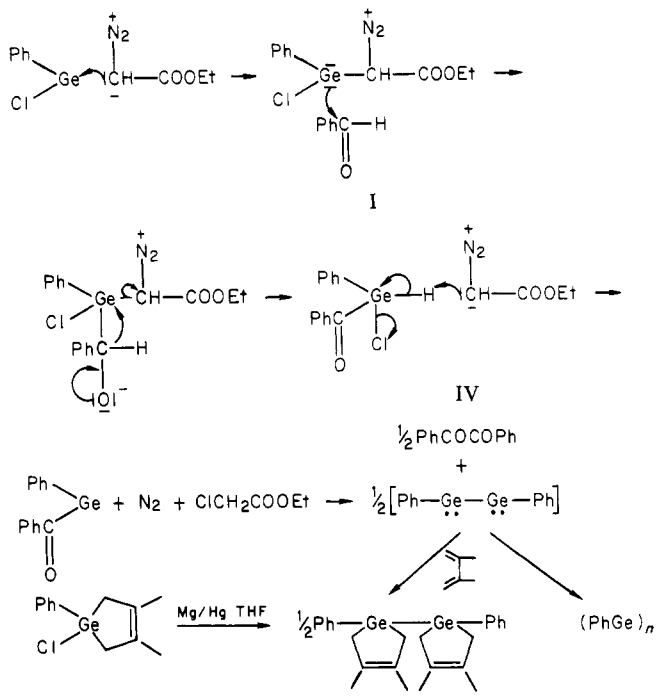
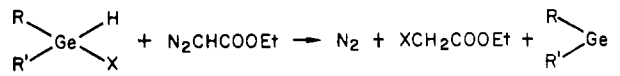
Scheme IV



Scheme V



4, Scheme III).[18] The high reactivity of the halogermylene compared to the diphenylgermylene and the reactivity of the germanium-halogen bond itself with germene trapping reagents make the characterization of such species more difficult. In the reaction of alcohols, nitrosobenzene, or nitrones, the main reactions are those of the starting halogermylenes.[7,19]

Although no reaction occurs between phenylchlorogermylene or ethyl diazoacetate and benzaldehyde at 20 °C in C_6H_6, complex I (Scheme III) of phenylchlorogermylene and ethyl diazoacetate reacts readily with this aldehyde in the same conditions, mainly leading to the corresponding halo ester and unstable phenylbenzoylgermylene (Scheme IV).

The proposed first step for this reaction is a nucleophilic attack of the metal in I on the carbonyl group of benzaldehyde, leading to chlorophenylbenzoylgermane IV. Such nucleophilic attacks of chlorogermyl anion on carbonyl have been recently observed in the base-catalyzed addition of chlorohydrogermanes to benzaldehyde.[20] IV is then dehydrochlorinated in situ by the diazo compound to yield the corresponding functional germylene and halo ester (Scheme IV). Thus, the last reaction can be used as a general method for the preparation of various germylenes through an α-elimination process (Scheme V).[20] Benzoylgermylene instability explains the formation of benzil[21] and digermane E (Scheme IV) during its characterization by cycloaddition to dimethylbutadiene (Carius tube, 2 h at 100 °C).

However, in the reaction of I with benzaldehyde (Scheme IV), traces of PhCH=CHCOOEt[13] were detected and suggest a partial pseudo-Wittig reaction of germene (formed from I as in Scheme III) with this carbonyl compound similar to those observed in the case of II obtained from diphenylgermylene (reaction 3, Scheme II).

(18) In this reaction, the mixture PhGeCl and $N_2CHCOOEt$ (in $PhCH_3$) has to be added at 0 °C to F_2Ge in ether, leading to oligomer D. Reduction of D with $LiAlH_4$/ether leads to PhH_2GeGeH_3[13] (13%): NMR (C_6D_6) δ 4.60 (q GeH_2), 3.27 (t, GeH_3 J = 4 Hz).

(19) P. Rivière, M. Rivière-Baudet, and J. *Satgé*, *J. Organomet. Chem.*, **96**, C7 (1975).

(20) P. Rivière, A. Castel, and J. Satgé, unpublished results.

(21) M. Massol, J. Barrau, P. Rivière, and J. Satgé, *J. Organomet. Chem.*, **30**, 27 (1971).

In summary, the present work demonstrates that ylide complexes resulting from interactions between germylenes and diazo compounds decompose and react in different ways, which gives evidence consistent with the transient existence of molecules containing a (p,p) π germanium-carbon bond: a "germene".

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Isolation of the [6 + 4]π Cycloadduct and Facile Successive Cope Rearrangements of the [2 + 4]π Cycloadduct in a Frontier-Controlled Pericyclic Reaction of Oxepin with Cyclopentadienone

Sir:

The cycloaddition reaction of heteropine has received attention in the past decade.[1] Interestingly, all cycloaddition reactions of oxepin (**1**) proceed via arene oxide (**1a**), and no example is yet known in which the seven-membered ring acts as either a 4π or a 6π donor.[1] Recently, Anastassiou et al.[2] found that prolonged exposure of **1** to 2,5-dimethyl-3,4-diphenylcyclopentadienone (MPC) (**2**) in boiling benzene led to the formation of the endo-[2 + 4]π cycloadduct **3** (Scheme I). However, all attempts at further thermal decarbonylation or sigmatropic rearrangement of the adduct **3** were unsuccessful, and only cycloreversion occurred.

We now report the first example, so far as we know, of the novel exo-[6 + 4]π cycloadduct **5**, which could not be predicted by consideration of the nonplanar conformation,[1b] and of facile tandem Cope-Claisen rearrangement of the initially formed endo-[2 + 4]π cycloadduct **6**.

When a solution containing a large excess of **1** and 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone (CPC) (**4**) in benzene was stirred at room temperature for 1 day, two crystalline 1:1 adducts [**5** (mp 180-182 °C, 12%) and **6** (mp 158-161 °C, 65%)] were afforded (Scheme II). The structure of **5** is assigned on the basis of the NMR data of the double-resonance technique, in which the bridgehead protons at δ 5.46 (2 H, H_a, d, J = 4.6 Hz) are strongly coupled with the adjacent vinyl protons at δ 6.59 (2 H, H_b, ddd, J = 9.4, 4.6, 3.5 Hz) and the olefinic protons at δ 5.89 (2 H, H_c, dd, J = 9.4, 3.5 Hz). Comparison of the NMR spectral patterns of the adduct **6** reveals that it is grossly similar to the adduct **3** [δ 3.76 (2 H, H_a, m), 5.12 (2 H, H_b, ddd, J = 8.7, 3.6, 2.5 Hz), 6.38 (2 H, H_c, d, J = 8.7 Hz)], indicating their skeletal resemblance.

The ^{13}C NMR spectra of these adducts also exhibited their symmetrical structures (sp^3 carbon at 51.80, 72.62, and 78.40 ppm for **5** and at 42.30, 52.21, and 70.37 ppm for **6**). The IR spectra of the adducts **5** and **6** showed the corresponding bridged carbonyl bands at 1780 and 1790 cm^{-1}. From these data, the adducts **5** and **6** were assigned the exo-[6 + 4]π and endo-[2 + 4]π cycloadducts, respectively.

The lack of dependence of rate on change in solvent polarity for the formation of the adducts **5** and **6** ruled out a dipolar intermediate. Both reactions are symmetry-allowed processes, and the secondary orbital interaction would lead the [6 + 4] and [2 + 4] cycloadditions to the exo and endo adducts, respectively.

(1) For reviews, see: (a) Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 165-173. (b) Vogel, E.; Gunther, H. *Ibid.* **1967**, *6*, 385-401. (c) Paquette, L. A. In "Non-benzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York and London, 1969; Vol. 1, pp 249-309. (d) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 402-413. (e) Harano, K.; Ban, T.; Yasuda, M.; Kanematsu, K. *Tetrahedron Lett.* **1979**, 1599-1602.

(2) Anastassiou, A. G.; Reichmanis, E.; Girgenti, S. J.; Schaefer-Ridder, M. *J. Org. Chem.* **1978**, *43*, 315-322.

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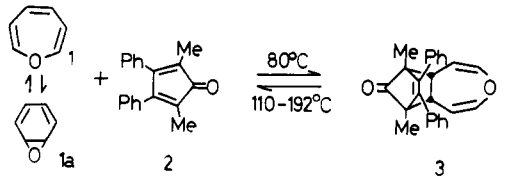
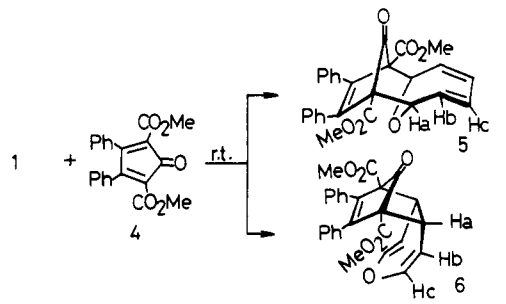
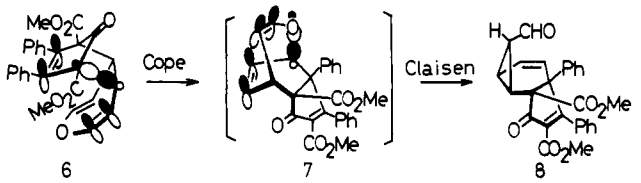
Scheme I



Scheme II



Scheme III



However, a striking contrast for thermal stability between **5** and **6** is observed: **5** is very stable during prolonged exposure to boiling benzene. On the other hand, **6** was converted to **8** (mp 241-244 °C) in near quantitative yield upon refluxing in benzene for 3 days. Compound **8** showed a positive response to Tollens reagent (a solution of silver ammonium hydroxide and sodium hydroxide), suggesting the presence of an aldehyde group. In fact, the IR spectrum showed three types of carbonyl bands at 1700 (enone), 1710 (aldehyde), and 1745 (ester) cm^{-1}. The NMR spectrum exhibited characteristic signals of the aldehyde proton at δ 9.45 (1 H, d, J = 7.1 Hz), the cyclopropane ring protons at δ 1.26 (1 H, ddd, J = 8.6, 8.6, 3.7 Hz), δ 1.70 (1 H, ddd, J = 8.6, 8.6, 7.1 Hz), and δ 2.29 (1 H, t, J = 8.6 Hz), and the olefinic protons at δ 5.39 (1 H, dd, J = 10.5, 3.7 Hz) and δ 5.55 (1 H, d, J = 10.5 Hz). The ^{13}C NMR spectrum showed well-resolved patterns (seven detectable sp^3 carbons at 18.34, 24.49, 33.93, 51.97, 52.32, 57.36, and 62.81 ppm). From these data, the structure of **8** was determined as a rearrangement product, as depicted in Scheme III.

The results indicate that the initial Cope rearrangement of **6** is more significant because the effective orbital interactions in three systems activate groups among the HOMOs of the two π bonds (the vinyl ether and diphenylethylene moieties) and the LUMO of the σ bond adjacent to the electron-attracting ester group. This is in sharp contrast to Anastassiou's conclusion for the adduct **3**.[2] Furthermore, it is apparent that successive Cope rearrangements (Claisen rearrangements) lead to the highly strained compound **8**.

From these results, it is noted that the success of **1** in functioning as a 6π donor toward **4** could conceivably be caused by the frontier-control and dominant donor-acceptor interaction.[3] The powerful electron-attracting **4**[4] should be more readily trapped by electron-donating oxepin, *even in the existence of the valence-tautomeric equilibrium between benzene oxide and the nonplanar conformational isomers.*[5]

(3) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693-4701.

(4) It is interesting that the CNDO/2 MO calculation indicates a 0.7-eV lowering of the LUMO energy for **4** as compared to **2**: Yasuda, M.; Harano, K.; Kanematsu, K. *Tetrahedron Lett.* **1980**, 627-630.

Finally, treatment of the adduct **6** with silicic acid in a protic solvent gave compound **9** [mp 185-187 °C, $C_{26}H_{24}O_5$, mass

9

spectra, m/e 416 (M^+)] in a moderate yield. The absence of the bridged carbonyl band in the IR, three detectable sp^3 carbons (39.44, 50.77, and 51.89 ppm) in the ^{13}C NMR, and characteristic signals at δ 3.17 (2 H, H_c, m), δ 3.18 (6 H, s, $CO_2Me \times 2$), δ 3.66 (2 H, H_d, d, J = 6.8 Hz), δ 5.17 (2 H, H_b, dd, J = 7.2, 6.2 Hz), and δ 6.22 (2 H, H_a, dd, J = 7.2, 1.3 Hz) in the NMR suggested the structure of **9** resulting from decarbonylation followed by hydrogen abstraction from the polar solvent, although further studies are necessary to settle the formation mechanism.

In addition, qualitative similarities in reactivity between two dienes are expected from the calculated FMO energy levels of **2** and tetracyclone,[4] but there is a large difference in reactivity between the reactants: tetracyclone reacts with **1** much slower (for about 1 month) than with **2** or **4**, even under more drastic conditions. We are currently examining the cycloadditivity and periselectivity of **1** with other cyclopentadienones on the basis of the frontier-controlled donor-acceptor interaction theory.[3]

(5) (a) Especially noteworthy is the fact that the absence of valence tautomerism of the 1*H*-azepine-azanorcaradiene form is contrasted with those for oxepin; see ref 1. (b) After the work had been submitted for publication, study of the benzene oxide-oxepin valence isomerization was reported: Hayes, D. M.; Nelson, S. D.; Garland, W. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1980**, *102*, 1255-1262.

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Chirality at a Pro-pro-prochiral Phosphorus Center. Stereochemical Course of the 5'-Nucleotidase-Catalyzed Reaction

Sir:

We report the first study on a stereochemical problem involving a pro-pro-prochiral phosphorus center,[1] the hydrolysis of AMP[2] to adenosine and P_i catalyzed by the venom 5'-nucleotidase, by use of chiral [^{16}O,^{17}O,^{18}O]thiophosphates (Ps_i).

Scheme I summarizes our experimental approaches. Reaction of $PSCl_3$ with adenosine,[3] followed by $H_2{}^{18}O$ (99%) hydrolysis, gave [$^{18}O_2$]AMPS (**1**) (>98% ^{18}O). Chemical phosphorylation[4] of **1** yielded [α-$^{18}O_1$]ADPαS (A + B) (**2**). Incubation of **2** with pyruvate kinase[5] gave [α-$^{18}O_1$]ATPαS (A) (**3**) and unreacted [α-$^{18}O_1$]ADPαS (B) (**4**).[6] Reaction of **3** and **4** with alkaline

(1) Problems involving a chiral, prochiral, or pro-prochiral ($ROPO_3^{2-}$) phosphorus center have been solved recently: Knowles, J. R. *Annu. Rev. Biochem.*, in press.

(2) Abbreviations used: P_i, inorganic phosphate; Ps_i, inorganic thiophosphate; O, oxygen-16; ⊖, oxygen-17; ●, oxygen-18; AMP, adenosine 5'-monophosphate; AMPS, adenosine 5'-thiophosphate; ADPαS, adenosine 5'-(1-thiodiphosphate); ATPαS, adenosine 5'-(1-thiotriphosphate); ADPβS, adenosine 5'-(2-thiodiphosphate); ATPβS, adenosine 5'-(2-thiotriphosphate); ATPγS, adenosine 5'-(3-thiotriphosphate). The diastereomers A and B are designated on the basis of their enzymatic activity (ref 4).

(3) Murray, W. A.; Atkinson, M. R. *Biochemistry* **1968**, *7*, 4023-4029.

(4) Eckstein, F.; Goody, R. S. *Biochemistry* **1976**, *15*, 1685-1691.

(5) (a) Richard, J. P.; Ho, H. -T.; Frey, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 7756-7757. (b) Jaffe, E. K.; Cohn, M. *J. Biol. Chem.* **1979**, *254*, 10839-10845.

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