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DEOXYGENATION BY ATOMIC CARBON. INTRAMOLECULAR REACTIONS OF HYDROXY AND ALKOXY SUBSTITUTED CARBENES.

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Previous work[2] has demonstrated that atomic carbon reacts with ketones and aldehydes during their codeposition at a liquid nitrogen cooled surface to yield carbon monoxide and

$$R_1R_2C{=}O \quad + \quad :C: \longrightarrow CO \quad + \quad R_1R_2C:$$

carbenes. We now wish to report what, to our knowledge, is the first instance of a carbene having a hydroxyl group bound to the divalent carbon: hydroxymethylcarbene from the deoxygenation of acetic acid. Esters were also found to deoxygenate and give products <u>via</u> an intramolecular route.

The codeposition of acetic acid (8 g) with atomic carbon (0.48 mmole) at a liquid nitrogen cooled surface[3] resulted in the formation of carbon monoxide and acetaldehyde (0.13 mmole) in 37% yield. The mechanism of acetaldehyde formation is of considerable

$$CH_3CO_2H \quad + \quad :C: \xrightarrow{-CO} CH_3{-}\ddot{C}{-}OH \longrightarrow CH_3CHO$$

interest since, as in the deoxygenation of methyl formate to produce methoxycarbene,[4] hydroxymethylcarbene is one of the intermediates involved in the production of acetaldehyde. It is possible to envision three distinct pathways for the formation of acetaldehyde from hydroxymethylcarbene in an acetic acid matirx: The migration of a hydrogen atom from the

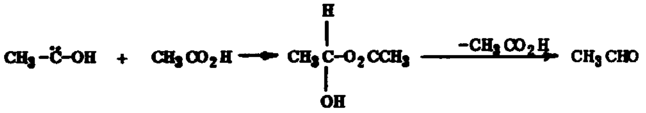
$$\overset{\curvearrowright}{CH_3}{-}\ddot{C}{-}OH \xrightarrow{\sim H} H_2C{=}CHOH \longrightarrow CH_3CHO \qquad (1)$$

methyl group would give vinyl alcohol, which could then tautomerize to the aldehyde (1);

the migration of the hydroxyl proton to the divalent carbon, giving the acetaldehyde

$$CH_3-\overset{\curvearrowright}{\ddot{C}-OH} \xrightarrow{\sim H} CH_3CHO \qquad (2)$$

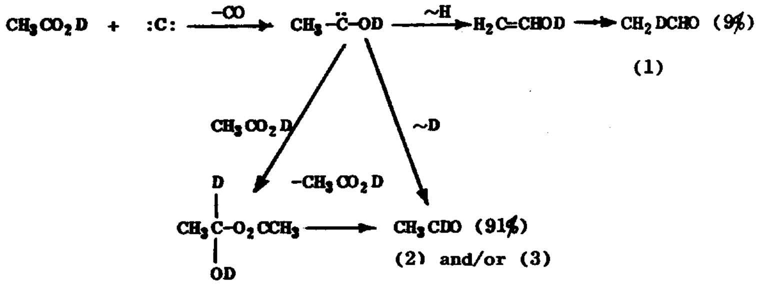
directly (2); and the reaction of hydroxymethylcarbene with a molecule of acetic acid from the matrix to give the hemiacylal which then eliminates acetic acid to yield the product (3).



$$CH_3-\ddot{C}-OH + CH_3CO_2H \longrightarrow CH_3\overset{H}{\underset{OH}{C}}-O_2CCH_3 \xrightarrow{-CH_3CO_2H} CH_3CHO \qquad (3)$$

A partial distinction may be made among these possibilities by examining the isotopic labeling of the acetaldehyde resulting from the deoxygenation of acetic acid-d. The distinction is shown in Scheme I. An examination of the acetaldehyde formed from the deoxygenation of

SCHEME I



acetic acid-d by NMR showed it to be a mixture of 91% CH_3CDO and 9% CH_2DCHO. The mass spectrum of the acetaldehyde confirmed that only acetaldehyde-d_1 was present and the infrared spectrum was identical to that published for CH_3CDO[5] with the exception of a small absorption centered at 3.7μ for the protium (9%) incorporated into the acyl position. This result precludes the significant intervention of vinyl alcohol in the hydroxymethylcarbene-acetaldehyde transformation. However, the result does not permit distinction between paths (2) and (3). It has been demonstrated that intramolecular hydrogen atom migration to divalent carbon may occur in acetic acid medium[6] and, if this is the route to acetaldehyde, it would require that migration from oxygen be more rapid than migration from carbon in the hydroxymethylcarbene molecule. However, it is also known[7] that atomic carbon reacts with alcohols to give alkoxy carbenes which undergo addition of a second molecule of alcohol to

$$\mathrm{ROH} + :\mathrm{C}: \rightarrow \mathrm{RO{-}\ddot{C}{-}H} \xrightarrow{\mathrm{ROH}} \mathrm{(RO)_2CH_2}$$

give an acetal. It may be that both pathways are competetive in an acetic acid matrix.

In earlier experiments with methyl formate[4], no appreciable ($<1\%$) amount of intramolecular rearrangement product (acetaldehyde) was obtained from the methoxycarbene intermediate although the carbene's presence was demonstrated by its addition to olefins under the reaction conditions. This result indicates that methyl migration from oxygen to divalent carbon (the analogy of (2)) is slower than intermolecular addition to olefin. In this context, the deoxygenation of methyl acetate was examined to see if 1,2-hydrogen migration in methylmethoxycarbene was more rapid than intermolecular addition to olefin under deoxygenative conditions.[8]

When methyl acetate and carbon vapor were cocondensed at a liquid nitrogen cooled surface, carbon monoxide was liberated and methoxy ethylene was produced in 35% yield

$$\mathrm{CH_3CO_2CH_3} + :\mathrm{C}: \xrightarrow{-\mathrm{CO}} \mathrm{CH_3{-}\ddot{C}{-}OCH_3} \xrightarrow{\sim\mathrm{H}} \mathrm{H_2C{=}CHOCH_3}$$

(based on C_1 vaporized). When carbon vapor and 1:1 mixtures of methyl acetate and isobutylene were codeposited at a liquid nitrogen cooled surface, methoxy ethylene was always the major product derived from methyl acetate. When the product mixture from the methyl acetate-olefin reaction was examined by combined gas chromatography-mass spectroscopy no peak with a molecular weight of 114 (C_4H_8 + C_3H_6O) could be observed. Intramolecular hydrogen migration in methylmethoxycarbene is more rapid than intermolecular addition to olefin.

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