as deriving from cyclopropene singlet excited state ring opening,[2,6] whereas various $^{3}A''$ counterparts to **9**, generated by photochemical extrusion of nitrogen from diazoalkenes, have been observed directly by ESR.[18] It thus appeared possible to selectively generate vinylcarbenes **8** and/or **9** (R = *tert*-butyl) independently from cyclopropene **2b** and diazoalkene precursors **10** and **11** (Chart II) as a means for assessing their role in allene photochemistry. The results are summarized in Table I and Chart II, and in each case the characteristic reactivity is cyclization to cyclopropene **2b** and indene **4b**, which is the typical fate of other vinylcarbene examples reported.[2,3,11,12] Atypical are the minor amounts of allene **1b** produced presumably via 1,2-H shift from C_2 to C_3 in **8**. Most significant, however, is the absence of alkyne **3b** (Table I), which strongly mitigates against vinylcarbenes **8** and **9** as exclusive intermediates in allene photochemistry but does not preclude their participation in cyclization since equilibrium among species **6–9** is difficult to assess.

To account for alkyne **3** formation from allene **1*** (Chart I), we envision singlet excited state decay to a potential-energy surface of cyclopropene ring opening at a geometry approximating vinylmethylene diradical **6** rather than anti stereoisomer **7**, which seems less attractive as a precursor to alkynes due to the possibility of a low barrier to cyclization. Decay to a bisected vinylmethylene in which C-1 rotation has not occurred in concert with 1,2-H shift would provide a suitable geometry for a second 1,2-H shift to C-1 competitive with the alternative cyclization pathways described above. In any case, decay occurs to the least stable of $^{1}A''$, $^{1}A'$, and $^{3}A''$ type species[4], i.e., vinylmethylenes related to $^{1}A''$. Vinylmethylene diradicals have also been considered[19a–c] as intermediates in cyclopropene to propyne thermal isomerizations,[19] although such a pathway would be more energy demanding than that for reversible ground-state ring opening involving a carbenic species.[4b,5]

Rotational decay of **1*** to the ground state would be a process competitive with rearrangement, thus accounting for the low quantum yields observed for allene **1b**. This is further substantiated by quantum yields as high as 0.96 for racemization of optically active 1,3-diphenylallene.[20] It is reasonable to expect energy minima on the excited-state surface at planar allene geometries,[21] in which case the close proximity to a ground-state surface would lead to decay. Such decay presumes efficient delocalization of excitation throughout the allenic moiety, which is not necessarily the case; the fast rate of radiationless decay intrinsic to the diphenylvinyl chromophore[10] and/or the possibility of 1,2-H shift being an activated process would also account for inefficient photoisomerization.

The generality of the photoisomerization with allenes of differing substitution pattern is currently under investigation.

Acknowledgment. Support of this research by a Cottrell Grant from the Research Corp., a grant by the donors of the Petroleum Research Fund, administered by the American Chemical Society, NSF Grant THI-8020268 for an NMR spectrometer, and the Office of Research Support, Marquette University Graduate School, for a summer fellowship and a regular research grant is gratefully acknowledged.

Registry No. **1a**, 81740-69-4; **1b**, 81740-70-7; **2b**, 42842-57-9; **10** sodium salt, 81740-71-8; **11**, 42842-76-2.

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Novel Palladium(II)-Catalyzed Copolymerization of Carbon Monoxide with Olefins

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Received February 5, 1982

We report that the series of cationic palladium(II) compounds, $[Pd(CH_3CN)_4](BF_4)_2{\cdot}nPPh_3$ (n = 1–3), were found to catalyze the copolymerization of carbon monoxide with a range of olefins under unusually mild conditions. The first example of copolymerization of carbon monoxide with olefins involved the free radical initiated copolymerization of carbon monoxide with ethylene under high pressure and temperature. Only low molecular weight random copolymer with the CO/C_2H_4 ratio deviating substantially from 1 was obtained.[1] High-pressure copolymerization of carbon monoxide and ethylene can also be induced by γ-rays.[2] More recently there have been two reports of copolymerization of carbon monoxide with norbornadiene catalyzed by $PdCl_2$.[3] There have also been a number of claims in the patent literature concerning palladium-catalyzed copolymerization of carbon monoxide and ethylene to yield high molecular weight polyketones.[4] These involve as catalysts either $Pd(CN)_2$[4a] or $HPd(CN)_3$,[4d] which lead to heterogeneous reaction conditions, or the tertiary phosphine complexes $Pd(Ph_3P)_2Cl_2$[4b] and $Pd(Ph_3P)_4$.[4c] *These catalytic systems all require reaction temperatures in excess of 100 °C and, in particular, we find that the latter two compounds were completely inactive at 25 °C (vide infra).*

The compound $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ (**1**) was synthesized through the reaction of $[Pd(CH_3CN)_4](BF_4)_2$ with excess PPh_3 in CH_2Cl_2, as has been reported earlier.[5] The other members of the series, $[Pd(CH_3CN)_4](BF_4)_2{\cdot}nPPh_3$ (n = 2, 3), were prepared in situ by similar procedures. All three compounds in the series were found to catalyze the rapid dimerization of ethylene at 25 °C (eq 1).[5] However, in the presence of both ethylene and carbon monoxide, high molecular weight alternating ethylene–carbon monoxide copolymer (E–CO copolymer) was formed (eq 2). In a typical reaction, 0.2 g of **1**, dissolved in $CHCl_3$, was exposed to a mixture of CO (350 psi) and C_2H_4 (350 psi) at 25 °C for 1 day. At the end of this period, little further drop in pressure was observed, and following depressurization, 1.4 g of a white polymer was found precipitated in the reaction vessel. The overall reaction represented a combined "turnover" of 300 equiv (relative to **1**) of CO and C_2H_4.

$$CH_2{=}CH_2 \xrightarrow[25\ ^\circ C,\ CHCl_3]{[Pd(CH_3CN)_4](BF_4)_2\cdot nPPh_3\ (n\ =\ 1-3)} C_4H_8 \qquad (1)$$

$$CH{=}CH_2 + CO \xrightarrow[25\ ^\circ C,\ CHCl_3]{[Pd(CH_3CN)_4](BF_4)_2\cdot nPPh_3\ (n\ =\ 1-3)} (-CH_2-CH_2-C(O)-)_n \qquad (2)$$

The E–CO copolymer is a white solid with melting point of 260 °C. It is virtually insoluble in all common organic solvents, probably due to its high crystallinity rather than to any cross linking (vide infra). Analysis of the E–CO copolymer indicates a CO/C_2H_4 ratio of 1. (Anal. Calcd for $C_2H_4{\cdot}CO$: C, 64.26; H, 7.14. Found: C, 63.97; H, 7.05.) The structure of the copolymer can be discerned from the ^{13}C NMR spectrum of the solid (Figure 1).[6] There are two resonances, at 38.3 and 211.8 ppm,

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(6) Recorded by A. Wong at the Materials Research Laboratory of Case Western Reserve University (see acknowledgment).

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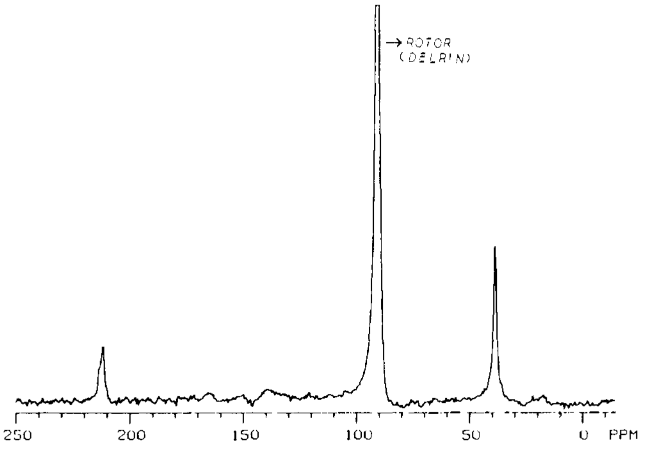
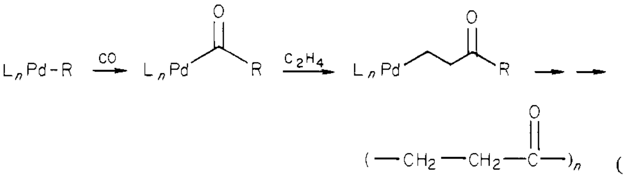


Figure 1. ^{13}C NMR spectrum (37.7 MHz) of solid E-CO copolymer. The rotor, (Delrin) consists of $-CH_2O-$ units.

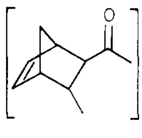
with an approximate intensity ratio of 2:1. The resonance at 211.8 ppm can be ascribed to the carbonyl carbons and falls nicely in the range expected for $-CH_2-C(O)-CH_2-$ unit.[7] The 38.3-ppm absorbance is due to the α-methylene carbons. The absence of any resonance at ~24 ppm (observed in case of random E-CO copolymers)[8] indicates the absence of any β-methylene carbons, leading to the conclusion that our E-CO copolymer has a regular structure with alternating ethylene and carbon monoxide units. Its IR spectrum exhibited a broad band centered around 1695 cm^{-1}.

A rational mechanism for the formation of E-CO copolymer would involve the alternate insertion of CO and C_2H_4 into a preformed Pd-alkyl bond (eq 3). Indeed, we found that the species generated by reactions of $AgBF_4$ with $Pd(PPh_3)_2MeI$ (**2**) and $Pd(PPh_3)_2(C(O)Me)Cl$ (**3**) (i.e. presumably $Pd(PPh_3)_2(Me)(solv)^+$ and $Pd(PPh_3)_2(C(O)Me)(solv)^+$, respectively[9]) were also active catalysts for the copolymerization of CO and C_2H_4 under conditions identical with those used for $[Pd(CH_3CN)_4](BF_4)_2 \cdot nPPh_3$ (n = 1–3). Most significantly, the corresponding neutral compounds **2** and **3** as well as $Pd(Ph_3P)_2Cl_2$ and $Pd(Ph_3P)_4$ were completely inactive under these conditions, perhaps indicative of the crucial need for easily accessible coordination sites. This is also supported by the observation that although catalyst preparations with a PPh_3/Pd^{2+} ratio of 1–3 were active (vide supra), those with ratios 4 and 6 were found to be inactive. Also inactive was $[Pd(CH_3CN)_4](BF_4)_2$, which was rapidly reduced by CO. The origin of the initial Pd-alkyl species is uncertain but is almost certainly related to the observed catalytic dimerization of C_2H_4 by **1** and related compounds (eq 1). A possible source would be a Pd-H species formed through the interaction of the Pd(II) compounds with protic impurities present in the reaction mixture. Indeed, the addition of 1 equiv of MeOH to the reaction mixture has no discernable effect, although an excess of methanol stops the copolymerization reaction.



$$L_nPd-R \xrightarrow{CO} L_nPd-C(O)-R \xrightarrow{C_2H_4} L_nPd-CH_2CH_2-C(O)-R \longrightarrow \longrightarrow (-CH_2-CH_2-C(O)-)_n \quad (3)$$

We have also examined the copolymerization of carbon monoxide with norbornadiene and norbornylene, using **1** as catalyst. The reactions were carried out in $CHCl_3$, at 60 °C with an initial CO pressure of 800 psi and a catalyst concentration of 5–9 × 10^{-3} M. In the case of norbornadiene, with a monomer to **1** ratio of 200:1, quantitative yield of the copolymer was obtained in 1 day (molecular weight 3380).[10] The norbornadiene–carbon monoxide copolymer (NBD–CO copolymer) is soluble in $CHCl_3$ and C_6H_6, probably due to its lower crystallinity (vide infra). We believe that our NBD–CO copolymer has structure I rather than II on the basis of broad resonances at ~6.2 and ~129 ppm that are present in its ^1H NMR and ^{13}C NMR spectra, respectively, which indicate the presence of vinylic hydrogens and carbons in the copolymer. However, the ^1H NMR spectrum reveals that the ratio of vinylic protons to the other protons present in our NBD–CO copolymer was significantly lower than that predicted on the basis of structure I. This would seem to indicate the carbonylation of some of the second C=C bonds of norbornadiene units that are present in structure I and should lead to a carbon monoxide to norbornadiene ratio of more than 1. Indeed C and H analysis of our NBD–CO copolymer reveal a CO:NBD ratio of 1.5. (Anal. Calcd for $C_7H_8 \cdot (CO)_{1.5}$: C, 76.46; H, 6.06. Found: C, 76.11; H, 6.16.) The overall reaction is represented by eq 4. A final problem is to determine whether the carbonyl groups of the copolymer have a cis or a trans configuration. Now, it has been reported[3a] that compound **4** exhibits two vinylic resonances, at 6.2 and 5.9 ppm, respectively, in its ^1H NMR spectrum, whereas compound **5** shows only a single absorption at 6.2 ppm. Thus our copolymer which exhibits a single broad vinylic resonance at ~6.2 ppm would appear to have a cis (exo- or endo-) configuration of carbonyl groups.



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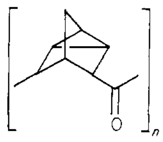

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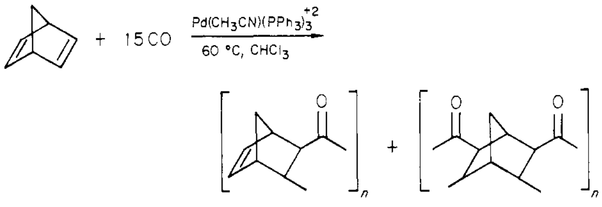

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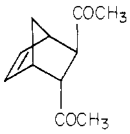

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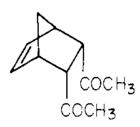

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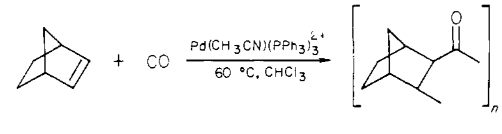
In the reaction of carbon monoxide with norbornylene, a norbornylene to **1** ratio of 60:1 was used, and this led to a 50% yield of the cooligomer in 3 days (molecular weight = 350).[10] The ^1H NMR spectrum of this cooligomer was similar to that corresponding to the NBD–CO copolymer, except for the absence of any vinylic resonances in the former spectrum. The C and H analysis of the cooligomer indicate a norbornylene to carbon monoxide ratio of 1. (Anal. Calcd for $C_7H_{10} \cdot CO$: C, 78.69; H, 8.19. Found: C, 78.11; H, 7.91.) The overall catalytic reaction is depicted in eq 5.



(5)

Acknowledgment. We thank Professor W. Ritchey and Professor J. P. Fackler of Case Western Reserve University for the

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(10) Molecular weights were measured by osmometry in $CHCl_3$.

^{13}C NMR spectrum of the E–CO copolymer. We also thank Johnson Matthey Inc. for a generous loan of palladium metal. This research was financially supported through grants from the Research Corp., NY, the Pennsylvania Research Corp., and the Department of Energy, Office of Basic Energy Sciences.

Registry No. **1**, 78736-29-5; **2**, 53228-65-2; **3**, 41910-22-9; E-CO copolymer, 25052-62-4; E–CO cooligomer, 49603-60-3; NBD–CO copolymer, 28475-06-1; carbon monoxide–norbornylene copolymer, 53580-34-0; carbon monoxide–norbornylene cooligomer, 81725-14-6; CO, 630-08-0; $CH_2{=}CH_2$, 74-85-1; NBD, 121-46-0; norbornylene, 498-66-8; $[Pd(CH_3CN)_4](BF_4)_2$, 21797-13-7.

Stabilities of Carbocations in Solution. 13. A Leaving-Group and Solvent Effect on the Thermodynamics of Carbocation Formation in Superacidic Media

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Received February 5, 1982

In previous studies,[1] we have shown close correlations with essentially unit slopes between enthalpies of ionization of alkyl, alicyclic, and aralkyl chlorides and fluorides in SO_2ClF, SO_2, SO_2F_2, CH_2Cl_2, "magic acid", and the gas phase. These thermochemical studies correlate closely with the NMR observations of Olah's group,[2] which show remarkably little effect of the leaving group on the nature of the carbocations which are formed from many types of precursors (halides, alcohols, alkenes, haloformates, thiols) provided that the superacid medium is strong enough to cause ionization and that halonium ions are not formed.[1b,3,4] The results presented here are the first departure known to us from this simple and consistent pattern.

Figures 1 and 2 show the relationship between enthalpies of ionization (ΔH_i) for a series of alcohols by excess SbF_5 or magic acid in SO_2 solvent compared to ΔH_i's for the corresponding chlorides with SbF_5 in SO_2ClF. Both series were measured at temperatures between −40 and −55 °C. Unlike all our previous studies referred to above, the alcohols in SO_2 show a much greater variation of ΔH_i with changing structure than do the halides in SO_2ClF. Thus, the slope of the line through points for the aliphatic and alicyclic cations with SbF_5 is 4.5 ($r = 0.98$, seven points) and 3.8 with 1:1 (mol/mol) SbF_5/FSO_3H ($r = 0.95$, seven points), and the points for cumyl, *p*-methylcumyl, trityl, benzhydryl, and 2-methyl-2-norbornyl cations are badly displaced, suggesting, perhaps, another line with slope close to unity. Evidence that this behavior is characteristic of alcohols in SO_2 is provided by Figure 3, which shows good correlation with unit slope for the same series of alcohols in SbF_5/SO_2 and in $SbF_5/FSO_3H/SO_2$. No displacement of the aralkyl ions is seen from this line. In all cases the low-temperature proton spectra (60 MHz, −55 °C) correspond to those that we have found in the other superacids and those reported by Olah's group for these ions.

Ionization appears to be rapid and complete as evidenced both by ^1H NMR spectra and the sharpness of the strip-chart thermograms.[1a,b] We are therefore presented with the interesting fact that the thermochemical behavior for ionization of the alcohols in two media containing SO_2 is sharply different from that in other media, even though the ^1H NMR spectra are identical. Figure 4 shows that the peculiar thermochemical behavior depends on *the presence of alcohols and SO_2*, since replacement of this solvent with SO_2ClF returns us to the usual unit slope correlation for halides in superacid media. Alkyl halides with SbF_5 in SO_2 behave normally (except for 2-propyl and cyclopentyl[1a,b]).

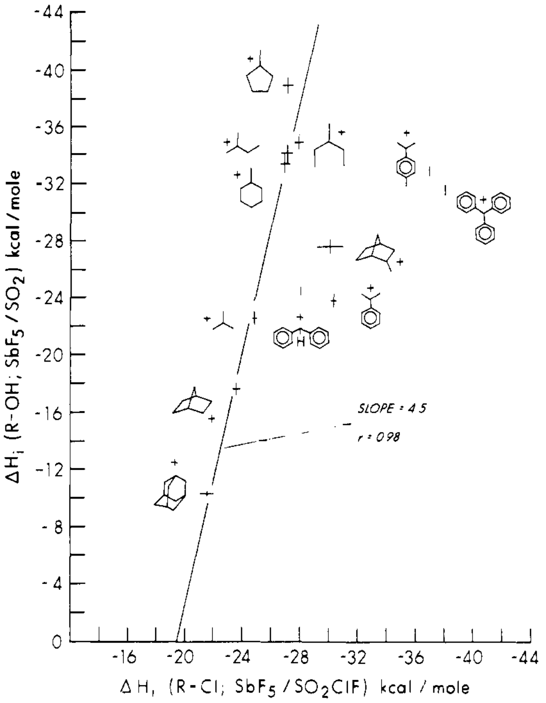

Figure 1. Plot of the heats of ionization for a series of alcohols with SbF_5 in SO_2 vs. the corresponding chlorides ionized with SbF_5 in SO_2ClF.[12] A regression line was calculated for the alkyl ions only (except 2-methyl-2-norbornyl).

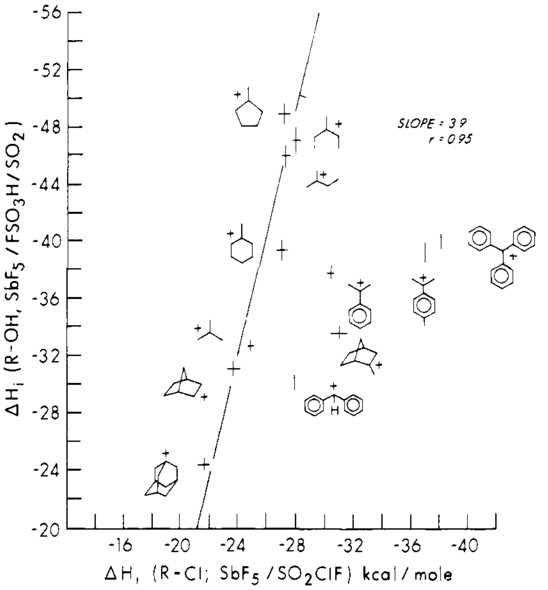

Figure 2. Plot of the heats of ionization for a series of alcohols with 1:1 (mol/mol) SbF_5/FSO_3H in SO_2 vs. the corresponding chlorides ionized with SbF_5 in SO_2ClF.[12] A regression line was calculated for the alkyl ions only (except 2-methyl-2-norbornyl).

The most reasonable way to account for these unusual results is to consider that they are caused by strong interactions between the carbocations and the complex antimony anions, which are produced by complete ionization. If ionization were not complete, it would be obvious from the spectra—if dissociation were complete, there is no reason why interaction with the anion should vary with the structure of the cations, as is the case here.

Considerable evidence is available from ^{19}F NMR[5] studies to show that the anions produced by ionization of alkyl halides with

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