Reactions of Germylenes with Diazo Compounds. New Route for the Formation of Germanium-Carbon Double-Bonded Intermediates

Sir:

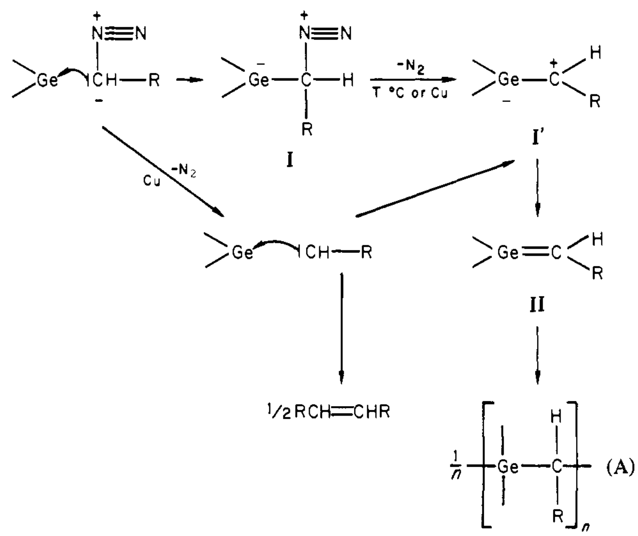
Evidence consistent with the transient existence of germyl derivatives containing (*p,p*) π-bonded germanium has accumulated in the last few years.[1-4] In this field of research, germylenes are a useful starting material for such double-bonded germanium intermediates. For example, oxidation of germylenes or their reactions with azides, nitroso compounds, oxaziridines, or nitrones led to transient $>Ge{=}Y$ derivatives (Y = O, NR).[5-7] We report a novel reaction which gives some chemical evidence for the existence of intermediates, recently characterized by Barton et al.[1a] or postulated[1b,c] in the literature, with germanium double bonded to carbon.

The reactions of germylenes $>Ge$ (Ph_2Ge, PhGeCl, F_2Ge)[8-10] with diazo compounds ($PhCHN_2$, $EtOOCCHN_2$) in C_6H_6 show an increasing germylene reactivity according to their relative electrophilic character[11] (F_2Ge; exothermic reaction; PhGeCl; 20 °C; Ph_2Ge; 80 °C). Thus, it is possible to postulate an initial nucleophilic attack of the germylene by the diazo compound which leads to a complex of ylide type I. Similar structures have been observed during the reactions of such diazo compounds with zinc dichloride.[12]

With the experimental conditions described above the complex I proceeds with evolution of nitrogen to germene II through a transient zwitterionic form I′. Moreover, when copper is used as catalyst in these reactions (Ph_2Ge, Cu powder, C_6H_6, Et_3N, 60 °C, 4 h), germene II can also be produced by a direct interaction between germylene and generated carbene (Scheme I).

Intermediates II (Scheme II), obtained from nonhalogenated germylenes (Ph_2Ge[8]), mainly polycondense, leading to oligomers A [(R = Ph: 10-15%, NMR (C_6D_6) δ 3.03 (s, CH); R = COOEt: 20-25%, δ 2.65 (s, CH)] chemically characterized (Scheme II, reaction 1). However, strong chemical evidence for the formation of II has been obtained:

Scheme I



(1) Their addition to methanol (Carius tube, 100-140 °C, in stoichiometric conditions) leads to the corresponding alkoxygermanes (reaction 2): R = Ph, $Ph_2Ge(OMe)CH_2Ph$ 8%, NMR (C_6D_6) δ 2.57 (s, CH_2), 3.57 (s, OCH_3); R = COOEt, $Ph_2Ge(OMe)CH_2COOEt$ 10%, δ 2.77 (s, CH_2), 3.60 (s, OCH_3), $Ph_2Ge(OMe)_2$,[13] CH_3COOEt[13] 16% (from methanolysis).

(2) They also give pseudo-Wittig reactions with aldehydes (reaction 3, above conditions). But these reactions, similar to those observed in the case of silenes,[14] occur with lower yields ($PhCH{=}CHCOOEt$[13] 7%).

(3) Cycloaddition of II (R = Ph) to nitrosobenzene (reaction 4) occurs when PhNO is added slowly to the mixture of Ph_2Ge and $PhCHN_2$ in the presence of copper at 40 °C (C_5H_{12}) and leads to germoxane $(Ph_2GeO)_n$ [ν(GeOGe) 870 cm^{-1}][15] and to the corresponding imine ($PhCH{=}NPh$[13] 17%). In this reaction, the nitrone, which should be formed at room temperature by direct interaction between PhNO and the diazo compound, has only been observed in traces. This result suggests that the complexing of diazo compounds to germylenes, which leads to I, is really the first step of the reaction. Since under the experimental conditions used diphenylgermylene does not react with PhNO or with the nitrone mentioned above, a reasonable pathway for the formation of both germoxane and imine is the cycloaddition of II (from Scheme I) to PhNO. The transient germaoxaazetidine[7] then formed decomposes according to reaction 4 (Scheme II) through an initial cleavage of the N-O bond.[7]

(4) The similar cycloaddition of II to α-diphenylnitrone is not observed at room temperature. However, at 100 °C (Carius tube), the formation of germoxane $(Ph_2GeO)_n$ and the corresponding alkene ($PhCH{=}COOEt$[13] 7%) and azo compound ($PhN{=}NPh$[13]), although in very low yield (reaction 5, Scheme II), suggests the formation of a transient heterocycle: a 2-germa-1-oxa-5-azolidine which decomposes like the analogue 2-germa-1-oxa-3,5-diazolidine.[16] This low yield is explained by the competitive reaction of the starting germylenes to the nitrone under the same experimental conditions, which leads to germoxane and imine $PhCH{=}NPh$[7] (48%).

We also studied the reaction of halogermylenes, XYGe[8] (X = Ph, Y = Cl, X = Y = F), with ethyl diazoacetate (Scheme III). In these reactions, the intermediates I formed react in two different

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[1] $>Ge{=}C<$: (a) T. J. Barton, E. A. Kline, and P. M. Garvey, *J. Am. Chem. Soc.*, **95**, 3078 (1973); (b) M. D. Curtis, *ibid.*, **91**, 6011 (1973); (c) N. S. Nametkine, L. E. Gusel'nikov, R. L. Ushakova, V. Yu. Orlov, O. V. Kuz'min, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **194**, 1096 (1970).

[2] $>Ge{=}N-$: (a) M. Rivière-Baudet, P. Rivière, and J. Satgé, *J. Organomet. Chem.*, **154**, C23 (1978); (b) M. Rivière-Baudet, P. Rivière, J. Satgé, and G. Lacrampe, *Recl. Trav. Chim. Pays-Bas*, **98**, 42 (1979); (c) M. Rivière-Baudet, G. Lacrampe, and J. Satgé, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **289**, 223 (1979).

[3] $>Ge{=}O$, $>Ge{=}S$: (a) H. Lavayssiére, J. Barrau, G. Dousse, J. Satgé, and M. Bouchaut, *J. Organomet. Chem.*, **154**, C9 (1978); (b) *ibid.*, **161**, C59 (1978); (c) *Helv. Chim. Acta*, **62**, 152 (1979).

[4] $>Ge{=}P-$: C. Couret, J. Satgé, J. D. Andriamizaka, and J. Escudie, *J. Organomet. Chem.*, **157** C35 (1978).

[5] J. Barrau, M. Bouchaut, A. Castel, A. Cazes, G. Dousse, H. Lavayssière, P. Rivière, and J. Satgé, *Synth. React. Inorg. Met.-Org. Chem.*, **9**, 273 (1979).

[6] P. Rivière, A. Cazes, A. Castel, M. Rivière-Baudet, and J. Satgé, *J. Organomet. Chem.*, **155**, C58 (1978).

[7] P. Rivière, J. Satgé, A. Castel, and A. Cazes, *J. Organomet. Chem.*, **177**, 171 (1979).

[8] F_2Ge is used pure[9] and PhGeCl pure in benzenic solution.[10] Ph_2Ge is freshly prepared by complete dehydrochlorination reaction of Ph_2ClGeH with an excess of Et_3N.[11] It is stabilized by 1 mol of Et_3N as the complex $Ph_2Ge + NEt_3 \rightleftarrows Ph_2Ge^{-}\text{-}{}^{+}NEt_3$ (forward, room temp; reverse, >room temp). The reactions of these germylenes with the used reagents have been previously investigated,[5-7] and their participation, in the experimental conditions used, is generally negligible.

[9] E. L. Muetterties and J. E. Castle, *J. Inorg. Nucl. Chem.*, **18**, 148 (1961).

[10] J. Satgé, M. Massol, and P. Rivière, *J. Organomet. Chem.*, **56**, 1 (1973).

[11] P. Rivière, J. Satgé, and A. Castel, *C. R. Hebd. Seance Acad. Sci., Ser. C*, **281**, 835 (1975).

[12] W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, 1971.

[13] All these compounds were identified by comparison of their GLC retention times (Varian Aerograph 1400, SE 30, and DEGS) and their NMR and IR data with those of authentic compounds.

[14] (a) T. J. Barton, C. L. McIntosh, and E. A. Kline, 3rd International Symposium on Organosilicon Chemistry, Madison, WI, Aug 1972; (b) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973); (c) D. N. Roark and L. H. Sommer, *ibid.*, 167 (1973).

[15] M. Lesbre, P. Mazerolles, and J. Satgé, "The Organic Compounds of Germanium", Wiley-Interscience, New York, 1971.

[16] M. Rivière-Baudet, P. Rivière, A. Castel, and G. Lacrampe, *Bull. Soc. Chim. Fr.*, in press.

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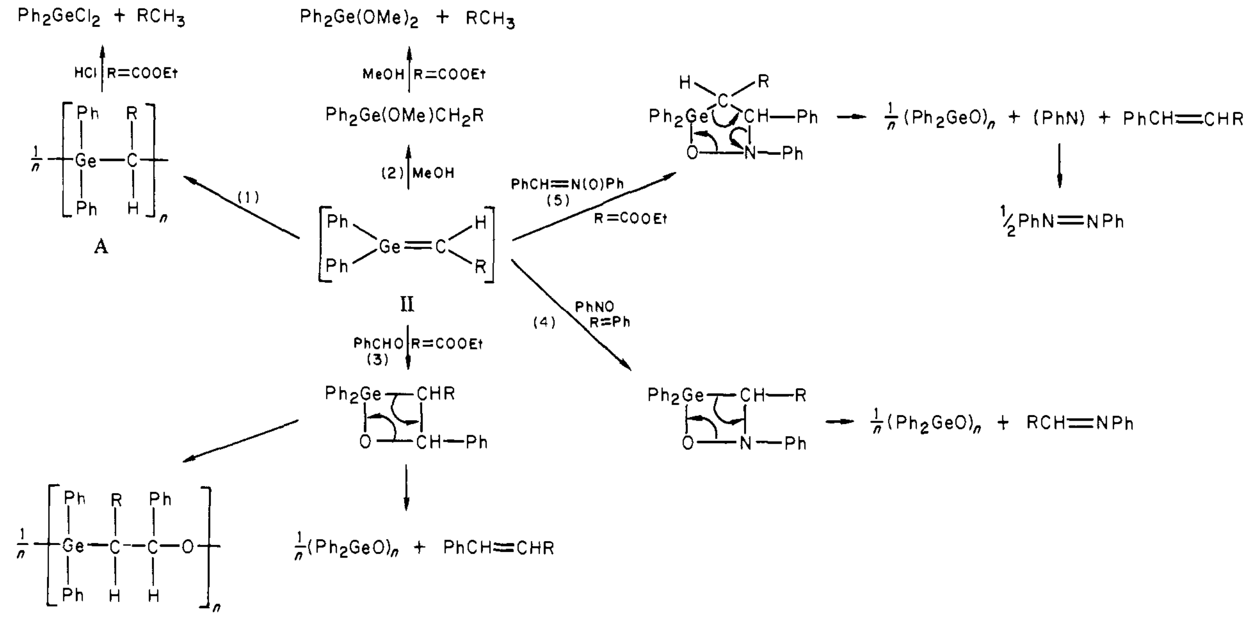
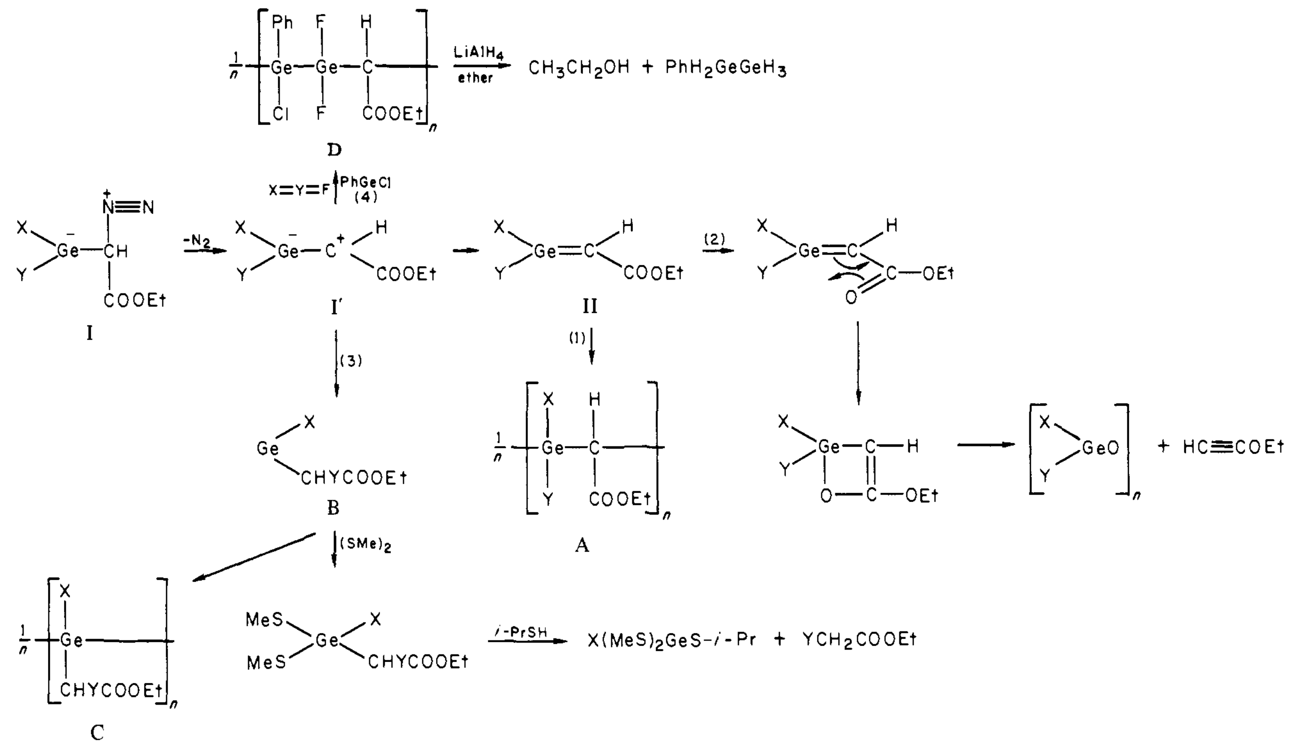
Scheme II



R = Ph; R = COOEt

Scheme III



X = Ph; Y = Cl

ways: (1) The decomposition of I can lead through I′ to the transient germene II, which partly polycondenses into oligomers A (reaction 1) [X = Ph, Y = Cl, 7%, NMR (C_6D_6) δ 2.60 (s CH), 3.90 (q, OCH_2), 0.97 (t, CH_3)]. Rearrangement of II also occurs through germanotropic tranposition[15] facilitated in this case by the higher electrophilic character of such germanium centers (reaction 2). The transient 2-germa-3-oxacyclobutene then formed decomposes readily through a β-elimination process, giving the observed germoxanes [(X = Ph, Y = Cl: $(PhClGeO)_n$[6] ν(GeOGe) 895 cm^{-1}] and ethoxyacetylene[13] (25–30%) extracted from the mixture in an azeotropic distillation with C_6H_6. (2) The migration of halogen in I′ from the metal to the carbonium in the α position (reaction 3, Scheme III) leads to a new germylene (B) partly trapped with dimethyl disulfide[11] with formation of Ph$(SMe)_2$GeCHClCOOEt.[17] Such migrations have been observed in the interaction between diazo compounds and $ZnCl_2$.[12] Without any reagent, germylene B polycondenses, mainly leading to oligomers C [X = Ph, Y = Cl, NMR (C_6D_6) δ 3.60 (s CH), 3.90 (q, OCH_2), 0.97 (t, CH_3)]. Digermylated oligomers D can also be formed in this reaction when it is carried out with an excess of germylene. This is demonstrated in the reaction of the complex of F_2Ge and $N_2CHCOOEt$ with phenylchlorogermylene (reaction

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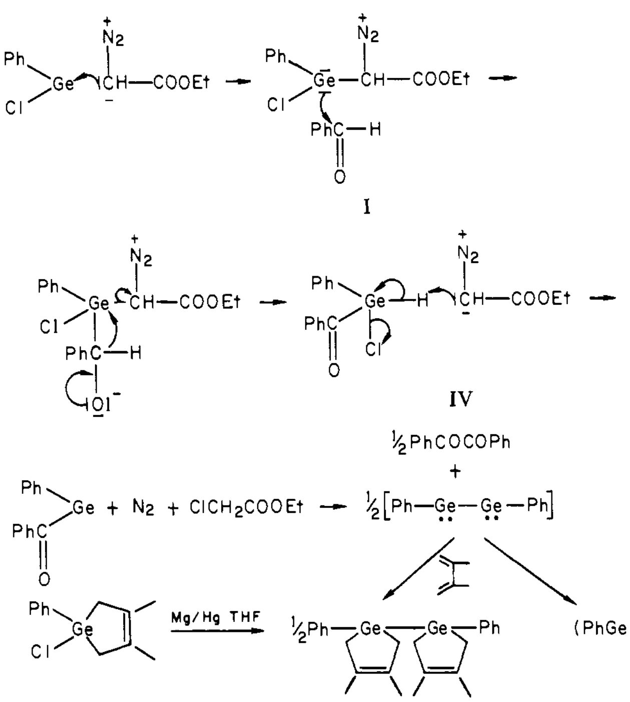
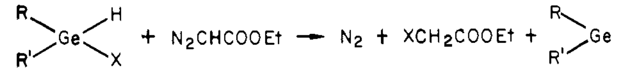
[17] Ph$(SMe)_2$GeCHClCOOEt is too unstable to be isolated by distillation and is chemically characterized by cleavage of the Ge–C bond by i-PrSH (Scheme III). i-PrSH (1 equiv) is added to the mixture (PhGeCl, $N_2CHCOOEt$, CH_3SSCH_3 200% excess) previously heated at 60 °C. After 1 h at 40–50 °C, we obtained Ph$(MeS)_2$GeS-i-Pr[13] (19%): NMR (C_6D_6) δ 2.00 (s, SMe), 3.06 (septet, CH), 1.33 (d, CH_3, J = 6,5 Hz), $ClCH_2COOEt$.[13]

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).

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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[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).

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.

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[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.