Table I. Rate Constants for Decay of Radical Concentrations[a]

R	Theory	This study	Ref 8
Me$_2$CCN	7	2.2 ± 1	0.10
◯—CN	7	2.2 ± 1	

[a] Rate constant $\times 10^{-9}$ M^{-1} sec^{-1}.

The results are not highly precise, but almost certainly accurate within the indicated limits of error, and are certainly gratifying to those who have attributed measured inefficiency in radical production to geminate recombination. The calculated diffusive encounter rate may not correspond exactly to the actual encounter rate for solute molecules[10] so the discrepancy between calculated and measured values may have no significance at all. The very large difference between the rates of recombination of small cyanoalkyl radicals and the growing radicals from methacrylonitrile is surprising and suggests that the near constancy of the reactivity of polymer radicals probably does not apply to radicals near monomeric size. There is support in the literature for such a suggestion. North and Reed have shown that the ratio of rate constants for chain termination to propagation decreases in a series of alkyl methacrylates as the alkyl group gets larger, and they have attributed this to a decrease in the termination constant.[11] Hughes and North have shown that in the low-temperature polymerization of methyl methacrylate termination reactions involving small radicals are more efficient than those involving large radicals.[12]

Further support for the high value of k_r comes from preliminary measurements at different temperatures. Stationary-state radical concentrations were measured in solutions of AIBN in *m*-xylene irradiated under identical conditions at -40 and $+30°$. The radical concentration changed by less than 50%, so k_r varies less than twofold between the two temperatures. A nearly diffusion-controlled rate should show very small dependence of the rate on temperature,[13] in contrast to the 5-kcal mole^{-1} activation energy reported for the termination reaction of polymethacrylonitrile radicals.[5]

(10) R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 4529 (1964).
(11) A. M. North and G. A. Reed, *J. Polymer Sci.*, **1A**, 1311 (1963).
(12) J. Hughes and A. M. North, *Trans. Faraday Soc.*, **60**, 960 (1964).
(13) Note that changes in solvent viscosity should have approximately, or exactly, compensating effects on the value of *f* and the diffusive encounter rate.

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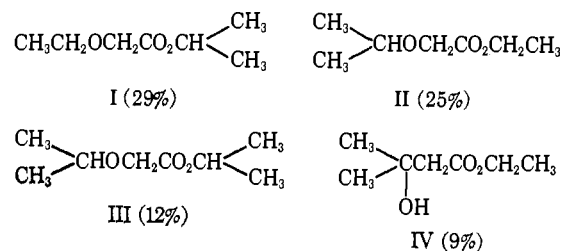## Rearrangement and Polar Reaction of Carbethoxymethylene in 2-Propanol

Sir:

Although intermolecular reactions of carbalkoxymethylenes are widely recorded in the literature,[1a,b]

(1) For a review see (a) W. Kirmse "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine "Divalent Carbon," The Ronald Press, New York, N. Y., 1964. (c) Professor F. H. West-

intramolecular reactions of these intermediates have not been observed.[1c] We wish to report here the rearrangement of carbethoxymethylene to ethoxyketene and its polar addition to 2-propanol as well as the *in situ* photolysis of this novel ketene.

Photolysis of ethyl diazoacetate in 2-propanol solution (2 g in 150 ml) was carried out by a Hanovia (450-W) medium-pressure mercury arc with a Vycor filter. The reaction was complete in 0.5 hr when nitrogen ceased to evolve and the yellow solution became colorless. Fractionation of the reaction mixture gave little actone (2,4-DNP mp 125°) and a small amount of ethyl acetate (2–3%). Distillation of the oily residue under reduced pressure gave a volatile fraction (1.8 g, bp 80–85° (18 mm)) which was separated by preparative gas chromatography (20-ft SE-30 column) to give I–IV.

$$CH_3CH_2OCH_2CO_2CH\langle{}^{CH_3}_{CH_3}$$
I (29%)

$${}^{CH_3}_{CH_3}\rangle CHOCH_2CO_2CH_2CH_3$$
II (25%)

$${}^{CH_3}_{CH_3}\rangle CHOCH_2CO_2CH\langle{}^{CH_3}_{CH_3}$$
III (12%)

$${}^{CH_3}_{CH_3}\rangle CCH_2CO_2CH_2CH_3$$ (with OH)
IV (9%)

All four products were structurally characterized by ir, nmr, and mass spectrometry in conjunction with unambiguous syntheses.

The products formed may be rationalized by assuming a carbethoxymethylene intermediate which inserts into the carbon–hydrogen bond to give IV. The formation of I involves a migration of the ethoxy group and most probably proceeds from an isomeric ketene analogous to the Wolff rearrangement.[2]

$$N_2CHCO_2Et \xrightarrow{h\nu}$$

$$N_2 + :CHCO_2Et \begin{cases} \xrightarrow[\text{2-PrOH}]{\text{insertion}} IV \\ \xrightarrow{\text{rearrangement}} EtOCH=C=O \xrightarrow{\text{2-PrOH}} I \end{cases}$$
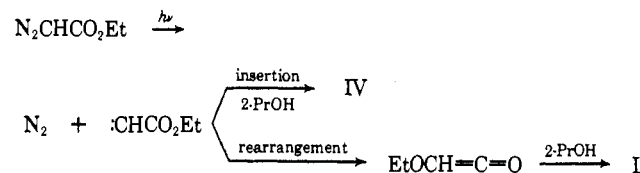
Product II may be explained by a polar addition of the carbene to the alcohol.

$$HC\langle{}^{OEt}_{O} \leftrightarrow HC=C\langle{}^{+OEt}_{O^-} \xrightarrow{ROH}$$

$$HC=C\langle{}^{+OEt}_{O^-} \text{ (with RO—H)} \rightarrow HC=C\langle{}^{OEt}_{OH} \text{ (with OR)} \rightarrow II$$
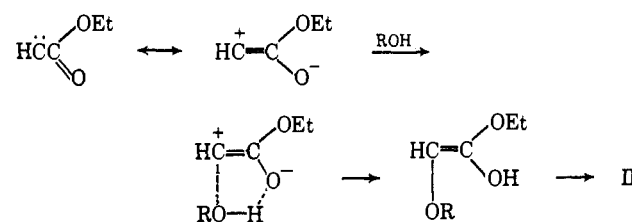
An ester interchange on II could account for III.

The possibility of the intervention of a carbonium ion produced *via* protonation of either the photoexcited

heimer has kindly called our attention to one of his earlier works (J. Shafer, P. Baranowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966)) and also an unpublished recent manuscript describing the rearrangement and insertion reactions of carbalkoxy carbenes. The observations and their interpretation are consistent with and complementary to ours.
(2) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p 38.

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, sum-

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

| | Yield of products,[b] % | |
Acid	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.

marized 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 S_N2 (diazonium ion) than of an S_N1 (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.

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

(3) W. Kirmse, *Ann.*, **666**, 669 (1963).
(4) D. Curtius and S. Gerber, *J. Am. Chem. Soc.*, **74**, 4052 (1952).

Scheme I

is consistent with and lends additional support to the proposed carbene → ketene rearrangement.

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]

(5) R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958).
(6) (a) W. von E. Doering and L. H. Know, *J. Am. Chem. Soc.*, **78**, 4947 (1956); (b) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

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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

(1) M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).