

turnings (0.38 g, 0.016 mol), and 10 ml of anhydrous ether by combining all three components and starting the reaction with a small amount of MeMgI in ether. After refluxing for 1 hr under Ar, the solution was filtered under Ar, added dropwise to a mixture of triphenyllead chloride (Alfa Inorganics) (5.0 g, 0.011 mol), and refluxed under Ar for 2 hr. Hydrolysis with 20% ammonium chloride followed by ether extraction, drying over magnesium sulfate, and evaporation of the solvent yielded pale yellow crystals which were recrystallized from ethanol: yield, 3.3 g (55%) white crystals, mp 114.5–116°. Nmr and ir spectra are consistent with the structure $\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{Ph}$.

Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Pb}$: C, 57.44; H, 4.45. Found: C, 57.43; H, 4.53.

Anisole (7) (bp 152–153° (760 mm)) and benzyltrimethylsilane (14) (bp 95° (35 mm)) were distilled before use.

Both phenylcyclopropane (bp 86–87° (4 mm), n_D^{25} 1.5304, lit.^{56a}

(55) E. A. Zollner, *Iowa State Coll. J. Sci.*, **9**, 213 (1934).

(56) (a) D. Davidson and J. Feldman, *J. Amer. Chem. Soc.*, **66**, 488 (1944); (b) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 949 (1913), [*Chem. Abstr.*, **7**, 3964 (1913)].

bp 174° (760 mm), n_D^{20} 1.5316) and 7-phenylnorcarane (bp 141° (14 mm), n_D^{25} 1.5452, lit.⁵⁷ no properties recorded) were prepared by the pyrazalone method of Kishner.^{56b} Both were chromatographed on Matheson Coleman and Bell alumina using methylene chloride immediately before use. Neither decolorized potassium permanganate.

The 1-vinyl-5,5-dimethylbicyclo[2.1.1]hexane (XI) supplied by Professor Hammond⁵⁸ was purified by gas-liquid chromatography before use. Vinylcyclopentane (X) and ethyl vinyl ether (XII) were from Aldrich.

Acknowledgment. We wish to express our appreciation to the Air Force Office of Scientific Research for financial support (Grant AF-AFOSR-514-66) and to Professor George Hammond and Dr. J. L. Charlton for a sample of 1-vinyl-5,5-dimethylbicyclo[2.1.1]hexane.

(57) G. L. Closs and L. E. Closs, *Tetrahedron Lett.*, **26** (1960).

(58) R. S. H. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1892 (1964).

Deoxygenation by Atomic Carbon. II. The Generation of Carbenes from the Reaction of Carbonyl Compounds with Metastable Singlet State Carbon Atoms¹

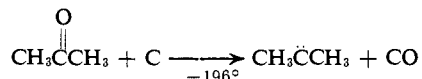
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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received July 18, 1969

Abstract: Carbon atoms produced in a low-intensity carbon arc under high vacuum react with ketones and aldehydes at -196° to produce carbenes and carbon monoxide. The distribution of the intramolecular rearrangement products is the same as from tosyl hydrazone derived carbenes.

The large value of the bond strength of carbon monoxide (256.7 kcal/mol)³ suggests that the reaction of carbon atoms with oxygen containing compounds to form carbon monoxide should be a thermodynamically favorable process. Atomic carbon produced by nuclear transformation has been reported^{4,5} to give carbon monoxide on reaction with oxygen, ethylene oxide, and carbon dioxide.

We have reported¹ that carbon atoms from a low-intensity arc are efficient deoxygenating agents: acetone reacts with carbon atoms on codeposition at a liquid nitrogen cooled surface to produce propylene and carbon monoxide as the major products. This process is calculated to be exothermic by 85–100 kcal/mol on



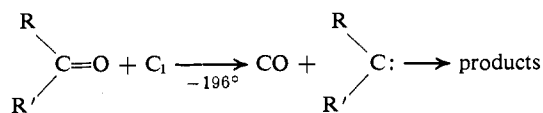
the basis of bond strengths.¹

Results and Discussion

A. The Deoxygenation Process. Simultaneous deposition at a liquid nitrogen cooled surface of aldehydes

- (1) A preliminary communication has appeared: P. S. Skell, J. H. Plonka, and R. R. Engel, *J. Am. Chem. Soc.*, **89**, 1748 (1967).
- (2) National Institutes of Health Predoctoral Fellow, 1967–1970.
- (3) A. E. Douglass, *J. Phys. Chem.*, **59**, 109 (1955).
- (4) C. MacKay and R. Wolfgang, *Radiochim. Acta*, **1**, 42 (1962).
- (5) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).

and ketones with carbon vapor results in extensive formation of carbon monoxide and hydrocarbons (olefins and cyclopropanes) characteristic of the corresponding carbene. This process has been named deoxygenation.



Several quantitative predictions concerning the deoxygenation of ketones and aldehydes can be made.

- (1) The amount of carbene-derived products should equal the amount of carbon monoxide produced.
- (2) In an experiment employing ¹⁴C-enriched carbon vapor, the carbene derived products should be radioinactive, while the carbon monoxide should be radioactive.
- (3) If no competitive pathways for carbon monoxide production are operative, it should have a relative molar activity of unity. The observation of such a value would eliminate a photochemical decomposition caused by light emission from the arc.

Table I demonstrates the correspondence of carbon monoxide yields with the yields of carbene derived products for the deoxygenations of acetone and 2-butanone. The observation of such a close correlation

Table I

Precursor	% yield of CO ^a	Yield of carbene ^a derived products
Acetone	50	44
2-Butanone	60	55

^a Yield = millimoles of product/millimoles of C₁ vaporized (assuming 40% of carbon vapor is monatomic carbon: see R. F. Harris, Ph.D. Thesis, Pennsylvania State University, 1968).

precludes any decomposition pathway producing carbon monoxide.

It should also be noted that all of the carbon monoxide produced in ketone deoxygenations is liberated during the codeposition of the carbon vapor and the substrate since subsequent warming of the matrix and collection of noncondensable gases does not yield additional quantities of carbon monoxide. This indicates that there are no adducts formed between the carbon atoms and the carbonyl compounds which are stable at liquid nitrogen temperature and generate carbon monoxide and carbene on warm-up.

The possibility that polyatomic forms of carbon (C₂ and C₃) may be responsible for oxygen abstraction can be eliminated in two ways: first, the process would be energetically unfavorable as evidenced by the high dissociation energy of the C₂ molecule (144 kcal/mol)⁶ which would give the process a ΔH of $\sim +70$ kcal/mol,



and second, reactions with thermally vaporized carbon (known to contain substantial amounts of C₂ and C₃)⁷ produce no appreciable deoxygenation (see Table VII).

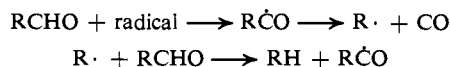
The correlation observed in Table I for ketone deoxygenations is not observed for aldehydes, as shown in Table II. The failure to observe an adequate mass

Table II

Precursor	—Yield based on C ₁ vap ^a —	
	% CO	% carbene product
Acetaldehyde	34	32
Propanal	88	44
Butanal	77	41
Pentanal	52	40
2-Methylpropanal	60	46
2-Methylbutanal	81	40
2,2-Dimethylpropanal	282	48

^a Calculated as in footnote a, Table I.

balance for the deoxygenation mechanism is attributable to simultaneous production of carbon monoxide by free-radical decarbonylation of the aldehyde to give the corresponding hydrocarbon. The increasing carbon monoxide yield with greater stability of R· is



in accord with the pattern established for aldehyde decarbonylations.⁸

(6) J. Drowart, R. P. Burns, G. DeMaria, and M. Inghram, *J. Chem. Phys.*, **31**, 1131 (1959).

(7) P. S. Skell, R. F. Harris, and J. E. Villaume, unpublished results.

(8) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

To distinguish between deoxygenative carbon monoxide and radical-chain decarbonylation carbon monoxide, reactions were carried out with ¹⁴C-enriched carbon vapor.⁹

The relative molar activities of carbon monoxide from aldehydes plus ¹⁴C can be predicted from Table II by using the amount of carbene-derived product as a measure of the radioactive carbon monoxide; decarbonylation gives inactive carbon monoxide. A comparison of predicted relative molar activities and the experimental values are presented in Table III.

Table III

Precursor	Calcd ^a rel molar act. of CO	Exptl ^b rel molar act. of CO
2-Methylbutanal	0.50	0.56
2-Methylpropanal	0.77	0.77
2,2-Dimethylpropanal	0.17	0.20

^a (Per cent carbene product)/(per cent CO formed), from Table II.
^b Allene was taken as a molar activity standard: it has a C₃ precursor;^{9c} therefore relative molar activity of CO = 3(curies/mole)_{CO} / (curie/mole)_{allene}.

Some carbon monoxide is given off ($\sim 20\%$) in the deoxygenation of 2,2-dimethylpropanal upon warm-up of the matrix; however, this carbon monoxide contains no radioactivity. All radioactive carbon monoxide is released from the matrix during deposition (prior to warm-up) indicating deoxygenation behavior identical with ketones although accompanied by free-radical decarbonylation.

The reactions of acetone and 2-butanone with ¹⁴C-enriched carbon vapor are summarized in Table IV.

Table IV

Precursor	Product	Rel molar act. ^a
Acetone	Carbon monoxide	0.91
	Propylene	0.00
	Acetylene	(2.00)
	Allene	2.75
2-Butanone	Carbon monoxide	0.89
	2-Butenes	0.00
	1-Butene	0.00
	Methylcyclopropane	0.00
	Acetylene	(2.00)
	Allene	2.87

^a Acetylene was taken as the standard in this table and has a C₂ precursor.^{9a} Therefore relative molar activity = 2(curies/mole)_{sample} / (curie/mole)_{C₂H₂}. The error of the relative molar activity is $\pm 5\%$.

The data presented in Table I demonstrated that any nondeoxygenative route to carbon monoxide must be minor; therefore, carbon monoxide should have a molar activity near unity. Acetylene was chosen as a molar activity standard for these compounds since it cannot have a molar activity greater than 2.00 (both carbons of C₂H₂ coming from the arc). This assignment correlates well with the carbon monoxide activity (derived from C₁) and with the allene molar activity (derived from C₃). The ability to observe an integral

(9) (a) P. S. Skell and R. F. Harris, *ibid.*, **88**, 5933 (1966); (b) *ibid.*, **90**, 4172 (1968); and (c) *ibid.*, **91**, 699 (1969).

Table V

Precursors	Products	Yield (% of C ₁ vaporized) ^a	Mole % of monomeric carbene products	
			Deoxygenation ^b	Comparison ^c
2-Butanone	<i>trans</i> -2-Butene	55	67 ^e	67 ^d
	<i>cis</i> -2-Butene		21	28
	1-Butene		10	5
	Methylcyclopropane		2	Trace
3-Pentanone	<i>trans</i> -2-Pentene	55	63	70 ^f
	<i>cis</i> -2-Pentene		33	28
	Ethylcyclopropane		4	2
	2-Methyl-2-butene		77	90 ^f
3-Methyl-2-butanone	3-Methyl-1-butene	42	15	5
	1,2-Dimethylcyclopropane		8	5
	3,3-Dimethyl-1-butene		82	52 ^d
3,3-Dimethyl-2-butanone	1,1,2-Trimethylcyclopropane	46	17	47
	<i>trans</i> -2-Pentene		55	
2-Pentanone	<i>cis</i> -2-Pentene	48	22	
	1-Pentene		19	<i>h</i>
	1,2-Dimethylcyclopropane		4	
<i>n</i> -Butyraldehyde	1-Butene	41	93	92 ^d
	Methylcyclopropane		7	5
2-Methylpropanal	2-Methylpropene	46	65	62 ^d
	Methylcyclopropane		35	38
<i>n</i> -Pentanal	1-Pentene	40	98	91 ^f
	Ethylcyclopropane		2	9
Propanal	Propene	39	95	90 ^d
	Cyclopropane		5	10
2,2-Dimethylpropanal	1,1-Dimethylcyclopropane	48	93	92 ^d
	2-Methyl-2-butene		6	7
	2-Methyl-1-butene		1	1
2-Methylbutyraldehyde	2-Methyl-1-butene	41	78	63 ^{d,g}
	Ethylcyclopropane		10	20
	<i>cis</i> -1,2-Dimethylcyclopropane		7	12
	<i>trans</i> -1,2-Dimethylcyclopropane		5	5

^a Calculated as in footnote a, Table I. ^b Temperature in reaction zone -150 to -180°. ^c Decompositions at 160°. ^d L. Friedman and H. Shecter, *J. Am. Chem. Soc.*, **81**, 5512 (1959), diazo decomposition. ^e *cis/trans* ratios were reversed in ref 1 and are corrected here. ^f A. Mansoor and J. R. D. Stevens, *Tetrahedron Lett.*, 1733 (1966), diazirine decomposition. ^g W. Kirmse and G. Wächtershäuser, *Tetrahedron*, **22**, 63 (1966), diazo decomposition. ^h No data available.

increase in molar activities for these three materials increases our confidence in the assignment of their precursors.

B. Carbenes Produced by Deoxygenation. Table V lists the product distributions for the deoxygenation of several carbonyl compounds and corresponding data for thermal decompositions of diazirines and diazo compounds. There is a close similarity in product composition despite the great difference in temperature (~350°), medium, and precursors.

This correspondence of products is strong evidence for the intermediacy of carbenes in the deoxygenation of aldehydes and ketones by C₁. Further, the correspondence among products for reactions taking place under such divergent conditions is a strong argument for noninvolvement of medium and leaving group; *both methods generate free carbenes*. Deoxygenation must be catalogued as a low-temperature, thermal process for generating free carbenes.

It should be noted for the reactions listed in Table V that carbene dimers are not formed.



The same product distributions for the low- and high-temperature reactions of carbenes indicates the differences in activation energy for intramolecular

carbene reactions are negligible, leaving steric and conformational effects in control. The rates of these reactions may be greater than rotational equilibration about the carbon-carbon bonds and thus the product geometries may reflect the configuration of the precursor at the time of carbene formation. Such steric and geometric explanations have been used to explain the selectivities of isomeric cyclopropane formation from hydrocarbon reactions with atomic carbon¹⁰ and in diazo decompositions.^{11,12}

Efforts were made to trap the dimethylcarbene from acetone deoxygenation by having both acetone and cyclohexene present in the matrix. The decrease in carbon monoxide and propylene yields with increasing cyclohexene content was measured to see if any appreciable portion of the dimethylcarbene was not appearing as propylene. The data in Table VI illustrate that the propylene-CO remains constant (0.95) over the concentration range studied. Also listed in the table is the statistical yield of carbon monoxide to be expected if a carbon atom reacted at random with the first molecule it encountered in the matrix. The total carbon monoxide yield observed correlates well with the statistical value, indicating no substantial difference in the rela-

(10) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **88**, 4883 (1966).

(11) G. L. Closs, *ibid.*, **84**, 809 (1962).

(12) See footnote g, Table V.

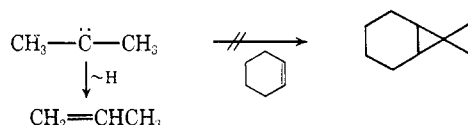
Table VI

Mole % acetone in matrix	Yield ^a		
	Carbon monoxide	Propylene	CO(stat) ^b
83.3	34.4	32.2	41.6
55.0	23.0	22.0	27.5
16.0	8.0	7.5	8.0

^a Calculated as in footnote a, Table I. ^b Calculated by taking CO yield without cyclohexene present (50.0%) and multiplying by mole per cent acetone in matrix.

tive reactivity of acetone and cyclohexene toward atomic carbon.

The small differences between observed yields of carbon monoxide and propylene were not found to correspond to trapping since analysis of liquid fraction of the reaction mixture by combined gc-mass spectroscopy gave no peak with the proper molecular weight for the 7,7-dimethylnorcaradiene under conditions where the corresponding bisethanoallene¹³ (C₁₅H₂₀) eluted from the column. These results indicate that a ketone



may compete for atomic carbon in the presence of an olefin and that intramolecular stabilization of alkyl-carbenes by product formation is more rapid than olefin addition, even at -196° .

It is generally assumed in carbene chemistry that intramolecular reactions to give olefins and cyclopropanes occur through a singlet structure, by analogy to carbonium ion behavior. Recently Moritani and coworkers have obtained more direct evidence¹⁴ indicating that singlet states are required. It follows from these considerations that the deoxygenative carbenes are singlet. The intermediacy of a triplet carbene would require the presently unobserved rearrangement of a 1,1 to a 1,2 diradical.

C. Spin State of Deoxygative Carbon. Carbon vapor from resistively heated carbon has been shown to produce much less excited state species^{9c} than arc vaporizations; electron bombardment in the arc plasma producing excited states. From a resistively heated surface, ground-state species predominate (³P for C₁).

Ground-state species of carbon vapor have very little, if any, deoxygenating capacity (Table VII), yields

Table VII

Precursor	Yield of CO ^a	
	Thermal vap	16-V arc
Acetone	2.9	50
2-Butanone	2.1	60
2-Methylbutanal	2.7 ^b	41 ^b

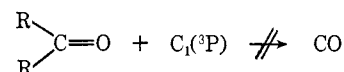
^a Calculated as in footnote a, Table I. ^b Using carbene product yields to eliminate CO from decarbonylation.

of carbon monoxide being dramatically reduced although the C₁ content is not changed. Clearly, C₁

(13) Formed from two molecules of cyclohexene plus a C₃ molecule: see P. S. Skell, L. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).

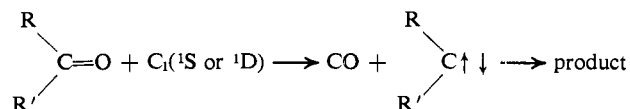
(14) I. Moritani, Y. Yamamoto, and S. I. Murahashi, *Tetrahedron Lett.*, 5697, 5755 (1968).

(³P) cannot be the species which deoxygenates carbonyl compounds. Residual capacity to produce carbon



monoxide may be attributable to excited state carbon, produced either by bombardment of vaporized species by thermal electrons, accelerated by the potential drop along the axis of the carbon rod, or by microarcing at poor contacts.

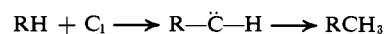
With arc vaporized carbon, the flight to wall of the reactor from the plasma requires 10^{-5} sec,¹³ permitting all allowed transitions to the ground and metastable states to occur before contacting the substrate. Thus C₁ (¹D and/or ¹S) is implicated as the species of atomic carbon which produces deoxygenation. This is consistent with results based on spin conservation



which would predict a singlet species being required to produce a singlet carbene.

While the ability to abstract oxygen is a general property of singlet carbon atoms,^{1,15} it is not unique. There are indications that methylene may abstract oxygen from carbon dioxide¹⁶ and Mahler has recently reported¹⁷ that bis(trifluoromethyl)carbene may remove oxygen from carbonyl fluoride.

Carbenes generated by carbon atom insertion into alkane carbon-hydrogen bonds¹⁰ in the condensed phase exhibit a totally different chemistry from the carbenes discussed in this paper, having an ability to abstract hydrogen to produce saturated products. These differences have also been noted by Wolf¹⁵ in the



case of cyclopropylcarbonyl carbene.

Experimental Section

The reaction system employed has been described previously.¹³ The atomic carbon was produced, along with C₂, C₃, and traces of C₄, from a 16-V (ac) carbon arc under vacuum ($\sim 1 \times 10^{-4}$ mm). Reactions occur in the condensed phase on a liquid nitrogen cooled surface.

Substrates were purchased commercially and purified by distillation until they were at least 99.9 mole % pure.

Products were isolated by gas chromatography and their infrared and mass spectra and retention times compared to authentic samples.

¹⁴C-enriched carbon vapor reactions were run as previously described.¹⁵ The enriched vapor was produced by replacing the lower arcing electrode by one enriched with carbon-14. These were obtained from the United Kingdom Atomic Energy Authority.

Blank reactions demonstrated that none of the materials listed as products in Table V were present in the starting materials. Since the matrix is formed in high dilution (weight of substrate)/(weight of carbon vaporized) ≈ 600 -1000, it is improbable these products could arise from reactions with substrate impurities.

Acknowledgments. We gratefully acknowledge the financial support of the Air Force Office of Scientific Research and the Public Health Service for a fellowship to J. H. P.

(15) P. S. Skell and R. F. Harris, *J. Am. Chem. Soc.*, **91**, 4440 (1969).

(16) G. B. Kistiakowski and K. Sauer, *ibid.*, **80**, 1066 (1958).

(17) W. Mahler, *ibid.*, **90**, 523 (1968), and references therein.

(18) P. B. Shevlin and A. P. Wolf, *ibid.*, **88**, 4735 (1966).