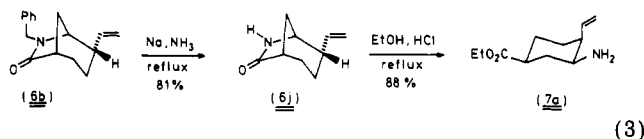


of the carbon adjacent to nitrogen is lost on forming the planar *N*-acyliminium ion. The allylsilanes **5c** and **5f** were prepared from the corresponding propargylsilanes in excellent yields by using the partial hydrogenation procedure of Brown.¹²

The products⁵ of the cyclization experiments are shown in the last column of Table I. Comparison of entries 1 and 3 reveals the favorable effect of silicon in the *N*-acyliminium ion cyclization reaction.¹³ Whereas **5a** yielded only the product of ethanol elimination **8a** on treatment with CF₃CO₂H in CH₂Cl₂, **5c** afforded a good yield of cyclization products **6bc**, along with a slight amount of **8b**, resulting from protodesilylation and ethanol elimination. In general, formic acid appeared to be a better medium for cyclization, since the amount of elimination was reduced (entries 1 and 3). In the cyclization of **5a** with formic acid there was obtained, in addition to 50% of **8a**, a complex mixture of three rather unstable products (possibly resulting from ring closure) which was not further investigated. Cyclization of the other allylsilanes (entries 4 and 6) induced by Brønsted acid proceeded in good to excellent yields, leading to bicyclic amides with a vinyl substituent. The stereochemistry of the vinyl isomers (**6bc**, **6de**, **6gh**) was determined by using difference NOE in ¹H NMR spectroscopy. Cyclization of propargylsilanes (entries 2, 5, and 7) effected by Brønsted acid led to 1,1-disubstituted allenes in excellent yields except in the case of **5g**, where protodesilylation was probably faster than closure of the eight-membered ring. However, 1.5 equiv of SnCl₄ in CH₂Cl₂^{13d} did cause the desired ring closure to yield **6i**. In future experiments we will further explore this Lewis acid mediated procedure.

Our results indicate that **1a-c** are well suited as dipolar synthons for a general approach to various bicyclic nitrogen compounds.¹⁴ The vinyl and vinylidene substituents lend themselves for further manipulations. Starting materials **1** and **4** containing more functionality are easily available, which then may lead to more heavily substituted azabicycles. The presence of silicon appears to be crucial to the method in terms of yield and regiocontrol.

The cyclization products can readily be converted into amino acid derivatives as is shown in eq 3. Removal of



the *N*-benzyl group from **6b** with sodium in refluxing ammonia¹⁵ afforded a lactam **6j**, which underwent ring opening to the carbocyclic amino acid ester **7a** in refluxing acidic ethanol. γ -Amino acids are interesting compounds for neurochemical research, as they are analogues of the

(13) For reactions of *N*-acyliminium ions with allyl- and propargylsilanes, see: (a) Hiemstra H.; Speckamp, W. N. *Tetrahedron Lett.* 1983, 24, 1407. (b) Hart, D. J.; Tsai, Y.-N. *Ibid.* 1981, 22, 1567. (c) Aratani, M.; Sawada, K.; Hashimoto, M. *Ibid.* 1982, 23, 3921. (d) Kraus, G. A.; Neuenschwander, K. *J. Chem. Soc., Chem. Commun.* 1982, 134.

(14) Many methods are known for the synthesis of the 6-azabicyclo[3.2.1]octane skeleton **6a-c**; see, e.g.: Bonjoch, J.; Mestre, E.; Cortes, R.; Granados, R.; Bosch, J. *Tetrahedron* 1983, 39, 1723. Krow, G. R.; Shaw, D. A.; Jovais, C. S. *Synth. Commun.* 1983, 13, 575. The other bicyclic systems have incidentally been prepared by specialized methods. For 7-azabicyclo[4.2.1]nonanes **6d,e**, see, e.g.: Kawashima, K.; Agata, I. *Yakugaku Zasshi* 1969, 89, 1426; *Chem. Abstr.* 1970, 72, 21571p. Moriconi, E. J.; Hummel, C. F. *J. Org. Chem.* 1976, 41, 3583. For 6-azabicyclo[3.2.2]nonanes **6f-h**, see, e.g.: Mackiewicz, P.; Furstoss, R.; Waegell, B.; Cote, R.; Lessard, J. *Ibid.* 1978, 43, 3746, 3750. For 7-azabicyclo[4.2.2]decanes **6i**, see, e.g.: Wegener, P. *Tetrahedron Lett.* 1967, 4985. Paquette, L. A.; Barton, T. J. *J. Am. Chem. Soc.* 1967, 89, 5480.

(15) Sugawara, S.; Fujii, T. *Chem. Pharm. Bull.* 1958, 6, 587; *Chem. Abstr.* 1960, 54, 14242b.

inhibitory neurotransmitter GABA.¹⁶

Acknowledgment. We thank Mr. C. Kruk for providing the 250-MHz ¹H NMR spectra, in particular the NOE difference spectra.

(16) Allan, R. D.; Johnston, G. A. R. *Med. Res. Rev.* 1983, 3, 91. Krogsgaard-Larsen, P.; Brehm, L.; Schaumburg, K. *Acta Chem. Scand., Ser. B.* 1981, B35, 311.

(17) Some spectral data are as follows. **6a**: IR (CHCl₃) 1665, 1680 cm⁻¹; ¹H NMR (CDCl₃, 100 MHz) δ 7.33 (m, Ph), 4.94 (d, *J* = 15 Hz, CHPh), 4.70 (m, C=CH₂), 3.92 (d, *J* = 6 Hz, NCH), 3.88 (d, *J* = 15 Hz, CHPh), 2.62 (m, COCH), 1.45-2.47 (m, 6 H). **6b**: IR (CHCl₃) 1675 cm⁻¹; ¹H NMR (CDCl₃, 250 MHz) δ 7.30 (m, Ph), 5.66-6.07 (m, CH=CH₂), 5.17 (d, *J* = 15 Hz, CHPh), 4.91-5.31 (m, HC=CH₂), 3.91 (d, *J* = 15 Hz, CHPh); 3.54 (d, *J* = 6 Hz, NCH), 2.56 (m, COCH), 1.35-2.47 (m, 7 H); ¹³C NMR (CDCl₃, 63 MHz) δ 175.3 (s), 140.4 (d), 136.3 (s), 127.6 (d), 127.0 (d), 126.4 (d), 113.7 (t), 58.0 (d), 44.6 (t), 41.1 (d), 39.6 (d), 37.6 (t), 24.2 (t), 23.1 (t). **6d**: IR (CHCl₃) 1665 cm⁻¹; ¹H NMR (CDCl₃, 250 MHz) δ 7.32 (m, Ph), 5.49-5.90 (m, CH=CH₂), 4.85-5.18 (m, CH=CH₂), 5.04 (d, *J* = 15 Hz, CHPh), 3.96 (d, *J* = 15 Hz, CHPh), 3.49 (dd, *J* = 7, 1.5 Hz, NCH), 1.16-2.77 (m, 10 H); ¹³C NMR (CDCl₃, 25 MHz) δ 176.9 (s), 139.5 (d), 136.4 (s), 128.3 (d), 127.8 (d), 127.2 (d), 114.6 (t), 60.1 (d), 43.5 (t), 42.0 (d), 41.2 (d), 31.7 (t), 29.7 (t), 26.5 (t), 21.7 (t). **6f**: IR (CHCl₃) 1955, 1640 cm⁻¹; ¹H NMR (CDCl₃, 100 MHz) δ 7.33 (m, Ph), 5.15 (d, *J* = 15 Hz, CHPh), 4.62 (m, C=CH₂), 4.11 (d, *J* = 15 Hz, CHPh), 3.98 (m, NCH), 2.88 (m, COCH), 1.56-2.70 (m, 8 H). **6g**: IR (CHCl₃) 1635 cm⁻¹. **6i**: IR (CHCl₃) 1955, 1630 cm⁻¹; ¹H NMR (CDCl₃, 100 MHz) δ 7.32 (m, Ph), 5.40 (d, *J* = 15 Hz, CHPh), 4.62 (m, C=CH₂), 4.08 (m, NCH), 3.78 (d, *J* = 15 Hz, CHPh), 2.92 (m, COCH), 1.10-2.50 (m, 10 H). **7a**: IR (CHCl₃) 3365, 1725 cm⁻¹; ¹H NMR (CDCl₃, 100 MHz) δ 5.80-6.21 (m, HC=CH₂), 5.04-5.30 (m, HC=CH₂), 4.14 (q, *J* = 7 Hz, OCH₂CH₃), 2.84 (dt, *J* = 11, 4 Hz, HCNH₂), 2.23-2.60 (m, HCCO₂Et, HCCH=CH₂), 1.34-2.02 (m, 6 H), 1.28 (s, NH₂), 1.26 (t, *J* = 7 Hz, OCH₂CH₃).

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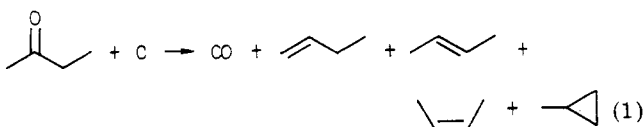
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Received December 2, 1983

Intramolecular Trapping of an Intermediate in the Deoxygenation of a Carbonyl Compound by Atomic Carbon

Summary: Deoxygenation of 2,3-butanedione by atomic carbon generates acetylenylidene, CO, CO₂, 2-butyne, and 1,2-butadiene.

Sir: The high energy of atomic carbon renders many otherwise difficult reaction pathways accessible.¹ An interesting example is the deoxygenation of carbonyl compounds, which generates carbon monoxide and a carbene. Thus, 2-butanone is deoxygenated to the products in eq 1.^{2,3}



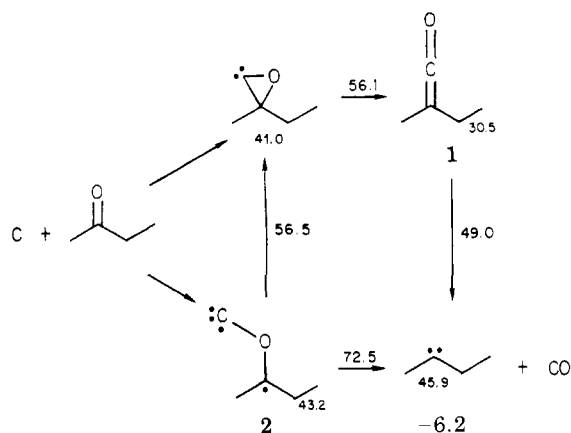
We have recently used MNDO calculations to investigate the reaction coordinate for the deoxygenation of 2-

(1) For recent reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel, J. J.; McGlinchey, M. J. *Acc. Chem. Res.* 1973, 6, 97-105. (b) MacKay, C. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol II, pp 1-42. (c) Shevlin, P. B. "In Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1-36.

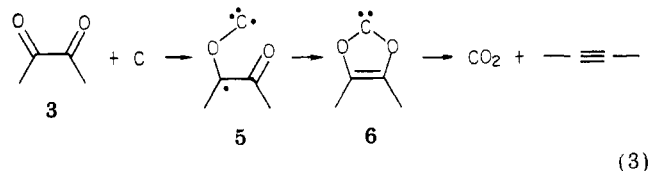
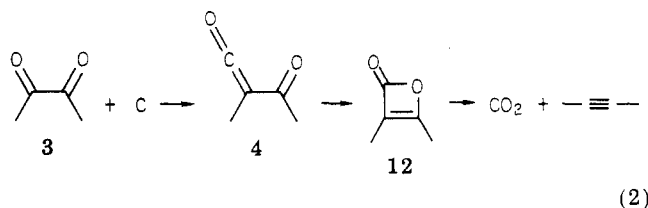
(2) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* 1970, 92, 836.

(3) Dewar, M. J. S.; Nelson, D. J.; Shevlin, P. B.; Biesiada, K. A. *J. Am. Chem. Soc.* 1981, 103, 2802.

Scheme I



butanone and have calculated the heats of formation for the intermediates and transition states (in kcal/mol) shown in Scheme I.³ These computations indicate that a route to the carbene involving loss of CO from a ketene intermediate, 1, may be competitive with direct loss of CO from an ylide-like species, 2. Although the calculations may not be sufficiently accurate to choose between reaction pathways, it is interesting that both 1 and 2 are predicted to lie in substantial energy wells and are potentially trapable. The design of an appropriate intramolecular trap for a species as reactive as carbon presents problems as there is always the chance that C will react preferentially with the trap. In order to avoid this difficulty, we have chosen as our trap a second carbonyl group equivalent to the first and have studied the reaction of carbon atoms with the α -diketone 2,3-butanedione, 3. In this case, the second carbonyl group may act as a trap for either ketene 4, as shown in eq 2 or ylide 5 (eq 3). Both of these pro-



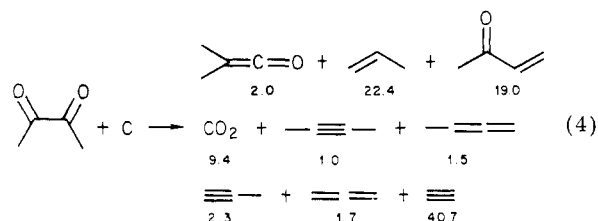
cesses appear likely to result in a dideoxylation with formation of CO₂ and possibly 2-butyne. Borden, Concannon, and Phillips have demonstrated the loss of CO₂ from the saturated analogue of carbene 6,⁴ and cycloaddition reactions between ketenes and carbonyl compounds to give lactones have been reported.⁵

When arc-generated carbon vapor, produced in an apparatus similar to that described by Skell and co-workers,⁶ was cocondensed with 3 at -196 °C, the products shown in eq 4, along with their relative yields, were detected. Carbon monoxide is not included in eq 4 as it was not condensable at -196 °C under the rapid pumping conditions of the reaction. However, when carbon atoms from

(4) Borden, W. T.; Concannon, P. W.; Phillips, D. I.; *Tetrahedron Lett.* **1973**, 3161.

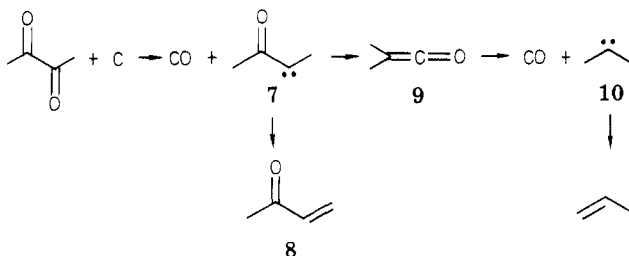
(5) Zaugg, H. E. *Org. React. (N.Y.)* **1954**, *8*, 305.

(6) Skell, P. S.; Wescott, L.; Jr.; Goldstein, J.-P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.



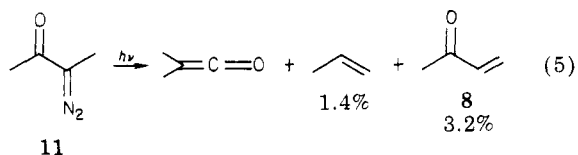
the decomposition of 5-diazotetrazole⁷ were reacted with 3 under static conditions, carbon monoxide was one of the major products.

This deoxygenation to generate CO is analogous to the deoxygenation of 2-butanone and is expected to generate acetylenylidene, 7. A 1,2-hydrogen migration in carbene



7 generates methyl vinyl ketene, 8, while a Wolff rearrangement will produce dimethylketene, 9. The formation of 9 in the carbon atom deoxygenation is expected to be extremely exothermic. This exothermicity will be channelled into the decomposition of the ketene to carbon monoxide and 2-propylidene, 10. Carbene 10 then rearranges to propene, a major product.

Both propene and methyl vinyl ketene have been observed when carbene 7 is generated in the gas or liquid phase by the photolysis of 3-diazo-2-butanone, 11.⁸ In order to determine if carbene 7 will behave similarly when generated in the condensed phase at -196 °C, we have slowly condensed 11 at -196 °C while photolyzing it under dynamic vacuum. The products of this reaction, shown in eq 5 along with their percent yields, are similar to those



observed in the reaction of carbon with 3 but in different ratios. The ratio of dimethylketene to propene is much greater in the condensed-phase photolysis than in carbon atom deoxygenation. This is due to the fact that photolysis generates the ketene with much less excess energy than in the extremely exothermic carbon atom deoxygenation. Thus, the ketene is formed with enough energy to lose CO in the carbon atom reaction but not in the photolysis.

The ratio of Wolff rearrangement products (9 + propene) to 1,2-hydrogen shift product 8 is also greater in the photolysis of the diazoketone than in the carbon atom deoxygenation. While there may be several causes for this difference, a major factor is the fact that excited diazoketone may also undergo the Wolff rearrangement.⁹

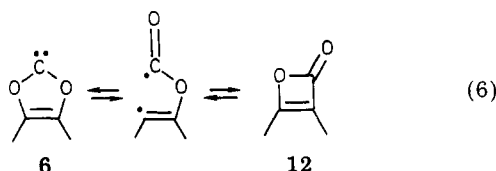
The fact that both carbon dioxide and 2-butyne are generated in the reaction of carbon with 3 indicates that the reaction(s) shown in eq 2 and/or 3 do take place. It is not possible to distinguish between the processes in eq

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

(8) Fenwick, J.; Frater, G.; Ogi, K.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 124.

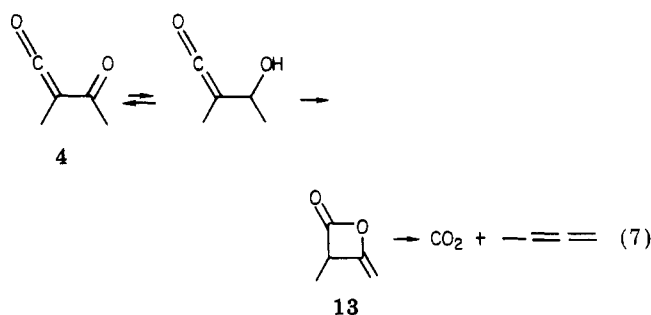
(9) Tomioka, H.; Okuno, H.; Izawa, Y. *J. Org. Chem.* **1980**, *45*, 5278.

2 and 3 for the formation of the 2-butyne. This system is complicated by the fact that 5 could convert to 4 by the pathway in Scheme I and that interconversion of the di-oxalenyldiene, 6, and the unsaturated lactone 12 is possible via the sequence in eq 6. The formation of 6 in a single

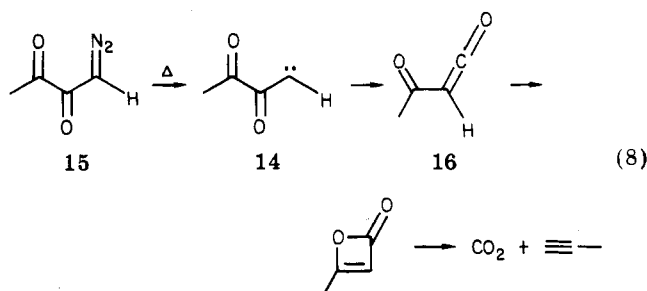


step by the reaction of C with 3 appears unlikely as very little of 3 is expected to be in the cisoid conformation.¹⁰

Since the product ratios in eq 4 demonstrate that considerably more CO₂ than 2-butyne is formed, there must be additional cleavage products corresponding to the CO₂. An obvious candidate is an isomer of 2-butyne, 1,2-butadiene, which could arise from cleavage of 13 (eq 7) or by stepwise bond rupture of one of the intermediates in eq 2 and 3.



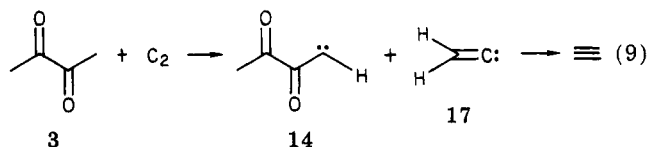
In order to test the possibility that a keto ketene will undergo an intramolecular cyclization of the type shown in eq 2 under the reaction conditions, we have generated pyruvylmethylidene, 14, by pyrolysis of the corresponding diazo compound 15 at 250 °C.¹¹ When 15 (12.2 mmol) is pyrolyzed and the products condensed at -196 °C under dynamic vacuum, both CO₂ (2.2 mmol) and propyne (2.9 mmol) are generated. Wolff rearrangement of carbene 14 (or its precursor) is expected to generate keto ketene 16. Cyclization of this species to an unsaturated lactone is followed by cleavage to CO₂ and propyne as shown in eq 8.



This result demonstrates that cyclization of keto ketenes and subsequent loss of CO₂ is possible under the conditions of the carbon atom reaction and nicely rationalizes the formation of 2-butyne and CO₂ in the deoxygenation of 3.

The reaction in eq 8 also serves to explain the formation of propyne and the additional CO₂ in the reaction of

carbon vapor with 3. Skell and Plonka have demonstrated that C₂, a species always generated in the carbon arc, can abstract two hydrogens from the same carbon to generate a carbene and ethenylidene, 17.¹² An analogous process, involving abstraction of two hydrogens from the 1-carbon of 3, would generate 14 and 17 (eq 9). Carbene 14 then reacts as shown in eq 8 to generate CO₂ and propyne.



These investigations demonstrate that the removal of two oxygens from an α,β-diketone by atomic carbon is competitive with monodeoxygenation and that the second carbonyl group most probably serves as a trap for an intermediate in the deoxygenation of carbonyl compounds by atomic carbon.

Acknowledgment. Financial support by the National Science Foundation under Grant CHE-8103034 is gratefully acknowledged.

(12) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* 1970, 92, 5620.

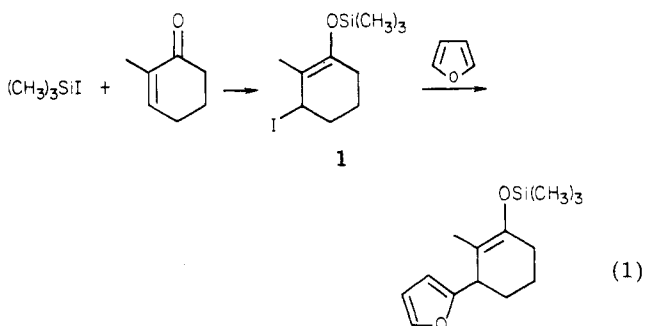
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Received December 20, 1983

Iodotrimethylsilane-Mediated Additions of Dienol Silyl Ethers to α,β-Unsaturated Ketones

Summary: (Trimethylsilyl)oxy-substituted dienes react with 1 at low temperatures to afford annulated products.

Sir: While examining methods for the construction of the quassinoid diterpenes, we recently discovered a direct and mild method (eq 1) for the conjugate addition of furans



and enol silyl ethers to enones.¹ Notably the reaction produced a regioselective enol silyl ether. In the course of studying the scope of this novel reaction, we encountered the transformation depicted in eq 2. We believe that the allylic carbocation generated by the reaction of the dienol silyl ether with 1 is intramolecularly trapped to produce 3. As evidenced by the entries in Table I, the trapping step is surprisingly stereoselective. Analysis of molecular models suggests that nonbonded interactions between R (in 2) and the methyl group attached to the enol silyl ether

(10) (a) Durig, J. R.; Hannum, S. E.; Brown, S. C. *J. Phys. Chem.* 1971, 75, 1946. (b) Danielson, D. D.; Hedberg, K. *J. Am. Chem. Soc.* 1979, 101, 3730. (c) Tyrrell, J. *Ibid.* 1979, 101, 3766.

(11) The diazo compound was prepared by the reaction of diazo-methane with pyruvyl chloride by a procedure adapted from ref 8.

(1) Kraus, G. A.; Gottschalk, P. *Tetrahedron Lett.* 1983, 24, 2727.