(in this case 366 nm) and 4a-FlEtOH at 350 nm in DMF. In a previous study the rate of decomposition of 4a-FlEtOO$^-$ in dry *tert*-butyl alcohol ($k = 4.6 \times 10^{-2}$ s^{-1}) has been shown to be independent of the concentration of *t*-BuO$^-$K$^+$.[12] Apparently in DMF the rate of decomposition of 4a-FlEtOOH in the presence of *t*-BuO$^-$K$^+$ is rapid and initially yields 4a-FlEtOO$^-$ (366 nm) prior to further decomposition products (315-, 325-, 340-nm bands).

Combination of FlEt· and $O_2^-\cdot$. The involvement of $O_2^-\cdot$ from 4a-FlEtOO$^-$ in dioxygenation reactions[12,14] and in the mechanism of the formation of 4a-hydroperoxyflavins from reduced flavin and oxygen[5,6,8] has been discussed previously. Thermodynamic calculations[6] demonstrate that an FlEt·–$O_2^-\cdot$ adduct is viable. When 1 equiv of FlEt· is combined with approximately 1 equiv of $O_2^-\cdot$ in DMF (or 1 equiv of FlEt$^+$ is combined with 2 equiv of $O_2^-\cdot$), products are formed whose spectroscopy and electrochemistry (Figures 4c and 5) are consistent with an initial transient formation of an adduct, FlEtOO$^-$. The transient anodic wave at +0.87 V vs. SCE is similar to that observed when *t*-BuO$^-$K$^+$ is added to FlEtOOH, and the UV spectrum of the FlEt·–$O_2^-\cdot$ combination is nearly identical with that found when *t*-BuO$^-$K$^+$ is added to FlEtOOH. While this spectrum is not solely that of FlEtOO$^-$, it indicates that both reactions follow similar pathways and probably involve FlEtOO$^-$ as a common intermediate.

The anodic waves at −0.27 and +0.31 V vs. SCE (Figure 4a) are the same as those observed for FlEt$^-$, which indicates that $O_2^-\cdot$ also reduces some FlEt· to FlEt$^-$ to liberate O_2 immediately after combination of FlEt· and $O_2^-\cdot$. That both O_2 and FlEt$^-$ can exist in the same solution reveals that thhe FlEt$^-$–O_2 reaction is not as facile as had been originally believed.

Acknowledgment. This work was supported by the National Science Foundation under Grants No. CHE-7922040 (D.T.S.) and PCM-8004816 (T.C.B.).

An Experimental and Theoretical Investigation of the Mechanism of Deoxygenation of Carbonyl Compounds by Atomic Carbon[1a]

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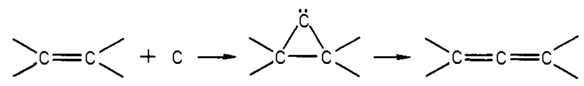
Abstract: The reactions of atomic carbon with butanal and butanone have been studied by both MNDO calculations and experiment. The calculations indicate the preferred path to involve addition of carbon across the C=O bond to form an oxiranylidene which rearranges to ketene. Since the ketene is formed with enough excess energy to undergo dissociation to carbon monoxide and a carbene, it should be detectable only under conditions where the excess energy is rapidly dissipated. While no ketene was observed when the reactions were carried out in the gas phase, a ketene intermediate was trapped by addition of water following the reaction of arc-generated carbon atoms with frozen butanal.

Atomic carbon is a highly reactive species which commonly attacks olefins and hetero-organic compounds at the point of maximum electron density and which has therefore been regarded as an electrophile.[2] A good example is the deoxygenation of carbonyl compounds, a reaction which provides a convenient route to carbenes.[3a]

These seem to take place by a donor–acceptor interaction between an occupied orbital of the substrate and an empty 2p AO of the carbon atom. In the case of an olefin, the only available donor orbital is the π MO of the double bond. The reaction therefore takes place by "sideways"[2a] addition of carbon to the π bond, leading to a cyclopropenacarbene (**1**) which rearranges to an allene.


(1)

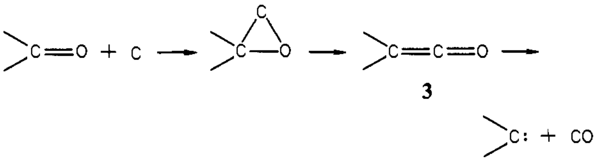
1

In the case of a molecule containing a π-bonded heteroatom, there is also the possibility of "end-on"[2a] attack via a lone-pair AO of the heteroatom. The products formed from various inorganic species with atomic carbon have been consistent with this alternative route. It seems to have been generally assumed[2] that the reactions of carbon atoms with carbonyl compounds also involve "end-on" attack on oxygen to form an ylide-like species (**2**) which dissociates into a carbene and carbon monoxide:

$$>C{=}O + C \rightarrow \underset{\mathbf{2}}{>\dot{C}{-}O{-}\dot{C}{:}} \rightarrow >C{:} + OC \qquad (2)$$

Here **2** may or may not be a stable intermediate, the reaction in the latter case involving a concerted transfer of oxygen from the substrate to the carbon atom.

There is, however, no compelling evidence for the "end-on" mechanism, at any rate in the case of the carbonyl reactions. The same products could equally well be formed by "sideways" attack, via an oxiranacarbene (**3**) and a ketene, the latter dissociating into the carbene and carbon monoxide, i.e.


3

(3)

It is true that the dissociation of a ketene into a carbene and carbon

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(1) (a) Presented at the Southwest Regional Meeting of the American Chemical Society, Austin, Texas, ORGN 34, December 5, 1979. (b) Robert A. Welch Predoctoral Fellow. (c) The University of Texas at Austin. (d) Auburn University.

(2) For recent reviews of the chemistry of atomic carbon, see: (a) C. MacKay In "Carbenes"; R. A. Moss and M. Jones, Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. 2, pp 1–42; (b) Skell, P. S.; Havel. J. S.; McGlinchey *Acc. Chem. Res.* **1973**, *6*, 97.

(3) (a) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 836. (b) Kammula, S.; Shevlin, P. B. *J. Am. Chem. Soc.* **1973**, *95*, 4441.

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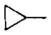
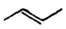
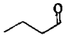
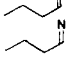
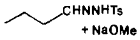
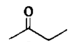
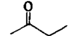
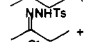
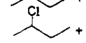
Table I. Product Ratios of Reactions Proceeding via Propyl and Methylethyl Carbenes

							Ref.
 + **8**	25.0	41.7	8.3	9.9	8.3	6.8	17
 + **8**			52.9	35.3	7.7	4.1	
 + $\ddot{C}$ [arc]			93	7	--	--	3a
 $\xrightarrow{h\nu}$			90	8	2		21
 + NaOMe			92	5	2	1	22
 + Na			86		4	3	23
 + **8**			3.1	25.6	46.1	25.2	
 + $\ddot{C}$ [arc]			10	2	67	21	21
 + NaOMe			5	0.5	67	28	22
 + K			60		28	12	23

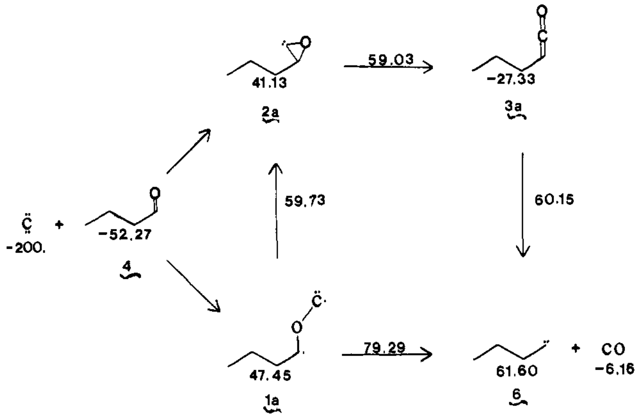
monoxide is extremely endothermic. However the initial addition of carbon to carbonyl to form the oxiranacarbene **2**, and the rearrangement of the latter to the ketene **3**, should both be extremely exothermic, so **3** should be formed with far more than enough energy to dissociate. Unless this excess energy is dissipated very rapidly indeed, the ketene **3** will not survive as such. Failure to observe ketenes among the products of such reactions would not then be surprising, particularly for reactions carried out in the gas phase. Furthermore, the carbon atom in its ground state ($(1s)^2(2s)^2(2p_x)(2p_y)$) can be regarded as a carbene, carbene itself being derived from it by using the singly occupied AOs to form CH bonds. As such it might be expected to undergo typical carbene reactions, in particular addition to multiple bonds.

This seemed a case where a distinction might be drawn between the two mechanisms on the basis of theoretical calculations. While various other reactions of atomic carbon have been studied theoretically, by both semiempirical[4] and ab initio[5] procedures, no one yet seems to have examined its reactions with carbonyl derivatives. We have therefore carried out such a study of two reactions of atomic carbon for which extensive experimental data are available, namely the deoxygenations of butanal (**4**) and butanone (**5**) to the carbenes **6** and **7**. The calculations were carried out with the use of the MNDO method. Extensive work in these laboratories had suggested that reliable conclusions should be obtained in this way. Since the calculations led to the somewhat unexpected conclusion that deoxygenation does in fact take place by the ketene route (eq 2), we have also carried out additional experimental work to test this prediction.

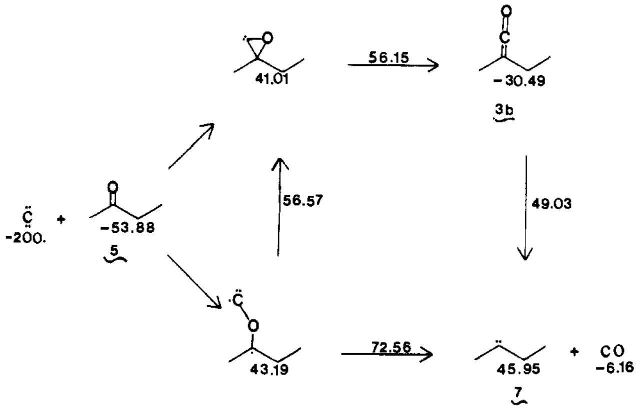
Experimental Data for the Reactions of 4 and 5 with Atomic Carbon

Table I summarizes the available experimental data for the reactions of **4** and **5**, with carbon atoms obtained from various precursors, both in the gas phase and in condensed phases. Gaseous carbon atoms were obtained by thermolysis of diazotetrazole (**8**). The products consisted of rearrangement products from the carbenes, **6** and **7**, together with higher boiling material formed by bimolecular reactions of **6** or **7** with other molecules. As would be expected, the yields of rearrangement products were greater for reactions in the gas phase where the relative rates of the bimolecular reactions must be less than those of the unimolecular rearrangements. Note also that no isobutene was formed in the reactions of **4** with atomic carbon. Its formation from propane (Table I) must be attributed to insertion of a carbon atom into a CH bond of the methylene group to form Me_2CHCH: (cf. ref 7).

Scheme I. Numbers below Structures (for Compounds and Intermediates) and at Arrows (for Transition States) Indicate ΔH_f (kcal/mol) for the Reaction of Atomic Carbon with Butyraldehyde



Scheme II. Numbers below Structures (for Compounds and Intermediates) and at Arrows (for Transition States) Indicate ΔH_f (kcal/mol) for the Reaction of Atomic Carbon with 2-Butanone



Theoretical Procedure

The calculations were carried out in the usual way,[8] with the use of a spin-unrestricted (UMNDO[9]) version of the MNDO method. The geometries of stable species were found by minimizing the total energy by using the standard[6] Davidon-Fletcher-Powell[10] (DFP) optimization procedure. Transition states were located approximately by the reaction coordinate method and then refined by minimizing the scalar gradient of the energy.[11,12] Each transition state was characterized as such by calculating[13] and diagonalizing the Hessian (force constant) matrix, and thus establishing that it had one and only one negative eigenvalue.[11,12] The corresponding eigenvector (transition coordinate) was also examined to make sure that the transition state corresponded to the desired reaction. Since Skell and Plonka[3a] have shown that the reactions involve singlet carbon and since the same is true for carbon generated from diazotetrazole,[3b] calculations were carried out only for the singlet potential surfaces.

Results and Discussion

The energetics of deoxygenations of **4** and **5**, as calculated by MNDO, are shown in Schemes I and II. The enthalpies of

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(4) (a) Figuera, J. M.; Shevlin, P. B.; Worley, S. D. *J. Am. Chem. Soc.* **1976**, *98*, 3820. (b) Dewar, M. J. S.; Bodor, N.; Maksic, Z. B. *Ibid.* **1973**, *95*, 5245.

(5) Blint, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1975**, *32*, 178.

(6) Dewar, M. J. S.; Thiel, W., *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(7) Shevlin, P. B.; Kammula, *J. Am. Chem. Soc.* **1977**, *99*, 2627.

(8) Dewar, M. J. S. "Further Perspectives in Organic Chemistry, Ciba Foundation Symposium 53"; Elsevier: Amsterdam, 1978; p 102. Dewar, M. J. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 197; *Chem. Br.* **1975**, *11*, 97; *Science* **1975**, *197*, 1037.

(9) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *Chem. Phys. Lett.* **1977**, *47*, 80.

(10) Fletcher, R.; Powell, M. J. S. *Comput. J.* **1963**, *6*, 163. Davidon, W. C., *Ibid.* **1968**, *10*, 406.

(11) McIver, J. W.; Komornicki, A., *J. Am. Chem. Soc.* **1972**, *94*, 2625; **1973**, *95*, 4512.

(12) Using a program written by Dr. P. K. Weiner.

(13) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, *J. Mol. Struct.* **1978**, *43*, 135.

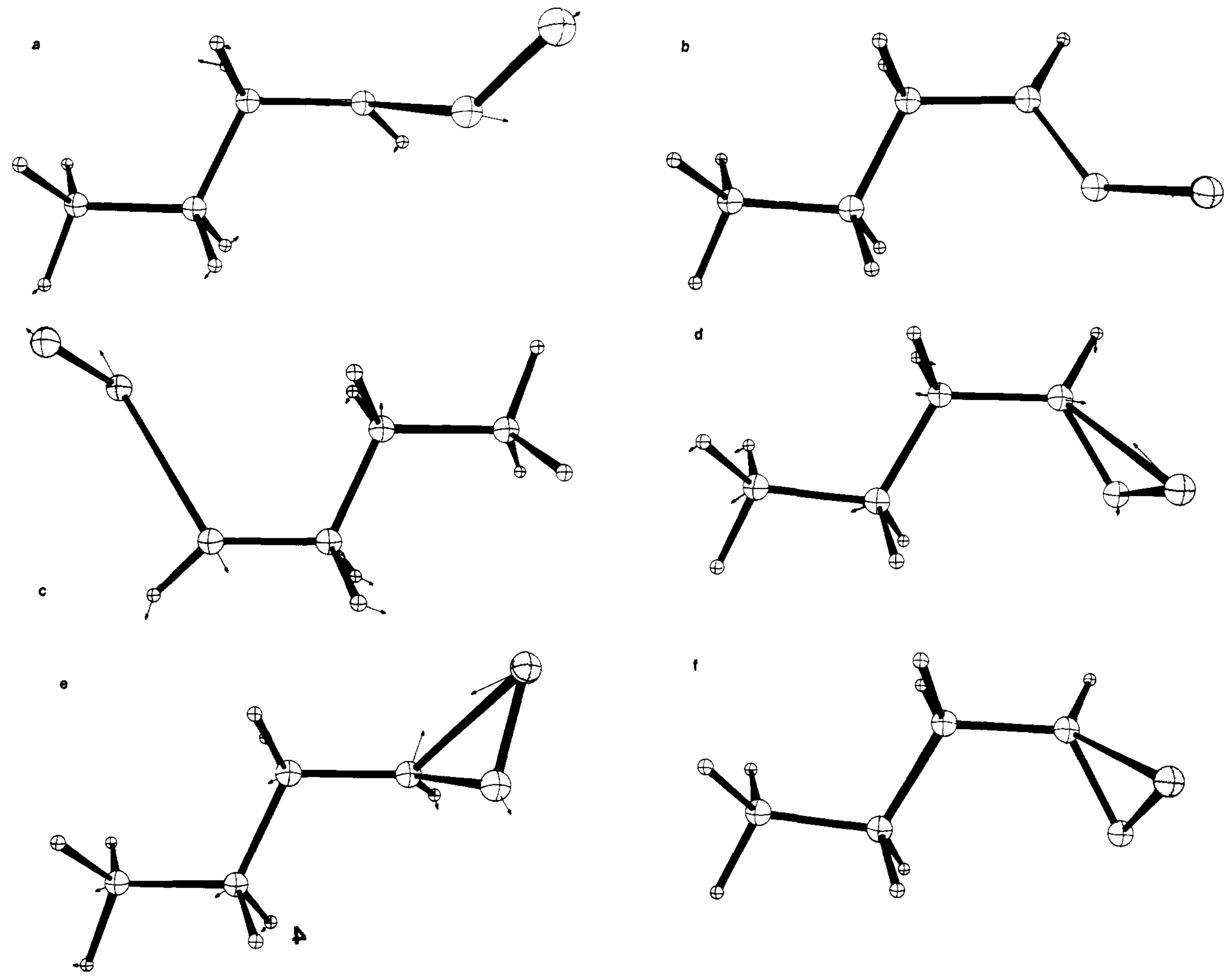

Figure 1. ORTEP plots for stable species and transition states derived from **4**. The arrows in the latter designate, by length and direction, the contribution of individual atomic motions to the transition coordinate: (a) oxiranylidene adduct (**2a**) resulting from π bond attack on **4** [butyraldehyde + C sideways]; (b) transition state for **2a** $\rightarrow$ **3a** [butyraldehyde transition state sideways to ketene]; (c) "end-on" adduct (**1a**) from **4** butyraldehyde transition state end-on to sideways]; (d) transition state for **1a** $\rightarrow$ **2a** [butyraldehyde transition state ketene to carbene]; (e) transition state for **3a** $\rightarrow$ **6** + CO [butyraldehyde + C end-on]; (f) [butyraldehyde transition state end-on to carbene].

deoxygenation of **4** to *n*-propylcarbene (**6**) (−92.6 kcal/mol) and of **5** to methylethylcarbene (**7**) (−106.2 kcal/mol) seem reasonable.[14]

First let us consider Scheme I.

MNDO predicts both modes of addition of carbon to take place without activation, giving the ylide (**1a**) and oxiranacarbene (**2a**) as stable intermediates. These reactions are, however, so very exothermic that neither will survive under conditions where the heat of reaction is not very rapidly dissipated, both dissociating to (**6** + CO), in the case of **2a** via the ketene **3a**.

The heats of formation of the transition states for the rearrangements (**1a** $\rightarrow$ **2a**) and (**2a** $\rightarrow$ **3a**) and for dissociation of **3a** ($\rightarrow$ **6** + CO) are similar, each being less by 20 kcal/mol than that for dissociation of **1a**. Under conditions where deactivation is not very fast, **1a**, **2a**, and **3a** may then all be formed. Since the activation energies for (**1a** $\rightarrow$ **2a**) and (**2a** $\rightarrow$ **3a**) are much less than for conversion of **3a** to **2a** or **6**, **6** is likely to be the main product among the intermediates.

Turning now to Scheme II, we see that the overall picture is similar to that in Scheme I and the same general conclusions should hold. There are, however, two important differences.

First, the differences in energy between the reactants and the various transition states are greater than in Scheme I. It should be correspondingly more difficult to trap intermediates.

Second, the transition state for dissociation of **3b** (to **7**) is lower in energy by 7 kcal/mol than that for formation of **3b** from **2b**. It should therefore be more difficult to trap the ketene intermediate (**3b**) from butanone (**5**) than that (**3a**) from *n*-butanal (**4**) because in the case of the latter, both transition states have similar energies.

A detailed search of each potential surface showed no low-energy path involving synchronous fission of the CC and CO bonds.

ORTEP plots of the geometries of the initially formed intermediates (**1** and **2**), and of all the transition states, are shown in Figures 1 and 2. The eigenvector corresponding to the imaginary vibration frequency for each transition state, i.e., the transition coordinate,[16] is indicated by arrows in each ORTEP plot. Note that these have the forms expected for the reactions in question.

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(14) The enthalpy of deoxygenation of formaldehyde to singlet carbene by a singlet (^{1}D) carbon atom is about −90 or −100 kcal/mol, the uncertainty arising from current uncertainty[15] concerning the S_0–T_1 separation in CH_2.

(15) The value (19.5 kcal/mol) reported by Lineberger et al. (Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731) now seems too large by ca. 11 kcal/mol. See: Lengel, R. K.; Zare, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 7495.

(16) The term "reaction coordinate" was originally introduced by Polanyi to describe an arbitrary geometrical parameter which varies during a reaction and whose instantaneous value can therefore be taken as a measure of the extent to which the reaction has proceeded. Its later use to describe the normal coordinate with an imaginary vibration frequency in a transition state seems unnecessarily confusing. The term "transition coordinate" seems to us a much better description of the latter.

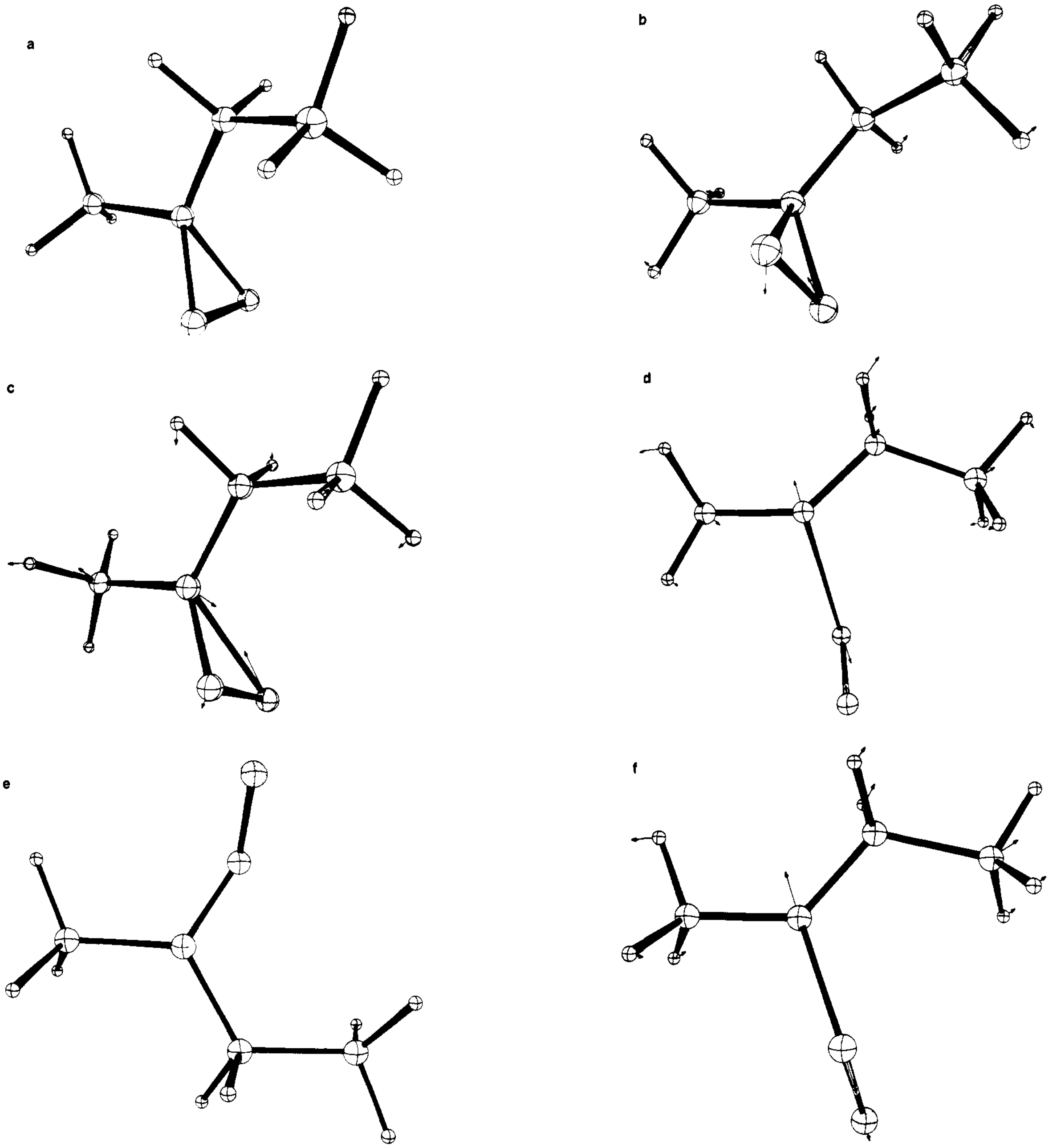
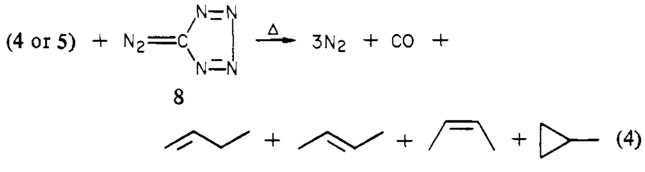


Figure 2. Plots analogous to Figure 1 for species derived from **5**: (a) oxiranylidene adduct (**2b**) resulting from π bond attack on **5** [2-butanone + C sideways]; (b) transition state for **2b** → **3b** [2-butanone transition state sideways to ketene]; (c) "end-on" adduct (**1b**) from **5** [2-butanone transition state sideways to end-on]; (d) transition state for **1b** → **2b** [2-butanone transition state ketene to carbene]; (e) transition state for **3b** → **7** + CO [2-butanone + C end-on]; (f) transition state for **1b** → **6** + CO [2-butanone transition state end-on to carbene].

The energetics of the reactions of **4** and **5** with carbon atoms are indicated schematically in Figure 3.

As we have already noted, ketenes have not previously been reported as even minor products of the reactions of carbon atoms with aldehydes or ketones. In view of our calculations, we decided to investigate the matter in detail. Initial attempts to trap the ketene were carried out with carbon atoms generated by thermolysis of 5-diazotetrazole (**8**)[17,18] in the presence of gaseous **4** or **5**. In each case water or methanol was added immediately after the reaction was complete, under conditions where the ketene, if formed, should have been converted to the corresponding carboxylic acid or its methyl ester. While these reactions yielded the products expected from the carbenes **6** or **7** (eq 4), none of the expected acid or ester could be detected, implying that no significant amount of ketene was present in the products. The same results were obtained when methanol was added at the same time as the substrate and the reaction run in the presence of methanol.



However, as we have already noted, failure to detect ketenes in these reactions does not prove that ketenes are not formed, because the ketene would be generated with much more than enough excess energy to dissociate into a carbene and carbon monoxide and because the excess energy could very well not be dissipated fast enough in the gas phase to prevent fragmentation of the ketene. We have therefore repeated the reactions of carbon atoms with **4** and **5**, using the arc method developed by Skell and co-workers.[2b] In this technique, carbon atoms are generated in the gas phase in a carbon arc and reacted with solid substrate

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(17) Shevlin, P. B.; Kammula, S. *J. Am. Chem. Soc.* **1977**, *99*, 2627.
(18) Dyer, S. F.; Shevlin, P. B. *J. Am. Chem. Soc.* **1979**, *101*, 1303.

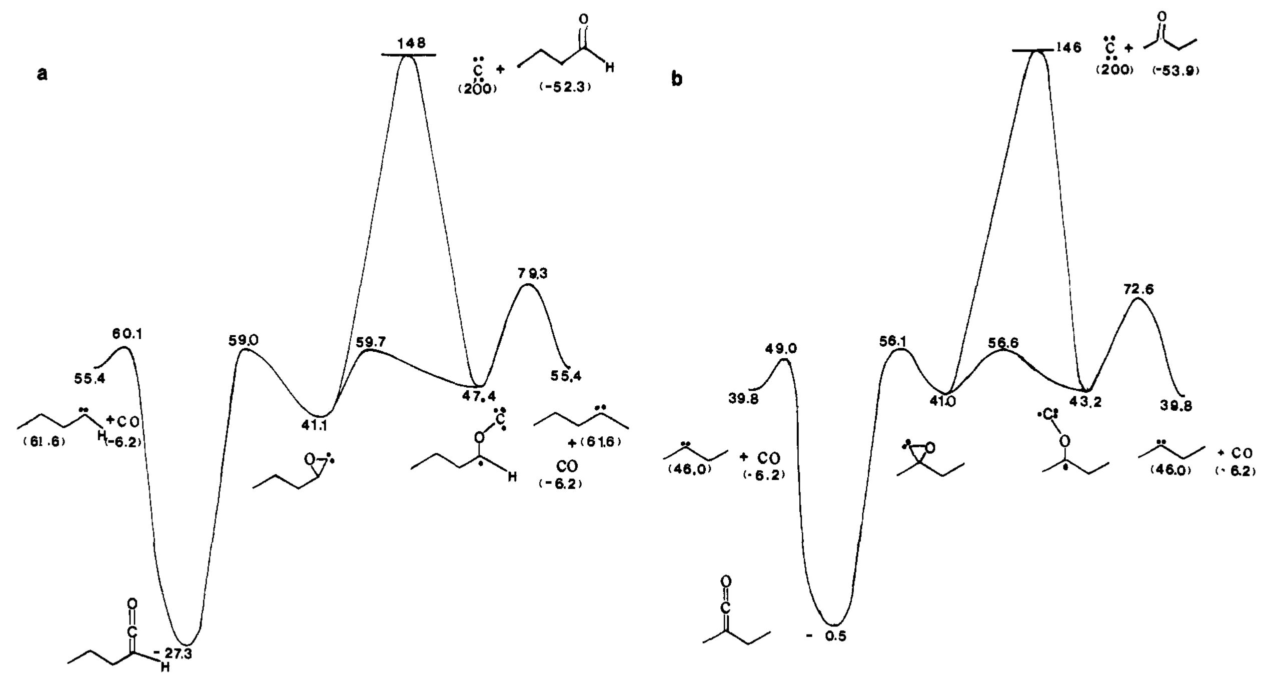
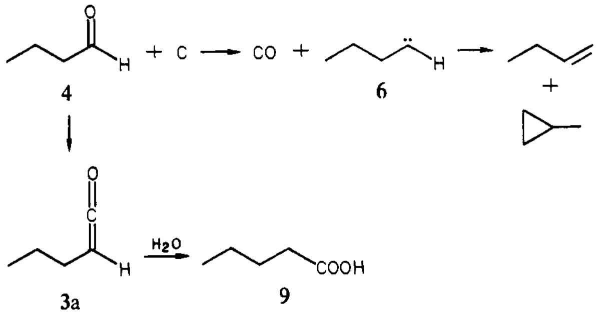


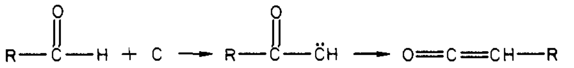
Figure 3. Schematic plots of the potential surfaces for (a) C + **4** and (b) C + **5**. The numbers indicate the calculated heats of formation (kcal/mol, at 25 °C).

cooled to a low temperature. It was thought that the cold surface would stabilize the ketene intermediate and allow it to be trapped. When **4** was reacted with arc-generated carbon at −196 °C and water was added before the reaction mixture was allowed to warm, pentanoic acid (**9**), as well as 1-butene and methylcyclopropane, were isolated from the reaction mixture. The detection of **9** in the reaction mixture constitutes good evidence for the intermediacy of ketene **3a**. Since 1-butene is the only other major product under these conditions, the observed molar ratio of **9** to 1-butene (1:3) suggests that almost one-quarter of the **4** that reacted was converted to the ketene (**3a**).



(5)

While this observation is consistent with the mechanism predicted by MNDO, the intermediate ketene (**3a**) could in principle have been formed by an alternative route, i.e., by insertion of carbon into the CH bond of the aldehyde to form a ketocarbene which would then undergo a Wolf rearrangement, i.e.



$$R-\overset{O}{\overset{\|}{C}}-H + C \longrightarrow R-\overset{O}{\overset{\|}{C}}-\ddot{C}H \longrightarrow O{=}C{=}CH-R \quad (6)$$

This, however, seems to us unlikely for several reasons.

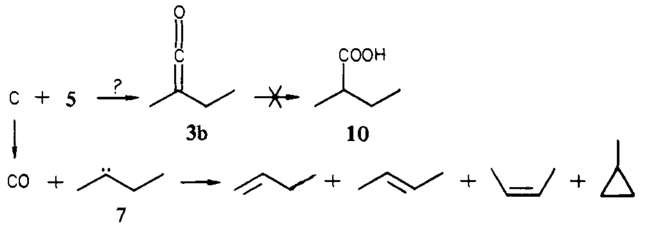
In the first place, all the available evidence suggests that carbon atoms, like singlet carbenes, undergo addition much more easily than insertion. One would therefore expect the mechanisms of eq 1 or 2 to be favored over that of eq 6.

If insertion nevertheless competes with addition, this should therefore imply that both reactions take place with exceptional ease, leading to low selectivity. Such a leveling is observed in the reactions of very reactive carbenes, e.g., in the case of singlet carbene (:CH_2) itself. Atomic carbon is, however, a very selective reagent. Thus it reacts with propane by insertion only at the CH bonds of the central methylene group and it reacts with **4** solely by addition to C=O rather than by CH insertion (Table I). Furthermore, insertion of carbenes into CH bonds formed by sp^2-hybridized carbon is usually less facile than insertion into CH bonds formed by sp^3-hybridized carbon, presumably because the former are stronger, and the difference should be accentuated in the case of -CHO by electron withdrawal by oxygen, atomic carbon acting apparently as an electrophilic reagent. It is true that the bond strength of aldehydic CH is low but this is only because breaking such bonds leads to unusually stable radicals (RCO). Their vibration frequencies indicate that they are in fact strong.

In agreement with these arguments, MNDO predicts insertion of carbon into the aldehydic CH of **4** to be a relatively high-energy process whereas addition to carbonyl requires no activation. Indeed, we were unable to find a transition state for insertion because of the ease with which any possible precursor collapsed to the adduct **3a**.

The two routes to **3a** might be distinguished by using isotopically labeled carbon atoms. However the Wolf rearrangement is known to take place with scrambling of the carbene and carbonyl carbon atoms, presumably by reversible cyclization of the intermediate carbenes to oxirenes.[19] Since similar rearrangements might occur in the case of the oxiranylidene intermediates postulated here, given that they should be formed with a very large amount of excess internal energy, it seemed very improbable that such a labeling experiment would lead to any unambiguous conclusions.

As an alternative, we studied the reactions of arc-generated carbon atoms with **5**, where the insertion mechanism of eq 6 is excluded. Here addition of water gave none of the acid (**10**) that would have been formed from the ketene **7**, the only products being carbon monoxide and a mixture of hydrocarbons derived from the carbene **3b**; see eq 5.[20]



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[19] Zeller, K. P.; Meier, H.; Kolshorn, H.; Muller, E. *Chem. Ber.* **1972**, *105*, 1875.

This result is, however, entirely consistent with our calculations, which, as we have pointed out, predict that it should be much harder to trap the ketene intermediate (**3b**) from **5** than that (**3a**) from **4**. The heat of formation of the transition state for dissociation of **3b** (into **7**) is lower by 7 kcal/mol than that for its formation from **2b**, whereas in the case of **3a**, both transition states are similar in energy. This difference is not unexpected because alkyl substituents stabilize carbenes. The conversion of **3b** to **7** should therefore be more facile than that of **3a** to **6**.

It would be of interest to try further trapping experiments under conditions where loss of thermal excitation might be expected to occur more readily than in our case. For example it should be possible to codeposit carbon atoms and **5** in a dilute argon matrix and then allow them to react by warming the matrix until it softens or melts.

Summary and Conclusions

The MNDO calculations reported here seem to suggest rather strongly that the deoxygenation of carbonyl compounds to carbenes by atomic carbon takes place by addition of carbon to the CO bond rather than by a direct electrophilic attack on oxygen, as has been commonly believed. The initial adduct, an oxiranylidene, rearranges to a ketene which undergoes decarbonylation by a "hot molecule" reaction, the necessary energy being provided by the extreme exothermicity of the two previous steps. When arc-generated carbon atoms reacted with cold butanal, the intermediate ketene could be identified in the products by hydration to butyric acid.

Experimental Section

Reaction of Chemically Generated Carbon Atoms with 4 and 5. 5-Diazotetrazole (**8**) was prepared as described previously,[17,18] and ~0.1 mmol was coated as a thin film on the walls of a 500-mL round-bottom flask. The flask was evacuated and 100 mm of gaseous carbonyl compound was admitted. The flask was closed and **8** was decomposed by immersing it in a 100 °C oil bath for 5 min. The flask was then opened on a vacuum line and the contents analyzed. The products were analyzed by pumping them through traps at −78 °C and −115 °C into a U-tube containing activated charcoal at −196 °C. The C_4 hydrocarbons, contained in the −115 °C trap, were analyzed by gas chromatography (GC) on a 20-ft 20% dimethylsulfolane (DMS) on a 40/60 firebrick column. The activated charcoal trap contained carbon monoxide which was analyzed by GC on a 16-ft 13× molecular sieve column.

Decomposition of **8** (~0.1 mmol) in the presence of an excess of **4** yielded carbon monoxide (3.1×10^{-2} mmol), 1-butene (7.2×10^{-4} mmol), methylcyclopropane (4.8×10^{-4} mmol), (*E*)-2-butene (1.05×10^{-4} mmol), and (*Z*)-2-butene (5.5×10^{-5} mmol). The pyrolysis of **8** (~0.1 mmol) in the presence of an excess of **5** yielded carbon monoxide (8.3×10^{-2} mmol), 1-butene (2.12×10^{-5} mmol), methylcyclopropane (1.6×10^{-4} mmol), (*E*)-2-butene (3.0×10^{-4} mmol), and (*Z*)-2-butene (1.61×10^{-4} mmol).

The above experiments were repeated, the flasks being immersed in liquid nitrogen immediately after pyrolysis. Transfer of either water or methanol to the cold flasks followed by warming to room temperature did not result in amounts of either esters or carboxylic acids detectable by mass spectrometry. Similar results were obtained upon decomposition of **8** in the presence of an excess of methanol and an excess of **4** or **5**.

Reaction of Arc-Generated Carbon with 4 or 5. Trapping of Ketene Intermediates. An apparatus, similar to that described by Skell and co-workers,[20] was used to generate carbon atoms. An intermittent arc was struck by passing a current of 100 A (AC) between two graphite electrodes. The carbonyl compound (**4** or **5**, 113 mmol) was introduced as a vapor and deposited on liquid N_2 cooled walls where it reacted with the carbon atoms. In a typical reaction, 0.5 g (41 mmol) of carbon was lost from the electrodes. However, some carbon was physically removed from the electrodes making a determination of the amount of carbon that was actually vaporized difficult. After the carbonyl compound had been added to the reaction, the arc was turned off and 10 mL of water was added. The reactor was warmed to room temperature and the volatile contents were pumped into traps at −78 °C and −196 °C. The reactor was opened, 10 mL of 5% $NaHCO_3$ was added, and the resultant solution was washed with ether. The $NaHCO_3$ solution was acidified with HCl and extracted with ether. In the case of **4**, evaporation of the ether yielded pentanoic acid (1.35×10^{-2} mmol by NMR), identified by comparing its spectral properties with those of an authentic sample. Analysis of the contents of the −196 °C trap by GLC showed that the yield of 1-butene in this experiment was 3.92×10^{-2} mmol.

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Thermal Rearrangements of Propargylic Trichloroacetimidates. Synthesis of (Trichloroacetamido)-1,3-dienes and -1,2-dienes

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Abstract: A new method for preparing (acylamino)-1,3-dienes is reported (Scheme I). Propargylic alcohols are condensed with trichloroacetonitrile to yield trichloroacetimidates **1**, which rearrange upon solution thermolysis to afford, depending on the structure of **1**, 1-(trichloroacetamido)-1,3-dienes (**3**), 2-(trichloroacetamido)-1,3-dienes (**4**), or 1-(trichloroacetamido)-1,2-dienes (**2**). The preparation of twelve 1-(trichloroacetamido)-1,3-dienes (Table I), three 2-(trichloroacetamido)-1,3-dienes, and five 1-(trichloroacetamido)-1,2-dienes is reported. Overall yields of 1,3-dienes from the starting propargylic alcohols range from 12 to 80%. More highly substituted 1,3-dienes are obtained in higher yields. The rearrangement is highly stereoselective and affords exclusively the (1*Z*,3*E*)-1-(trichloroacetamido)-1,3-diene isomer. In some cases the corresponding (1*E*,3*E*)-1-(trichloroacetamido)-1,3-diene could be prepared by base-catalyzed equilibration of the kinetic isomer. Several experiments which define important energetic and mechanistic details of isomer interconversions in this series are described, and a detailed mechanism for the thermal conversion of a propargylic trichloroacetimidate to a (trichloroacetamido)-1,3-diene is proposed (Scheme III).

Recent studies in our laboratory have demonstrated that the thermal [3,3]-sigmatropic rearrangement of allylic trichloroacetimidates is a superior method for the 1,3-transposition of alcohol and amine functionality (eq 1).[2,3] In order to further

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