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Unexpected Intramolecular Reactions of Intermediate Phosphacarbonyl Ylide Tungsten Complexes**

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Carbonyl ylides (**I**; Scheme 1) can be obtained by reactions of carbenes and carbenoids with aldehydes and ketones^[1, 2] or by electrocyclic ring opening of oxiranes.^[3] As 1,3-dipoles^[4] they are mechanistically and preparatively of interest for heterocycle syntheses, and can be detected by intra- and intermolecular trapping reactions.^[2] In reactions of carbonyl compounds with organophosphorus carbene analogues, such as phosphanediyls, electrophilic, terminal phosphanediyl metal complexes,^[5] iminophosphorus analogues (**II**–**V**) of carbonyl ylides has not yet



Scheme 1. Carbonyl ylides (I) and organophosphorus analogues (II-V) (R = alkyl, aryl; [M] = metal complex fragment).

been proved; thus, the course of the oxaphosphirane ring closure has not yet been elucidated. We recently reported the synthesis of an oxaphosphirane tungsten complex,^[8, 9] and postulated a terminal phosphanediyl tungsten complex with benzaldehyde as an intermediate to rationalize the reaction.^[10] Although a publication by Mathey et al. on Lewis acid/Lewis base adducts of electrophilic, terminal phosphanediyl tungsten complexes with phosphanes and amines has appeared,^[11] the reactions of these carbene analogues with carbonyls remain unexplained, as do those with imines, which proceed under the formation of three-membered heterocycles.^[12]

In order to investigate the course of the oxaphosphirane ring formation more closely, and to enable a comparison with the formation of azaphosphiridines, we have thermolyzed a 2H-azaphosphirene tungsten complex in the presence of benzophenone, acetophenone, and (E)-N-methyl(benzylidene)amine. Here we describe the new, and in some cases novel, complexes resulting from these reactions, and also report the first unam-

[**] Chemistry of 2H-azaphosphirene Complexes, Part 5. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Part 4: A. Ostrowski, J. Jeske, P. G. Jones, R. Streubel, J. Chem. Soc. Chem. Commun. 1995, 2507. biguous evidence for a phosphacarbonyl ylide complex in the oxaphosphirane ring formation.

The thermolysis of the 2*H*-azaphosphirene tungsten complex $1^{[13]}$ in toluene at 45 °C in the presence of benzophenone (2) or acetophenone (3) takes an unexpected course in both cases. With benzophenone, the products are benzonitrile,^[14] the oxaphosphirane tungsten complex 6, and the benz[c]-1,2-oxaphospholane tungsten complex 8. With acetophenone, the only product formed apart from benzonitrile^[14] is the tungsten complex 9, which bears a P-H function (Scheme 2). The prod-



Scheme 2. Thermolysis of 1 in the presence of benzophenone (2) and acetophenone (3).

ucts 8 and 9 can be readily separated by low-temperature chromatography and crystallization, whereas the oxaphosphirane tungsten complex 6 can only be obtained in reduced yield and is contaminated with 5-10% 8. The suggested constitutions of compounds 6, 8, 9 are based on their NMR spectroscopic, (Table 1) IR, and MS data,^[15] and are confirmed for 8 and 9 in the solid state by single-crystal X-ray structure analyses.^[16, 17]

Table 1. Selected NMR spectroscopic data of 6, 8, 9, and 12 [a].

6: ${}^{13}C{}^{1}H$ NMR: $\delta = 1.3$ (d, ${}^{3}J(C,P) = 4.7$ Hz, SiMe₃), 2.0 (d, ${}^{3}J(C,P) = 2.4$ Hz, SiMe₃), 31.8 (d, ${}^{1}J(C,P) = 17.3$ Hz, PCH), 71.7 (d, J(C,P) = 19.7 Hz, PCO), 127.9 (br, J(C,P) = 6.1 Hz, Ph), 128.2 (br, J(C,P) = 6.1 Hz, Ph), 128.3 (d, J(C,P) = 2.6 Hz, Ph), 128.4 (d, J(C,P) = 2.6 Hz, Ph), 128.6 (s, Ph), 129.2 (s, Ph), 130.1 (s, Ph), 132.4 (s, Ph), 195.5 (d, ${}^{2}J(C,P) = 8.1$ Hz, ercO), 196.5 (d, ${}^{2}J(C,P) = 34.1$ Hz, trans-CO); ${}^{31}P{}^{1}H{}$ NMR: $\delta = 52.2$ (d, ${}^{1}J(P,W) = 306.4$ Hz).

8: ${}^{13}C{}^{1}H$ NMR: $\delta = 2.8$ (d, ${}^{3}J(C,P) = 2.7$ Hz, SiMe₃), 3.2 (d, ${}^{3}J(C,P) = 1.9$ Hz, SiMe₃), 34.6 (d, ${}^{1}J(C,P) = 7.6$ Hz, PCH), 86.0 (d, J(C,P) = 7.5 Hz, OCH), 124.0 (d, J(C,P) = 7.6 Hz, Ar), 128.1 (d, J(C,P) = 13.8 Hz, Ar), 128.5 (d, J(C,P) = 8.6 Hz, Ar), 128.7 (s, Ph), 129.1 (s, Ph), 129.2 (s, Ph), 130.3 (d, J(C,P) = 1.4 Hz, Ar), 138.5 (d, J(C,P) = 1.1 Hz, Ph), 141.1 (d, J(C,P) = 12.9 Hz, Ar), 144.8 (d, J(C,P) = 29.2 Hz, Ar), 197.3 (dd, ${}^{2}J(C,P) = 7.7$, ${}^{1}J(C,W) = 126.6$ Hz, *cis*-CO), 200.3 (d, ${}^{2}J(C,P) = 24.0$ Hz, *trans*-CO); ${}^{31}P{}^{1}H$ NMR: $\delta = 140.4$ (d, ${}^{1}J(P,W) = 273.5$ Hz).

9: ${}^{13}C{}^{1}H$ NMR: $\delta = 0.4$ (d, ${}^{3}J(C,P) = 2.6$ Hz, SiMe₃), 2.3 (d, ${}^{3}J(C,P) = 3.4$ Hz, SiMe₃), 23.0 (d, ${}^{1}J(C,P) = 10.7$ Hz, PCH), 95.1 (d, ${}^{3}J(C,P) = 11.1$ Hz, $C = CH_2$), 127.2 (s, p-C), 127.3 (s, o-C), 128.8 (s, m-C), 135.4 (s, i-C), 156.7 (d, ${}^{2}J(C,P) = 9.1$ Hz, O-C = C), 196.4 (dd, ${}^{2}J(C,P) = 7.7$, ${}^{1}J(C,W) = 109.9$ Hz, cis-CO), 198.7 (d, ${}^{2}J(C,P) = 27.5$ Hz, trans-CO); ${}^{31}P{}^{1}H$ NMR: $\delta = 95.4$ (d, ${}^{1}J(P,W) = 276.5$ Hz).

12: ${}^{13}C{}^{1}H{}$ NMR: $\delta = 1.3$ (d, ${}^{3}J(C,P) = 3.9$ Hz, SiMe₃), 1.9 (d, ${}^{3}J(C,P) = 3.4$ Hz, SiMe₃), 18.2 (d, ${}^{1}J(C,P) = 27.5$ Hz, PCH(SiMe₃)₂), 41.9 (d, J(C,P) = 1.7 Hz, PCN), 56.4 (s, NCH₃), 127.4 (s, *p*-C), 127.6 (d, ${}^{3}J(C,P) = 1.6$ Hz, *o*-C), 128.3 (s, *m*-C), 136.3 (d, ${}^{2}J(C,P) = 4.1$ Hz, *i*-C), 196.4 (dd, ${}^{2}J(C,P) = 7.7$ Hz, ${}^{1}J(C,W) = 132.7$ Hz, *cis*-CO), 196.4 (d, ${}^{2}J(C,P) = 30.0$ Hz, *trans*-CO); ${}^{31}P{}^{1}H{}$ NMR: $\delta = -37.3$ (d, ${}^{1}J(P,W) = 269.1$ Hz).

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[[]a] Solutions of 6, 8, 9 and 12 in CDCl₃ at 25 °C; ¹³C NMR: 50.3, ³¹P NMR: 81.0 MHz. The deuterated solvents were used as internal standards, 85% H₃PO₄ as external standard.

It is noteworthy that the double phenyl substitution in the oxaphosphirane tungsten complex **6** leads to a significantly low-field-shifted resonance signal of the atoms of the three-membered ring, compared to those of the corresponding atoms in $10^{[8]}$ (6: $\delta^{31}P = 52.2$, ${}^{1}J({}^{31}P, {}^{183}W) = 306.4$ Hz; $\delta^{13}C = 71.7$, $J({}^{13}C, {}^{31}P) = 19.7$ Hz vs. $10: \delta^{31}P = 40.4, {}^{-1}J({}^{31}P, {}^{183}W) =$

 $[{Ph(H)C-O-PCH(SiMe_3)_2}W(CO)_5] \quad 10$

308.2 Hz; $\delta^{13}C = 59.7$, $J({}^{13}C, {}^{31}P) = 27.3$ Hz). The presence of the 1,2-oxaphospholane ring in **8** is demonstrated, for example, by the ${}^{31}P$ resonance signal ($\delta = 140.4$, ${}^{1}J({}^{31}P, {}^{183}W) =$ 273.5 Hz), the ${}^{13}C$ resonance signal of the carbon atom directly bonded to oxygen ($\delta = 86.0$; $J({}^{13}C, {}^{31}P) = 7.5$ Hz), and the presence of the signals of the arene unit. A remarkable spectroscopic feature of complex **9** is the ${}^{31}P$ resonance signal ($\delta = 95.4$, ${}^{1}J({}^{31}P, {}^{1}H) = 329.2$, ${}^{1}J({}^{31}P, {}^{183}W) = 276.5$ Hz) and also both resonance signals of the ethylene moiety in the ${}^{13}C$ NMR spectrum ($\delta = 95.1$ (d, ${}^{3}J({}^{13}C, {}^{31}P) = 11.1$ Hz, $C = CH_2$); $\delta = 156.7$ (d, ${}^{2}J({}^{13}C, {}^{31}P) = 9.1$ Hz, O - C = C)).

The molecular structures of compounds **8** (Figure 1) and **9** (Figure 2) in the crystal show some characteristic features. Compound **8** displays the typical envelope conformation of the 1,2-oxaphospholane unit (cf. ^[18]); the O atom lies 30 pm out of the P-C6-C7-C8 plane, and the tungsten atom adopts a distorted



Figure 1. Molecular structure of **8** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [$^{-}$]: P-W 249.17(10), P-C13 182.2(6), P-C6 164.1(2), P-C8 182.2(6); C8-P-C6 91.42(18), W-P-C13 125.21(12), W-P-C6 111.66(9), W-P-C8 114.14(11), C13-P-C8 106.0(2), C13-P-C6 102.74(14).



Figure 2. Molecular structure of **9** in the crystal (ellipsoids represent 50% probability levels: hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [$^{-1}$]: P1-W1 248.18(9), P1-C14 181.1(3), P1-O6 164.5(2), O6-C6 139.0(4), C6-C7 131.6(5); O6-P1-C14 100.45(14), O6-P1-W1 118.9(9), C14-P1-W1 102.40(12).

octahedral coordination with appreciably different C4-W-P and C3-W-P bond angles of 86.76(11) and $96.86(10)^\circ$, respectively. Compounds **8** and **9** display almost identical bond lengths at phosphorus, but a significant difference in the O6–C6 distances (146.3(4) vs. 139.0(4) pm).

In order to throw more light on the mechanism of the cyclizations, we have investigated the influence of the following reaction conditions on the product ratio of 6 to 8 by using ³¹P NMR spectroscopy: 1) the concentration of benzophenone (2 to 30 mmol), 2) the temperature (40 to $60 \,^{\circ}$ C), 3) the reaction time (10 to 50 h). In fact, the product ratio of 1:1.7 6:8 remained essentially constant, not significantly influenced by any of the above-mentioned parameters; the values varied between 1:1.6 and 1:1.8. Furthermore, warming 6 and 8 in toluene at 45 °C showed no interconversion of the oxaphosphirane to the oxaphospholane ring or vice versa (³¹P NMR spectroscopy). These observations lead us to postulate the carbonyl ylideanalogous intermediate 5 as the common precursor of compounds 7 and 8. The formation of 5 can be explained by a Lewis acid/Lewis base reaction of the transiently formed electrophilic phosphanediyl tungsten complex 4 with benzophenone,^[19] and the remaining steps of the reaction can be described in terms of two routes (Scheme 3). Route 1 provides the oxaphosphirane tungsten complex 6 by a 1,3 ring closure; whereas a 1,5 ring closure by nucleophilic attack of the phosphorus atom on the allyl-cationic ortho-phenyl carbon atom of 5 leads to the further intermediate 7 (route 2). An immediate 1,3 hydrogen shift and subsequent rearomatization leads to the formation of the benz-[c]-1,2-oxaphospholane tungsten complex 8. This suggestion would also be essentially consistent with the product ratio of about 1:1.7, but would not explain the deviation from the ideal



Scheme 3. Postulated reaction course for the formation of the three- and five-membered rings of the complexes 6 and 8, respectively.

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ratio of 1:2, since a priori each phenyl ring of the benzophenone can form part of an allyl cation system.

With acetophenone, compound 9 is formed rather than the corresponding oxaphosphirane- or benz[c]-1,2-oxaphospholane tungsten complex; this could be caused by a rapid rearrangement of a compound analogous to the intermediate 5, involving migration of a hydrogen atom of the methyl group to the phosphorus (cf. ref. [20]).

Thermolysis of the 2*H*-azaphosphirene tungsten complex 1 in toluene at 63 °C in the presence of (E)-*N*-methyl(benzylidene)-amine (11) leads to the azaphosphiridine tungsten complex 12, benzonitrile,^[14] and about 5% of an inseparable by-product^[21] [Eq. (a)].



The assumption that the terminal phosphanediyl tungsten complex 4 undergoes a [1,2] addition to the C-N double bond of 11, is also plausible for the formation of complex 12, since, for example, five-membered heterocycles were not observed as products of a phosphanitrile ylide (cf. ref. [8]). The constitution of the azaphosphiridine tungsten complex 12 is shown unambiguously by the NMR spectroscopic details (Table 1) and the mass spectrometric data.^[22] In comparison to the ³¹P resonance signal of noncomplexed azaphosphiridines,^[23] that of 12 $(\delta = -37.3, {}^{1}J({}^{31}P, {}^{183}W) = 269.1 \text{ Hz})$ is shifted to low field by $\Delta \delta \approx 30$. This effect of a metal complex fragment on the ³¹P resonance signal of phosphorus atoms in three-membered heterocycles has already been observed for other, related classes of compounds.^[24] Since the stereochemical arrangement of the ring substituents in 12 was not unambiguous from the spectra, and because no solid-state structural data were known for the azaphosphiridine ring system, we were particularly interested in an X-ray structure analysis of compound 12. The results^[25] (Figure 3) confirm the structural relationship of 12 to the oxaphosphirane tungsten complex 10 that we had described



Figure 3. Molecular structure of **12** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: W - P 249.64(10), P - C14 180.8(4), P - C6 183.5(4), C6 - N 147.8(5), P - N 172.8(3); W - P - C14 126.06(12), W - P - C6 108.7(2), W - P - N 123.04(11), C6 - P - C14 121.31(12), C6 - P N 48.9(2), P - C6 - N 61.8(2), P - N - C6 69.3(2).

previously.^[8] The formal replacement of the oxygen atom by an *N*-methyl fragment leads to an increase in the bond lengths of the three-membered ring, by which the bond lengths become more nearly equal. There is a marked increase in the exocyclic angle W-P-C14 (126.06(12)°) compared to the corresponding angle in **10** (121.4(2)°).^[8] whereas the endocyclic ring angles C6-P-N or C6-P-O of $48.9(2)^{\circ}$ and $50.3(3)^{\circ}$.^[8] respectively, remain roughly constant; this is consistent with a reduction of steric strain. Particularly interesting is the arrangement of the ring substituents. Future studies will investigate whether this stereochemistry indicates a concerted [2 + 1] cycloaddition of the *E* isomer **11** with the phosphanediyl tungsten complex **4** or a two-step reaction of the *Z* isomer of **11** with **4** analogous to that described in Scheme 3.

Experimental Section

6 and **8**: A solution of **1** (1.36 g, 2 mmol) in toluene (12 mL) was treated with benzophenone (**2**) (4.91 g, 27 mmol) under nitrogen at room temperature and stirred for 43 h at 45 °C (monitored by ³¹P NMR spectroscopy). The yellow reaction mixture was evaporated to dryness under reduced pressure and dissolved in pentane. Excess benzophenone was removed by crystallization at -60 °C and filtration. The products were separated by two column chromatography runs on silica gel (-20 °C, 1. hexane/Et₂O (97.5:2.5) and 2. hexane/toluene (8:2)). The eluates were evaporated to about 5 mL under reduced pressure and cooled to -30 °C. The resulting solids (**6**,**8**) were washed with a little pentane and freed of remaining solvent traces in vacuo (ca. 10^{-3} mbar). Crystallization from pentane at $+6^{\circ}$ C gave yellow crystals of **8**. **6**: colorless powder, yield: 0.05 g (0.07 mmol; 4%), m.p. 113 °C (decomp); **8**: light yellow powder, yield: 0.58 g (0.8 mmoi; 42%), m.p. 136 °C (decomp).

9: 1 (0.62 g, 1 mmol) in toluene (5 mL) was treated with acetophenone (3 g, 25 mmol); the mixture was stirred for 21 h at 45 °C. The yellow solution was evaporated to dryness under reduced pressure, and the residue subjected to column chromatography on silica gel (-15 °C, hexane/Et₂O). After the volume of the eluate had been reduced, 9 was obtained as a yellow powder. Crystallization from pentane at +6 °C gave yellow crystals of 9, yield: 0.43 g (0.68 mmol; 68%), m.p. 74 °C (decomp).

12: 1 (0.62 g, 1 mmol) was dissolved in toluene (3 mL) and treated with (*E*)-*N*-methyl(benzylidene)amine (11) (2.7 mL, 24 mmol). The mixture was stirred for 8 h at 63 °C and then evaporated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (-15 °C, hexane/Et₂O). After the volume of the eluate had been reduced, a yellow oil was obtained, from which 12 formed as a yellow solid. This was washed with a little cold pentane and recrystallized from pentane at -30 °C in the form of light yellow crystals: yield: 0.16 g (0.26 mmol; 26%), m.p. 136 °C (decomp).

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- [15] Selected IR spectroscopic and MS data of **6**, **8**, **9**; **6**: MS (EI, 70 eV, ¹⁸⁴W): m/z696 [M^+]; **8**: IR (KBr, $v_{C=0}$ region): $\tilde{v} = 2070.5 \text{ m}$, 1947.4 vs, 1921.6 s cm⁻¹; MS (EI, 70 eV, ¹⁸⁴W): m/z 696 [M^+]; 9: IR (KBr, $v_{C=0}$ region): $\tilde{v} = 2073.8 \text{ m}$, 1988.0 w, 1953.7 vs, 1904.9 s cm⁻¹ and $\tilde{v} = 1625.6 \text{ m} (v_{C=C})$; **9**: MS (EI, 70 eV, ¹⁸⁴W); $m/z = 634 [M^+]$; correct C,H elemental analyses for **6**, **8**, **9**.
- [16] Crystal structure analysis of **8**: $C_{25}H_{29}O_6PSi_2W$, monoclinic, space group $P2_1/c$, a = 1135.9(4), b = 1174.4(3), c = 2107.9(4) pm, $\beta = 100.87(2)^{\circ}$, V = 2.7615(12) nm³, Z = 4, $\rho_{celed} = 1.675$ Mg m⁻³, $\lambda = 0.71073$ pm, T = 173 K. The crystal ($0.44 \times 0.44 \times 0.38$ mm) was mounted in perfluoropolyether oil at -100 C on a Siemens P4 diffractometer. Intensities were collected by ω scans in the 20 range 5–60°. Of 8860 reflections, 8026 were independent ($R_{int} = 0.0169$). After a semiempirical absorption correction (ψ scans) the structure was solved with the heavy atom method and refined with full-matrix least-squares methods against F^2 (SHELXL-93, G. M. Sheldrick, Universität Göttingen). Hydrogen positions were included by using a riding model or rigid methyl groups. Final wR2 = 0.0692 based on F^2 for all data, conventional R(F) (R1) = 0.0309. 322 parameters and 165 restraints; max. Δp 1229 cnm⁻³ [25].
- [17] Crystal structure analysis of 9: $C_{20}H_{27}O_6PSi_2W$, monoclinic, space group $P2_1/n$: a = 1088.3(2), b = 1264.4(2), c = 1928.5(2) pm, $\beta = 102.807(8)^\circ$, V = 2.5878(7) nm³. Z = 4, $\rho_{calcd} = 1.628$ Mg m⁻³, $\lambda = 0.71073$ pm, T = 173 K. Details as for ref. [16], except: crystal dimensions $0.64 \times 0.48 \times 0.32$ mm, 20 range 6-50, 7188 reflections, 4540 independent ($R_{int} = 0.0200$). The structure was solved with direct methods and refined as in ref. [16], ref. [16], respectively was refined freely. wR2 = 0.0458, R1 = 0.0235, 281 parameters and 9 restraints; max. Δp 1074 enm⁻³.
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- [25] Crystal structure analysis of 12: $C_{20}H_{28}NO_5PSi_2W$, triclinic, space group PI, a = 929.81(12), b = 984.9(2), c = 1563.8(2) pm, $\alpha = 72.454(10)$, $\beta = 75.738(8)$, $\gamma = 76.715(10)^\circ$, V = 1.3046(3) nm³, Z = 2, $\rho_{calcd} = 1.613$ Mg m⁻³, $\lambda = 0.71073$ pm, T = 173 K. Details as in ref. [16]: crystal dimensions $0.68 \times 0.56 \times 0.42$ mm, 2θ range $6 - 50^\circ$, 4826 reflections, 4538 independent ($R_{int} = 0.0120$), structure solution as in ref. [17], refinement as in ref. [16]. The hydrogen atom H6 bonded to C6 was refined freely. wR2 = 0.0626, R1 = 0.0249, 283 parameters; max. Δp 1265 enm⁻³. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-141. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223) 336-033; e-mail: deposit@chemcrys.

Direct Study of a Nondegenerate Cyclopropene-to-Cyclopropene Isomerization**

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Until 1989 the mechanism of the thermal isomerization of cyclopropene (1) to propyne (2) was thought to proceed via the propene-1,3-diyl (3) intermediate formed by ring opening of 1. A subsequent 2,3 hydrogen-shift results in $2^{[1]}$ In that year, Yoshimine et al.^[2] proposed a different mechanism on the basis of ab initio calculations at the SDQCI(DZP) and MRCI*(DZP) levels. They suggested a propenylidene (4) intermediate, which is formed by ring opening with a synchronous 1,3 H-transfer. This is then followed by a 2,1 H-shift.



At that time, existing experimental studies were unable to distinguish between these alternatives. However, in 1992 Walsh et al.^[3] found that alkyne formation was 18 times slower for 1,3,3-trimethylcyclopropene (5) than for 3,3-dimethylcyclopropene. They argued that this is due to the 2-methyl-2-isopropylvinylidene intermediate (6, formed from 5), which is an analogue of 4 (formed from 1).

The reason why 6, rather than *trans*-4-methylpent-2-ene-2,4diyl (7), can lead to a rate reduction is provided by the second step of the isomerization $(6 \rightarrow 8)$, which involves an alkyl



(methyl or isopropyl) rather than an H-shift. The expected lower rate of the alkyl shift makes the second step rate-determining.^[3] This slows the overall reaction and implies reversibility of the first step $(5 \rightarrow 6)$. We have recently confirmed^[4] the generality of the mechanism of alkyne formation from cyclopropene via a

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