

it has become possible to apply a double tracer technique to the study of atoms produced by nuclear recoil.⁸ We report here preliminary results of such studies on carbon atom reaction mechanisms.

Technique.— C^{11} atoms are produced by $C^{12}(\gamma, n)C^{11}$ reaction induced by 40 Mev. Bremsstrahlung irradiation of the appropriate isotopically mixed system. (Either a mixture of protonated and deuterated molecules or a single partially deuterated compound is used.) Nuclear techniques for production of the recoil atoms under conditions of low radiation damage are described elsewhere.¹⁻⁴ Analysis of products involves gas chromatography followed by flow counting.¹⁻⁴ Isotopic separation is effected by a 100-ft. ethylene glycol-silver nitrate column (25° and 0°). This column was calibrated for isotopic ethylenes using C_2D_4 , C_2H_4 , C_2H_3D , CH_2CD_2 , and a mixture prepared by reducing C_2H_2 with D_2 on a platinum catalyst. The five equally spaced compounds found are assumed to correspond to $C_2H_nD_{4-n}$ ($n = 0-4$). No information on possible separation of the three $C_2H_2D_2$ isomers was obtained. Allene calibrations were based on C_3H_4 and C_3D_4 . Retention volumes of partially deuterated isomers were interpolated. These were checked by irradiation with C^{11} of a $C_2H_6-C_2D_6-C_2H_2$ mixture. The predicted unsymmetrical distribution of allenes, corresponding to the expected production⁹ of C_3H_4 , C_3H_3D , and $C_3H_2D_2$, was found. The effectiveness of the column for separating isotopic propylenes was checked using a propylene mixture prepared by catalytic reduction of $CH_3C\equiv CH$ with D_2 .

Allene from C Atom Reactions with Ethylene.—Allene is a principal product of the reaction of C with ethylene.¹ When produced from an equimolar mixture of C_2H_4 and C_2D_4 the following isotopic yield ratios were found: $C_2C^{11}H_4:C_2C^{11}H_3D:C_2C^{11}H_2D_2:C_2C^{11}HD_3:C_2C^{11}D_4 = 7:1 \pm 0.3:0.2:1 \pm 0.3:7 \pm 1$. Thus allene is produced predominantly by interaction of a carbon atom with a single ethylene molecule. This result is consistent with the two previously postulated mechanisms of insertion into the double bond,¹ and into the C-H bond,^{1,2} of ethylene. It seems plausible that the isotopic mixing that does occur is associated with radical production following insertion into the C-H bond.

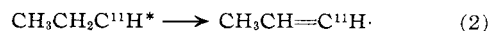
Propylene from C Atom Reaction with Ethane.—The formation of propylene from ethane has a formal similarity to the formation of allene from ethylene. However, it has a much lower yield.^{1,2} This was attributed to the different nature of the intermediates formed by the $C=C$ and $C-H$ insertions.¹ This difference in predominant mechanisms is reflected in the results on propylene formation from an equimolar mixture of C_2H_6 and C_2D_6 . Four propylene peaks are found, probably C_3H_6 , C_3H_5D , C_3HD_5 , and C_3D_6 . The peak ratios are $C_3H_6:C_3H_5D = C_3D_6:C_3HD_5 \cong 1.3:1$. Regardless of peak identities it is obvious that there is very extensive, though probably incomplete, isotopic mixing involving one hydrogen atom. Thus, unlike allene from ethylene, most propylene from ethane seems to have a radical precursor. This result is consistent with the previously postulated² carbon insertion into a C-H bond



The intermediate can de-excite by several modes and is thus a precursor for a number of products.¹⁻⁴ One such mode is H atom elimination

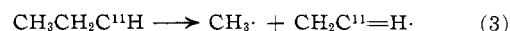
(8) The use of stable isotopes as tracers for recoil atom reactions should not be confused with their use to measure isotope effects.

(9) The allene produced in this system appears to result from addition to acetylene of methylene arising from reaction of C atoms with ethane.

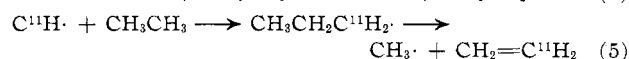


The resulting radical then abstracts a hydrogen atom from C_2H_6 (or C_2D_6).¹⁻⁴

Ethylene from C Atom Reaction with Ethane.—One of the more important products from the C atom reaction in saturated hydrocarbons is ethylene.²⁻⁴ When produced in an equimolar $C_2H_6-C_2D_6$ mixture we find approximately equal amounts of $CC^{11}H_4$, $CC^{11}H_3D$, $CC^{11}HD_3$, and $CC^{11}D_4$. The ratio of $CC^{11}H_2D_2$ to $CC^{11}HD_3$ is less than 1:5. This finding excludes a number of possible mechanisms, but is consistent with C atom insertion into a C-H bond. The intermediate formed by reaction 1 de-excites by C-C rupture (a favorable mode)



The vinyl radical then abstracts hydrogen from C_2H_6 or C_2D_6 . The data are equally consistent with a postulated alternative mechanism involving insertion into the C-H bond by a $C^{11}H$ intermediate.^{10,11}



Acknowledgments.—We are indebted to the operating staff of the Yale linear electron accelerator. This work was supported by the U. S. Atomic Energy Commission.

(10) Insertion by CH has been recognized as a possible alternative to insertion by C^2 . It was suggested as a specific precursor of ethylene by A. P. Wolf (Hot-Atom Conference, Amsterdam, May, 1963).

(11) It may be relevant to point out that the conclusions drawn from this work regarding the existence of radical precursors could not be derived from work with scavengers. Thus the yields of neither allene from ethylene nor ethylene from ethane are markedly oxygen-sensitive. Yet the double tracer experiments show that the former does not generally involve a radical precursor, while the latter does. This limitation of the scavenger technique in atomic carbon systems is probably due to the very high thermal reactivities of the radicals involved. (Scavengers are only effective when radicals have a relatively long lifetime in the given system.)

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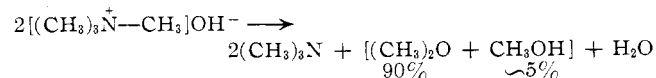
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RECEIVED OCTOBER 21, 1963

A Reinvestigation of the Pyrolysis of Tetramethylammonium Hydroxide

Sir:

The thermal decomposition of tetramethylammonium hydroxide has been found to yield *trimethylamine and dimethyl ether* as the major decomposition products rather than the reported products, trimethylamine and methanol.¹ The ether is formed in >90% yield based on the recovered trimethylamine. Minor prod-



ucts are methanol (*ca.* 5%), and apparently small quantities of higher alcohols and polyethylene.

The pyrolysis was carried out in a vacuum line using a stock solution of 10% tetramethylammonium hydroxide in water. Most of the water was removed by heating the solution at 65° to give a white amorphous solid. The solid decomposed at 135-140° and the products were collected continuously during the course of the reaction in a series of cold traps; water and methanol were removed at -78° (CO_2 -isopropyl alcohol bath), and the amine and ether at -196° (liquid N_2 bath).

(1) A. W. Hofmann, *Ber.*, **14**, 494 (1881).

The methanol was determined by gas-liquid chromatography with a flame ionization detector. The amine and ether mixture was condensed into a tared reaction tube and treated with a known amount of hydrogen chloride. The ether and excess hydrogen chloride were distilled and the amine content was determined by the isolation of the hydrochloride salt.² In a partial trap-to-trap fractionation of the original mixture, both the amine and ether fractions were analyzed by infrared spectroscopy. The spectrum of the ether fraction revealed traces of amine as the only impurity.

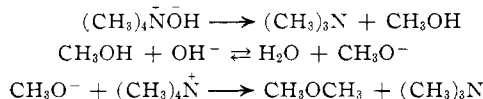
A typical decomposition using 2 ml. of 10% tetramethylammonium hydroxide (2.20 mmoles) gave the following products.

Products	Millimoles
(CH ₃) ₃ N	2.13 ^a
(CH ₃) ₂ O	0.97 ^b
CH ₃ OH	0.11 ^c
(CH ₂) _n	Trace

^a Recovered as the hydrochloride. ^b Recovered ether and HCl mixture less the HCl not used in forming the amine hydrochloride (see ref. 2). ^c Methanol and water mixture analyzed by gas-liquid chromatography with flame ionization detector.

A series of pyrolyses was carried out under a variety of conditions (a-e) without significant changes in the yield of products: (a) in an atmosphere of nitrogen, (b) in a rapid nitrogen flow system with a head pressure of 10 mm., (c) in an atmosphere of 25 mm. of water vapor, (d) in the presence of Ag⁺ ion, and (e) in an initially evacuated system without continuous collection of products.

Trace amounts (0.09%) of dimethyl ether have been reported³ as a product in the pyrolysis of cyclohexylmethyl-β-d-trimethylammonium hydroxide and its formation was explained by a three-step mechanism. An analogous mechanism for the decomposition of tetramethylammonium hydroxide would account for the observed products.



However, if methanol is formed under the present conditions it would be expected to leave the reaction zone rapidly. The formation of the methoxide ion and its subsequent reaction to form the ether in high yield would involve retaining the methanol completely but allowing the water to escape. Consequently, it is suggested that the hydroxide ion behaves as a proton-abstracting agent to give a nitrogen ylide and the observed products result from the decomposition of the ylide in various ways.

Nitrogen ylides have been shown to exhibit carbene character,⁴ and carbenes have been reported⁵ to react with alcohols to give ethers. Thus, the ether may be formed by the reaction of ylide with the small amount of water remaining at the decomposition temperature. Methanol may be formed either by the decomposition of the ylide in the presence of a large amount of water, or by a displacement reaction, whereas polyethylene is formed only in the latter stages of reaction when water is no longer present. The decomposition of this ylide in ether to form polyethylene and trimethylamine has been reported.⁶

(2) Dimethyloxonium chloride decomposes at -2° and can be removed completely from the amine salt.

(3) A. C. Cope, N. A. LeBel, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **83**, 3861 (1961).

(4) V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

(5) W. Kirmse, *Ann.*, **666**, 9 (1963).

(6) G. Wittig and R. Polster, *ibid.*, **599**, 1 (1956).

From this preliminary study, it appears that in the absence of hydroxylic solvent, or after the removal of hydroxylic solvent from the reaction site, α-hydrogen abstraction by strong bases⁷ (OH⁻, NH₂⁻, phenyl⁻) is the favored reaction. With weaker bases (Cl⁻, Br⁻, etc.)⁸ displacement may be the predominant reaction. It has been suggested³ that the mechanism of the Hofmann degradation may depend on the manner in which it is carried out. However, the mechanism may change during the course of reaction. In the presence of hydroxylic solvent^{9,10} or during the removal of solvent at elevated temperature, β-elimination appears to be the primary mode of decomposition. It is known that α-hydrogen abstraction occurs in the presence of these protonic solvents,^{10,11} but apparently reprotonation occurs before the ylide can decompose by any competitive path and alternative mechanisms are favored.^{3,9} As the solvent is removed, α-hydrogen abstraction becomes irreversible and the course of reaction depends on the mode of decomposition of the ylide.

Acknowledgment.—The author wishes to thank the National Science Foundation (GP-1704) and The University of California for supporting this research.

(7) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(8) A. T. Lawson and N. Collie, *J. Chem. Soc.*, **53**, 624 (1888).

(9) G. Ayrey, E. Bunce, and A. N. Bourns, *Proc. Chem. Soc.*, 458 (1961).

(10) V. J. Shiner and M. L. Smith, *J. Am. Chem. Soc.*, **80**, 4095 (1958).

(11) W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

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Chelation as a Driving Force in Organic Reactions.¹

A Generic Synthesis of Amino Acids by the Carboxylation and Alkylation of 3-Phenylhydantoin

Sir:

In the course of our work on the carboxylation of compounds containing activated methylene positions, we became interested in 3-phenylhydantoin. Wheeler and Hoffman² showed that the methylene position of hydantoin is sufficiently activated to condense with aromatic aldehydes, and thus hydantoin might be a member of the group of compounds which react with magnesium methylcarbonate.¹

When 3-phenylhydantoin³ was heated at 80° with magnesium methyl carbonate and the reaction mixture sampled periodically by diluting 1-ml. portions with methanol, a new absorption peak in the ultraviolet was observed at 278 mμ. A basic solution of 3-phenylhydantoin does not absorb in this region. This suggested that the 5-position of 3-phenylhydantoin has been carboxylated and the chelate formed. The new absorption peak immediately disappeared on addition of a trace of aqueous acid.

The identity of the carboxylation product was established by isolation of 3-phenyl-5-carbomethoxyhydantoin. The product was precipitated by pouring the reaction mixture into ether. After decanting the liquid phase, methanolic hydrogen chloride, at -50°, was added. After 2 days at room temperature most of the methanol was removed and the remainder poured into water. The infrared and nuclear magnetic reso-

(1) Previous related papers: H. L. Finkbeiner and M. Stiles, *J. Am. Chem. Soc.*, **85**, 616 (1963); H. L. Finkbeiner and G. W. Wagner, *J. Org. Chem.*, **28**, 215 (1963), and references cited.

(2) H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, **45**, 368 (1911). Subsequent work on hydantoins, their synthesis, and utility has been reviewed by E. Ware, *Chem. Rev.*, 403 (1950).

(3) This compound is prepared from the direct reaction of glycine with phenylisocyanate [J. R. Bailey and C. P. Randolph, *Ber.*, **41**, 2499 (1908)].