The readily available diketone (**1**)[6] underwent transannular ring closure to the diol (**2**) on reduction with zinc amalgam in aqueous HCl.[4] The crystalline diol,[7] mp 182–182.5 °C, was obtained in 92% yield. Its ^{1}H NMR spectrum (CDCl$_3$) showed δ 1.9–2.5 (m, 8 H), 3.15 (t, 2 H, J = 5 Hz), 3.73 (s, 2 H), 7.12 (s, 4 H); ^{13}C NMR (CDCl$_3$) δ 42.27 (d), 50.03 (t), 83.40 (s), 126.71 (d), 129.54 (d), 144.24 (s). Like the thionocarbonate prepared from catechol,[8] this derivative (**3**)[7] of the diol failed to give any indication of double bond formation on heating in refluxing triethyl phosphite. Heating the dimethylamino-dioxolane (**4**)[7,9] in refluxing acetic anhydride[10] also failed to give evidence of formation of the olefin (**6**). However, we found that pyrolysis of **4** in refluxing tetraglyme, containing 1 equiv of acetic acid[11,12] and diphenylisobenzofuran as trapping agent, gave, in 45–55% yield,[13] the crystalline Diels–Alder adduct of **6**,[7] mp 217–217.5 °C. When diphenylisobenzofuran was omitted from the reaction, the acetate (**5**)[7] was obtained in 14–17% yield.[13] In the absence of the trapping agent, the major product of this reaction was, however, a crystalline dimer,[7] mp >300 °C, which precipitated from the reaction mixture on cooling and could be isolated in up to 40% yield. The simplicity of the ^{1}H NMR ((CDCl$_3$) δ 1.52 (d, 8 H, J = 12.5 Hz), 2.48 (d of d, 8 H, J = 12.5 and 6 Hz), 3.42 (t, 4 H, J = 6 Hz), 7.07 (s, 8 H)) and ^{13}C NMR ((CDCl$_3$)[14] δ 44.13, 51.84, 56.83, 125.80, 129.04, 146.59) spectra of the dimer was consistent with the assignment of its structure as that resulting from a formal $_\pi 2_s + _\pi 2_s$ reaction.

Because the structure assigned to the dimer contains a novel feature, two [3.3.2]propellane[15] moieties that share a common cyclobutane ring, an x-ray study of crystals of the dimer, grown from a supersaturated mesitylene solution, was undertaken. Preliminary photographs showed monoclinic symmetry, and accurate lattice constants, determined by least-squares fitting of 15 2θ values, were a = 19.126 (5), b = 7.928 (2), c = 18.970 (5) Å, and β = 139.28 (1)°. The systematic absences conformed to $C_{2/c}$ and a measured density of ~1.29 g/cm^3 indicated z = 4. Thus $C_{14}H_{14}$ or one-half of the dimeric $C_{28}H_{28}$

structure forms the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114.1°$ were recorded on a four-circle diffractometer using graphite monochromated Cu Kα (1.541 78 Å) radiation. Of the 1274 reflections surveyed 1133 were judged observed after correction for Lorentz, polarization, and background effects. The structure was solved uneventfully by a multisolution, weighted sign determining procedure.[16] Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic hydrogens converged to a standard crystallographic residual of 0.036.[17]

Figure 1 is a drawing of the final x-ray model of the dimer, less hydrogens. The structure spans a crystallographic inversion center, and the two halves are strictly related only by this inversion center, although the molecule has experimental D_{2h} symmetry. The most noteworthy aspects of the structure are the long bonds in the planar cyclobutane ring and the short bonds leading away from it.[18] The cyclobutane bonds joining the halves (C(3)–C(7')) are 1.589 (3) Å, and the other two cyclobutane bonds (C(3)–C(7)) are 1.579 (4) Å. The four noncrystallographically equivalent bonds leading away from the cyclobutane ring have an average distance of 1.526 (10) Å.

These observations could be explained by assuming that each bridgehead carbon, in order to bond most effectively to two other bridgehead and to two nonbridgehead carbons, is constrained to use hybrids with large amounts of p character in forming the bonds of the four-membered ring. Analogous proposals have been advanced to explain the bond lengths found in other small-ring propellanes.[19] Alternatively, the long bonds found in the cyclobutane ring of the dimer could be attributed to steric crowding, since all four bridgehead atoms are tetrasubstituted. Similarly lengthened bonds between tetrasubstituted carbons are not uncommon.[20] While the former effect may be responsible, at least in part, for the long central bond in within each [3.3.2]propellane unit of the dimer, the two even longer bonds of the four-membered ring are almost certainly the result of the latter effect. The x-ray structure of the dimer shows a very short (1.93 Å) nonbonded contact between pairs of hydrogens that are attached to carbons (e.g., C(8) and C(4')), adjacent to the bridgeheads. Partial relief of van der Waals repulsions between the four pairs of such hydrogens in the dimer surely contributes significantly to the unusual length of the two bonds formed upon dimerization.

Further studies of the chemistry of **6** and that of its dimer are in progress.

Supplementary Material Available: The crystallographic data for the dimer, fractional coordinates (Table 1), bond distances (Table 2), bond angles (Table 3), and observed and calculated structure factors (Table 4) (9 pages). Ordering information is given on the masthead page.

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(12) In *refluxing* tetraglyme both methyl iodide and acetic anhydride also served to induce fragmentation of 4 to 6.
(13) Diol (2) was also isolated from the pyrolysis reaction in 20–30% yield. The origin of the diol is not clear. Although we took great pains to thoroughly dry the tetraglyme used, we cannot rule out small amounts of adventitious water in the solvent as being responsible, at least in part, for the formation of the diol. The yield of 2 was smallest when 4 and 1 equiv of acetic acid were pyrolyzed in the absence of solvent.
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(21) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1972–1977.

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Parallel Reaction Pathways in the Cobalt-Catalyzed Cyclotrimerization of Acetylenes

Sir:

A variety of transition metal compounds catalyzes the cyclotrimerization of alkynes to arenes.[1-3] In many cases, particularly with low valent metal catalysts, metalocyclopentadienes or metalloles (1, cf. Scheme I), formed by oxidative cyclization of two coordinated alkynes, have been implicated as intermediates in the catalytic cycle.[4]

Two modes of reaction of alkynes with metalloles have been suggested (Scheme I): (i) Diels–Alder addition of a coordinated alkyne to the diene moiety of the metallole generating bicyclic intermediate (2) and (ii) insertion of a coordinated acetylene into a metal–carbon σ bond leading to metalocycloheptatriene (3). In either case the final step is reductive elimination of arene with release of the coordinatively unsat-

Scheme I
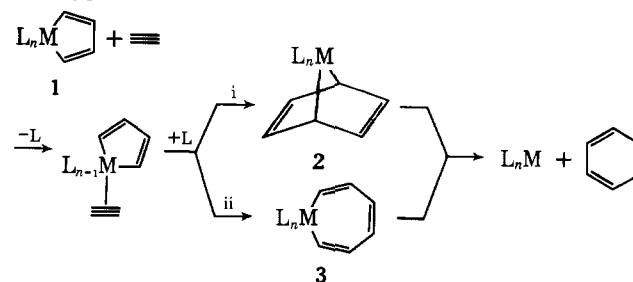
urated metal fragment. It has been tacitly assumed that coordination of the alkyne precedes either i or ii. Indeed, Collman and co-workers report that blocking the vacant coordination site of $IrCl(PPh_3)_2\{C_4(CO_2Me)_4\}$ with CO inhibits completely the cyclotrimerization of dimethylacetylene dicarboxylate by this metallole.[4a]

As part of an investigation of alkyne cyclotrimerization catalyzed by phosphine derivatives of (η^5-cyclopentadienyl)-cobalt, we have examined the reactions of alkynes with trialkyl- and triarylphosphinecyclopentadienylcobalta-2,3,4,5-tetramethylcyclopentadiene (4). We find that the mechanism of the reaction is critically dependent upon the nature of the alkyne.
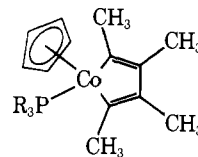
4a, $R = C_6H_5$
b, $R = C_2H_5$
c, $R = CH_3$

The reaction of (η^5-C_5H_5)Co(PPh$_3$)$_2$ (5) with 2 equiv of 2-butyne (6) in refluxing benzene affords yellow-brown 4a rapidly and in good yield.[5] In a sealed tube in benzene at 120 °C, 4a catalyzes the trimerization of 6 to hexamethylbenzene (7);[6] this process may be monitored conveniently by NMR spectrometry. In the presence of excess triphenylphosphine, the pseudo-first-order rate fits the expression:

$$\frac{d[7]}{dt} = k_{obsd} \frac{[4a][6]}{[PPh_3]}$$

This rate law is consistent with the mechanism outlined in Scheme II, involving substitution of PPh$_3$ by 6 via coordinatively unsaturated intermediate 8. Assuming this mechanism,

$$\text{rate} = \frac{d[7]}{dt} = \frac{k_1 k_3 [4a][6]}{k_{-1}[PPh_3] + k_3[6]}$$

so at high [PPh$_3$] where $k_{-1}[PPh_3] \gg k_3[6]$,

$$k_{obsd} = \frac{k_1 k_3}{k_{-1}} = 4.5 \times 10^{-5} \text{ s}^{-1}$$

This mechanism is also supported by kinetic data under conditions of high acetylene and low phosphine concentrations. If under these conditions $k_3[6] \gg k_{-1}[PPh_3]$, the rate law reduces to

$$\frac{d[7]}{dt} = k_1[4a]$$

Since the concentration of catalyst does not change, an overall zero-order rate is expected.[7] Accordingly, the rate of appearance of hexamethylbenzene at 74 °C in a benzene solution initially containing 1.90 M 6 and 0.19 M 4a was followed by ^{1}H NMR spectrometry and found constant (2.0×10^{-5} M s^{-1})