diazo compound or the carbene itself (as suggested by Kirmse[3] for diphenylmethylene) has been tested and discounted on the basis of experimental evidence.

Ethyl diazoacetate in 2-propanol was subjected to acid-catalyzed decomposition. The results, summarized in Table I, indicate a very low stability for the hypothetical carbethoxycarbonium ion; the solvolysis and competitive reactions with added nucleophiles can be more readily rationalized in terms of an SN2 (diazonium ion) than of an SN1 (carbonium ion) mechanism.[4] Since in no case was the rearrangement product detected, carbethoxycarbonium ion is not implicated in the photoreaction, at least not in the formation of the principal product, I.

Table I. Acid Decomposition of Ethyl Diazoacetate[a] in 2-Propanol

Acid	Yield of products,[b] % II	Other
HBr	12	Ethyl bromoacetate, 85
HCl	24	Ethyl chloroacetate, 75
$HOSO_2C_6H_4$-*p*-CH_3	98	None

[a] One equivalent of acid decomposed 4 mmoles of ethyl diazoacetate in 20 ml of 2-propanol at 0°. [b] Products identified by comparison with authentic samples and yields estimated by vpc.

Further evidence against any role of the carbethoxycarbonium ion intermediate comes from the irradiation of ethyl diazoacetate in 2-propanol solution of lithium bromide. The photolysis did not produce the expected bromoacetate and the original product distribution was not affected by the lithium bromide. Experiments with added triethylamine gave similar results (Table II).

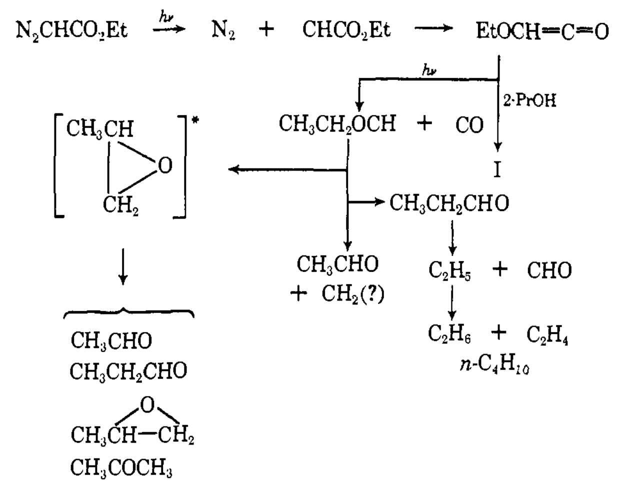
Table II. Photodecomposition of Ethyl Diazoacetate[a]

Phase	Added substance	Products and yield, or relative ratio[b]
Gas[c]	None	N_2 and CO in approximately equal amounts, considerable amounts of acetaldehyde and propionaldehyde, ethane, ethylene, butane, little acetone, and propylene oxide
	N_2 (700 torr) and 2-PrOH (50 torr)	Similar products and I in 8% yield
Liquid[d]	None	I, II, III, and IV, 29:25:12:9
	Et_3N[e]	I, II, III, and IV in unchanged ratio and small amounts of unidentified product
	LiBr[f]	I, II, III, and IV in unchanged ratio

[a] Medium pressure mercury lamp with Vycor or Pyrex filter. [b] Products identified by comparison with authentic samples and yield or relative ratio estimated by vpc. [c] 5 torr of ethyl diazoacetate at 45° in quartz cells. [d] 4 mmoles of ethyl diazoacetate in 20 ml of 2-propanol in quartz cells at room temperature. [e] 20–25% solution. [f] 4 mmoles.

Finally, the photolysis has also been examined in the vapor phase. The data along with the condensed phase results are summarized in Table II. The mechanism (Scheme I) accounts for all the observed products and is consistent with and lends additional support to the proposed carbene → ketene rearrangement.

Scheme I



In conclusion, carbethoxymethylene inserts into the tertiary C–H bond of 2-propanol, undergoes polar addition with the O–H bond, and rearranges to ethoxyketene. The latter process readily occurs in the gas phase as well. The *in situ* photolysis of the novel ethoxyketene affords ethoxymethylene which to a small extent stabilizes itself through isomerization but largely fragments (like the isomeric hot propylene oxide formed in the addition reaction of oxygen atom to propylene[5]) giving a variety of products. The predominance of rearrangement over intermolecular reactions in polar solvent is not due to solvent effect but simply to the decreased reactivity of the polar solvent as compared to hydrocarbons.[6]

Acknowledgment. The authors are grateful to the National Research Council of Canada for financial Support and to Professor P. Yates and Dr. J. Font for valuable comments.

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Thermal Rearrangement of $B_7C_2H_9{}^{2-}$ Ligand–Cobalt Complexes

Sir:

We wish to report the first example of the thermal polyhedral rearrangement of a transition metal complex in which the ligand comprises a fragment of a carborane system.

When the cesium salt of the recently reported complex ion $Co[B_7C_2H_9]_2^-$ (I)[1] was heated at 315° for 24 hr in a sealed tube, analysis of the product (II) was in agreement

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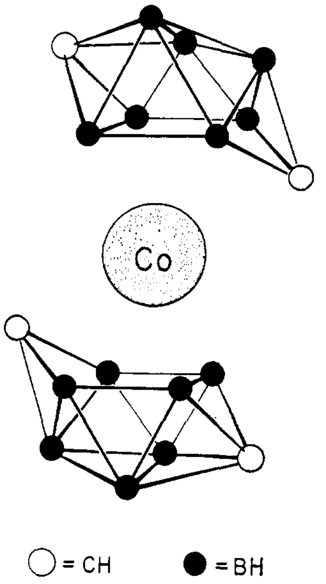

Figure 1. The proposed structure of the rearranged $\mathrm{Co[B_7C_2H_9]_2^-}$ ion.

with the same empirical formula, but the product differed in physical properties from the precursor ion. The salts of II were orange [λ_{max} 229 mμ (ϵ 19,100), 281

$$\underset{\mathrm{I}}{\mathrm{Co[B_7C_2H_9]_2^-}} \xrightarrow{315°,\ 24\ \mathrm{hr}} \underset{\mathrm{II}}{\mathrm{Co[B_7C_2H_9]_2^-}}$$

(8260), 348 (5360), and 483 (300)]. *Anal.* Calcd for $\mathrm{Cs(B_7C_2H_9)_2Co}$: C, 11.72; H, 4.43; B, 36.95; Cs, 32.95; Co, 14.38; equiv wt, 409. Found: C, 11.85; H, 4.50; B, 36.85; Cs, 32.81; Co, 14.29; equiv wt, 413. The isomerization was carried out in 98% yield.

The 32-Mc/sec ^{11}B nmr spectrum of I showed[1] it to be a low-symmetry system with seven unique boron atoms in each $\mathrm{B_7C_2H_9^{2-}}$ ligand. The 32-Mc/sec ^{11}B nmr spectrum of II appeared to represent a much more symmetrical system with no low-field doublet and two doublets of relative areas 3 and 4. The low-field doublet had previously[1] been assigned to an apex boron atom. The 60-Mc/sec ^{1}H nmr spectrum of the tetramethylammonium salt of II contained a sharp singlet of intensity 12 at τ 6.53 and two broad singlets, each of intensity 2, at τ 1.97 and 3.77. The former resonance was assigned to the methyl protons of the cation, and the other two resonances were assigned to two dissimilar sets of protons attached to the carbon atoms of the complex. A comparison between the 60-Mc/sec ^{1}H nmr spectrum of the tetramethylammonium salts of I and II showed that one of the carbon proton resonances associated with the $\mathrm{B_7C_2H_9^{2-}}$ ligand was approximately the same in both complexes (τ 3.77; *cf.* 3.40 for I) while the other carbon proton was significantly shifted downfield (τ 1.97; *cf.* τ 4.80 for I).

The mixed complex $\mathrm{(C_5H_5)Co(B_7C_2H_9)}$[1] can also be rearranged, under identical conditions, from the red complex III to an orange complex IV in 98% yield:

$$\underset{\mathrm{III}}{\mathrm{(C_5H_5)Co(B_7C_2H_9)}} \xrightarrow{315°,\ 24\ \mathrm{hr}} \underset{\mathrm{IV}}{\mathrm{(C_5H_5)Co(B_7C_2H_9)}}$$

mp 113° (*cf.* 158–159° for III); λ_{max} 198 mμ (ϵ 18,000), 236 (sh) (11,250), 254 (14,400), 327 (5220), and 455 (252). *Anal.* Calcd for $\mathrm{(B_7C_2H_9)Co(C_5H_5)}$: C, 36.12; H, 6.06; B, 32.80; Co, 25.31. Found: C, 36.14; H, 6.02; B, 30.57; Co, 24.51. High-resolution mass spectroscopy gave a parent ion peak at 234.1081 (calculated for $\mathrm{^{59}Co^{11}B_7{}^{12}C_7{}^1H_{14}}$, 234.1079).

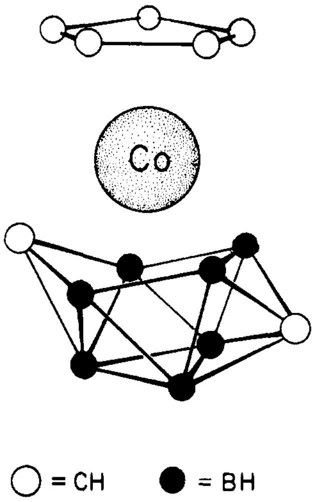

Figure 2. The proposed structure of rearranged $(\pi\text{-}\mathrm{C_5H_5})\mathrm{Co(B_7C_2H_9)}$.

The 32-Mc/sec ^{11}B nmr spectrum of IV was very symmetrical and consisted of four doublets of relative areas 1:2:2:2. No low-field doublet was observed. The 60-Mc/sec ^{1}H nmr spectrum of IV contained a sharp cyclopentadienyl resonance at τ 4.82, and the carbon proton resonances associated with the $\mathrm{B_7C_2H_9^{2-}}$ ligand appeared to be very broad singlets at τ 0.94 and 3.50. Again, a significant shift downfield had occurred for one of the two carbon protons (τ 0.94; *cf.* 6.50 for III) while the other had shifted only slightly (τ 3.50; *cf.* 2.31 for III).

Preliminary X-ray diffraction results[1] obtained on the tetraethylammonium salt of I showed that cobalt, assumed to be in the formal oxidation state +3, was sandwiched between two $\mathrm{B_7C_2H_9^{2-}}$ ligands in which each ligand has the two carbon atoms in the open-bonding face. The two carbon atoms were separated by a boron atom with one carbon atom occupying an apex position.

As a result of the high symmetry of the new $\mathrm{B_7C_2H_9^{2-}}$ ligand (shown by the ^{11}B nmr spectra), it is suggested that the thermal rearrangement has moved the nonapical carbon atom out of the open-bonding face of I and into the other apex position to generate II. The known thermal rearrangement of 1,6- to 1,10-$\mathrm{B_8C_2H_{10}}$,[2] which occurs at 350°, is an analogous rearrangement.

Our proposed structures for II and IV are shown in Figures 1 and 2.

Further work is in progress which involves the preparation and subsequent rearrangement of $\mathrm{B_7C_2H_9^{2-}}$ ligand–transition metal complexes other than those which contain cobalt.

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