= 15, 6, 1 Hz). Anal. Found: C, 63.59; H, 9.13; N, 8.59.

11a: IR (film) 2030, 2080 (br) cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H), 1.1-1.7 (m, 8 H), 2.27 (t, 2 H, J = 7 Hz), 4.79 (br s, 1 H), 4.92 (s, 1 H). Anal. Calcd for $C_9H_{15}NS$: C, 63.85; H, 8.93; N, 8.27. Found: C, 63.38; H, 8.97; N, 8.42.

11b: ^{1}H NMR δ 5.27 (d, 1 H, J = 1 Hz), 5.53 (d, 1 H, J = 1 Hz), 7.1-7.6 (m, 5 H).

11c: IR (film) 2070-2130 (br) cm^{-1}; ^{1}H NMR δ 1.04 (s, 9 H), 5.86 (s, 2 H); ^{13}C NMR δ 29.1 (q), 32.5 (s), 113.3 (d), 132.3 (s, N=C=S), 144.0 (d). Anal. Calcd for $C_7H_{11}NS$: C, 59.53; H, 7.85; N, 9.92. Found: C, 59.64; H, 8.07; N, 9.91.

Registry No. **1**, 87656-40-4; **2**, 87656-41-5; **3**, 87656-42-6; **4**, 87656-43-7; **5**, 87656-44-8; **6** (isomer 1), 87656-45-9; **6** (isomer 2), 87726-15-6; *threo*-**7**, 87656-46-0; *erythro*-**7**, 87656-47-1; **8a**, 87656-48-2; **8b**, 78386-96-6; **8c**, 87656-49-3; **8d**, 87656-50-6; **9a**, 87656-51-7; **9b**, 71055-61-3; **9c**, 87656-52-8; **9d**, 87656-53-9; (*Z*)-**9e**, 87656-54-0; (*Z*)-**9f**, 87656-55-1; (*E*)-**9f**, 77425-32-2; **10a**, 52566-12-8; **10b**, 2696-79-9; **10c**, 87656-56-2; **10d**, 87656-57-3; (*E*)-**10e**, 87656-58-4; (*E*)-**10f**, 87656-59-5; **11a**, 87656-60-8; **11b**, 87656-61-9; (*E*)-**11c**, 87656-62-0; cyclohexene, 110-83-8; cyclopentene, 142-29-0; cycloheptene, 628-92-2; cyclooctene, 931-88-4; (*Z*)-cyclododecene, 1129-89-1; (*E*)-cyclododecene, 1486-75-5; *cis*-4-octene, 7642-15-1; *trans*-4-octene, 14850-23-8; 1-octene, 111-66-0; styrene, 100-42-5; 3,3-dimethyl-1-butene, 558-37-2; phenylseleneyl chloride, 5707-04-0; mercuric thiocyanate, 592-85-8.

Intramolecular Carbon-Hydrogen Insertions of Alkylidenecarbenes. 1. Selectivity

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Base-promoted reaction between dialkyl ketones having γ-hydrogens and dialkyl (diazomethyl)phosphonates leads to formation of cyclopentenes in modest to high yields. The relative reactivity of various types of carbon-hydrogen bonds for the process, which involves insertion by an alkylidenecarbene, has been assessed, and the result has been compared to those reported when the carbene is generated by α elimination and by 1,2-shifts. The comparison suggests that a common species, viz., an alkylidenecarbene, may be responsible for formation of the cyclopentenes obtained from (a) flash vacuum pyrolysis of alkynes and (b) decomposition of diazoethenes, whereas that derived from α elimination of terminal vinyl halides is more selective, a result consonant with production of a carbenoid.

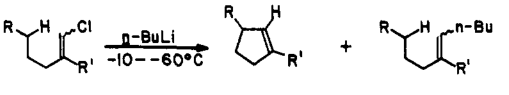
Recent years have witnessed a burgeoning interest in the generation and chemistry of unsaturated carbenes **1**.[2]

$$R_2C{=}({=}C{=})_n{=}C$$

1

These species undergo many of the same types of reactions as do their saturated relatives[3] among which is insertion into various types of σ bonds.[4,5] The present paper is concerned with the intramolecular insertion of alkylidenecarbenes **1** (n = 0) into carbon-hydrogen bonds.

Several previous studies of such an intramolecular reaction have been reported. Koebrich et al. in a brief communication noted that α elimination of terminal vinyl chlorides with n-butyllithium at -10 to -60 °C afforded cyclopentenes, accompanied by coupling products, in "good" yields (eq 1) and cited unpublished work showing that insertion occurs exclusively at C-5.[5c] Similarly, Wolinsky et al. found that base-promoted α elimination of vinyl bromides at 240 °C gave cyclopentenes (in yields ranging from 13% to 58%) along with alkynes and, in some cases, methylenecyclopropanes (eq 2).[5a,e] They were unable to detect products of insertion into the carbon-hydrogen bonds at C-4 or C-6, however.[6] This result reinforces the conclusion drawn from the earlier work[5d] that a considerable kinetic preference exists for reaction by way of a six-centered transition state. By assuming that the ratios of cyclopentenes to alkynes formed in their reactions were a reflection of the relative reactivities of the carbon-hydrogen bonds at C-5 toward insertion, Wolinsky et al. found the trend to be tertiary > secondary (benzylic) > secondary ≫ primary.[5e] Finally, Brown et al.[5d,f] and Dreiding et al.[5g,i,j] have made the remarkable observation



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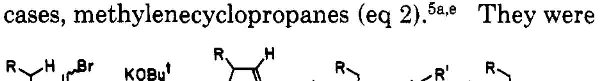

(2)

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[1] This work taken in part from the dissertations of U.W. and D.H.G., submitted in partial fulfillment of requirements for the Ph.D. degree, University of Texas at Austin, 1980 and 1981.

[2] Reviews: (a) Hartzler, H. D. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol II, Chapter 2. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (c) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.

[3] Reviews: (a) Gilcrist, T. L.; Rees, C. W. "Carbenes, Nitrenes and Arynes"; Appleton-Century Crofts, Inc.: New York, 1969. (b) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (c) Jones, M., Jr.; Moss, R. A., Eds. "Carbenes"; Wiley-Interscience: New York, 1973; Vol. I. (d) Barton, D. H. R.; Ollis, W. D. "Comprehensive Organic Chemistry"; Pergamon Press: New York, 1979; Vol. 2.

[4] Intermolecular: (a) Sakakibara, T.; Odaira, Y.; Tsutsumi, S. *Tetrahedron Lett.* **1968**, 503. (b) Newman, M. S.; Okorodudu, A. O. M. *J. Org. Chem.* **1969**, *34*, 1220. (c) Newman, M. S.; Beard, C. D. *J. Am. Chem. Soc.* **1970**, *92*, 4309. (d) Newman, M. S.; Patrick, T. B. *Ibid.* **1970**, *92*, 4312. (e) Gilbert, J. C.; Butler, J. R. *Ibid.* **1970**, *92*, 7607. (f) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *Ibid.* **1974**, *96*, 4562. (g) Gilbert, J. C.; Weerasooriya, U. *Tetrahedron Lett.* **1980**, *21*, 2041. (h) Gilbert, J. C.; Weerasooriya, U.; Wiechman, B.; Ho, L. *Ibid.* **1980**, *21*, 5003. (i) Stang, P. J.; Christensen, S. B. *J. Org. Chem.* 1981, *46*, 823. (j) Gilbert, J. C.; Weerasooriya, U. *Ibid.* **1983**, *48*, 448.

[5] Intramolecular: (a) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1143. (b) Walsh, R. A.; Bottini, A. T. *J. Org. Chem.* **1970**, *35*, 1086. (c) Fisher, R. H.; Baumann, M.; Koebrich, G. *Tetrahedron Lett.* **1974**, 1207. (d) Brown, F. C.; Eastwood, R. W.; Harrington, K. J.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2393. (e) Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* **1976**, *41*, 745. (f) Brown, R. F. C.; Eastwood, F. W.; Jackman, G. P. *Aust. J. Chem.* **1977**, *30*, 1757. (g) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 852. (h) Gilbert, J. C.; Weerasooriya, U.; Giamalva, D. *Tetrahedron Lett.* **1979**, 4619. (i) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1981**, *64*, 1123. (j) Karpf, M.; Huguet, J.; Dreiding, A. S. *Ibid.* **1982**, *65*, 13. (k) Hauske, J. R.; Guadliana, M.; Desai, K. *J. Org. Chem.* **1982**, *47*, 5019.

[6] The methylenecyclopropanes are believed[5e] to be formed by an addition-isomerization sequence rather than by insertion into the C-H bond at C-3.

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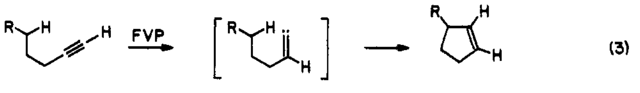
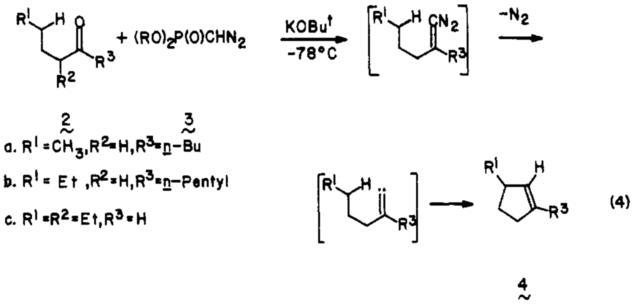
that cyclopentenes are produced in yields of up to 66% by flash vacuum pyrolysis of alkynes (eq 3). The mechanism of the reaction is ill-defined, but it is believed to involve an initial isomerization of the alkyne to an alkylidenecarbene, a rearrangement that is calculated to be endothermic by some 40 kcal/mol for the vinylidene–acetylene pair;[7] insertion then follows. The Swiss group of investigators found a preference for insertion into C–H bonds of higher degree, just as did Wolinsky et al., and provided data that suggest that the transition state for ring formation has a coplanar geometry of the five key carbon atoms.[5g]



The purpose of the present work was to investigate the nature of the intramolecular insertion process when diazoethenes are used as the precursors to the alkylidenecarbenes (eq 4).[9] It was anticipated that this method would permit study of the insertion reaction under conditions more mild than those previously reported.



Results and Discussion

The results of experiments to define the general course of base-promoted reaction between carbonyl compounds **2** having hydrogen atoms at the γ-position and dimethyl (or diethyl) (diazomethyl)phosphonate (DAMP, **3**, eq 4) are contained in Table I. It is seen (entries 1 and 2) that cyclopentenes are formed in modest yields when near-equimolar quantities of DAMP and a ketone are allowed to react. The result shown in entry 3 illustrates that yields are increased when an excess of DAMP is used, an outcome that is consistent with our belief that low conversions of ketones in this type of reaction are due to unproductive consumption of the DAMP rather than of the ketones.[4j] The data of entries 4 and 5, in combination with those of entry 1, demonstrate that the transformation of the ketone to the cyclopentene **4a** is indeed occurring at −78 °C. Formation of the enol ether **5** would have been expected under the reaction conditions of entry 5 if this were not true, but this ether could not, in fact, be detected by ^{1}H NMR and GLC analysis of the crude reaction mixture. Moreover, the results of entries 4 and 6 show that the intramolecular insertion cannot compete with either intermolecular trapping by protic solvents or with an intramolecular 1,2-shift of hydrogen. The latter is hardly surprising in view of the earlier reports that intramolecular insertion of alkylidenecarbenes is noncompetitive with 1,2 aryl migration[5e] and that the migratory aptitude of hydrogen in shifts of this sort is much greater than that of the aryl group, at least with saturated analogues.[10,11]

$(n\text{-Bu})_2C{=}CHOMe$ $CH_3(CH_2)_3CH(Et)C{\equiv}CH$

5 **6**

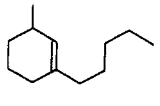


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Table I. Reactions of Ketones 2 with Dialkyl (Diazomethyl)phosphonate (3)

entry[a]	substrate	product	yield,[b] %
1	2a	4a[c]	33
2	2b	4b[d]	36
3[e]	2a	4a	51
4[f]	2a	5[g]	20
5[h]	2a	4a	33
6	2c	6[i]	79

[a] Unless otherwise noted, all reactions were performed for 2 h at −78 °C in anhydrous THF as the solvent and with a ratio of 1.0:1.1 of 2/3. [b] Reactions were not optimized. [c] Identified by comparison of spectral data to those published.[5e] [d] See text for a discussion of the assignment of the structure. [e] The ratio of 2a/3 used was 1.0:3.0; the yield is based on consumption of 2a. [f] Anhydrous methanol was used as the solvent, and the reaction was terminated after 10 h. [g] See the Experimental Section for structural data. [h] After 22 h, the reaction was quenched at −78 °C by addition of anhydrous methanol. [i] See ref 9 for proof of the structure.

The site selectivity with regard to insertion at C-5 vs. C-6 of the alkylidenecarbene was qualitatively assessed by examination of the crude reaction mixture obtained from **2b** (entry 2) for the presence of 3-methyl-1-(1-pentyl)cyclohexene (**7**). Had any insertion occurred to give **7**, the ^{1}H NMR spectrum of the reaction mixture should have exhibited resonances in the region of δ 1.6 for the four nonallylic cyclohexyl hydrogens, as is the case in 1-ethylcyclohexene;[12] these resonances were not observed. Moreover, the mass spectrum of the mixture did *not* contain an M − 15 peak. Such a fragmentation, signifying the loss of a methyl group, would have been expected were the cyclohexene **7** present as cleavage of allylic carbon–carbon bonds is an extremely efficient process in the mass spectra of these cycloalkenes.[13] The data suggest the absence of **7** in the product mixture. Judging from the integration of the ^{1}H NMR spectrum, the selectivity is estimated to be at least 10:1 in favor of insertion at C-5, a result in accord with the reports mentioned earlier.[5c,e,g,j] This preference likely has its origin in the enthalpic and entropic factors that favor six- vs. seven-membered cyclic transition states.[14]

The selectivity of the insertion into various types of C–H bonds was measured by analyzing the cyclopentenes

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(7) Ab initio techniques predict a heat of reaction of 40 kcal/mol,[8] whereas an SCF approach (MINDO/3) predicts 46 kcal/mol (Gilbert, J. C., unpublished results).

(8) Dykstra, C. E.; Schaefer, H. F. III. *J. Am. Chem. Soc.* **1978**, *100*, 1378.

(9) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *42*, 1837.

(10) Su, D. T. T.; Thornton, E. R. *J. Am. Chem. Soc.* **1978**, *100*, 1872.

(11) The migratory aptitudes of aryl and hydrogen appear to be comparable in cases where the alkylidenecarbene is generated by flash vacuum pyrolysis.[5d,f] However, preliminary data obtained in our laboratories show hydrogen to migrate exclusively, relative to either phenyl or *p*-anisyl, when the carbene is generated at −78 °C (Baze, M. E., unpublished results).

(12) "The Sadtler Standard Spectra"; Sadtler Research Laboratories: Philadelphia, PA, 1980; ^{1}H NMR, Spectrum No. 8185.

(13) Budzikiewicz, H.; Brauman, J. I.; Djerassi, C. *Tetrahedron* **1965**, *21*, 1855.

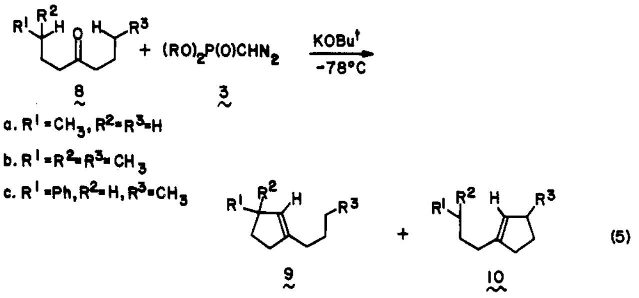
(14) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

Table II. Selectivity of C-H Insertion Reaction

		$\Delta\Delta G^{\ddagger}$,[b] kcal/mol				
reagent	relative rates[a]	primary	secondary (benzylic)	tertiary	temp, K	ref
RC(O)C=CR′	0.05:1.0:-:2.0	>5.4		−1.3	913	5j
R_2C—CHBr	>0.033:1.0:2.5:7.9[c]	>3.6	−0.93	−2.1	513	5e
$R_2C=CN_2$	>0.0030:1.0:7.5:18.6	>2.3	−0.78	−1.1	195	this work

[a] Ratios are primary/secondary (aliphatic)/secondary (benzylic)/tertiary; statistically corrected values. [b] These values are relative to insertion in a secondary aliphatic C–H bond. [c] Two values for the ratio of secondary C–H insertion/rearrangement, viz.; 0.28 and 0.33, are given in ref 5e. The average of these has been used in our calculations.

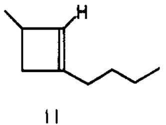
formed by treatment of unsymmetrically substituted dialkyl ketones with DAMP (**3**, eq 5). The composition of



(5)

the product mixture was determined with the aid of GCMS, and structural assignments were made by use of spectroscopic techniques, as described below.

The competition between a primary and a secondary aliphatic C–H bond was studied by use of 4-octanone (**8a**). A single product, formed in 22% yield (uncorrected for unchanged ketone), accounted for 96.6% of the volatile hydrocarbons. This was assigned as 3-methyl-1-propylcyclopentene (**9a**), a previously unknown alkene, on the basis of its spectral data (see Experimental Section). Briefly, the logic behind the assignment is as follows. The product is a cyclic monoalkene as evidenced by its molecular formula and the observation of two, and only two, resonances in the ^{13}C NMR spectrum having chemical shifts expected for sp^2-hybridized carbon atoms.[15] Consequently, acyclic dienes and alkynes[16] need not be considered as possibilities. Given that the ^1H NMR spectrum exhibits a methyl doublet, the cycloalkenes that are possible are limited to **9a** and the cyclobutene **11**. The latter



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can be eliminated because resonances for its vinylic hydrogen and carbon atoms would be at lower fields than those observed.[15] In contrast, **9a** is consistent with the data. Among other things, this isomer should have its double bond stretching vibration near 1650 cm^{-1} [17] and is calculated[15] to have its vinylic carbon atoms at δ 145.3 (C-1) and 126.8, values that are acceptably close to those observed experimentally.

The potential primary insertion product 1-butylcyclopentane (**10a**), derivable from **8a**, could not be detected by GCMS analysis of the crude reaction mixture; no other peak produced the necessary molecular ion of *m/e* 124. Furthermore, by coinjection of the reaction mixture derived from the reaction of DAMP with ketone **8a** with an authentic sample of **10a**, it was determined that as little as 0.5% of **10a**, were it present, could have been readily detected under the conditions of the analysis.

Competition between insertion into secondary and tertiary carbon–hydrogen bonds was measured by reaction of 2-methyl-5-nonanone (**8b**) with DAMP. Two isomeric compounds, in a 9.3:1 ratio and constituting 99.5% of the volatiles, were formed in 85% isolated yield. These isomers were assigned as the previously unknown hydrocarbons **9b** and **10b**, respectively, on the basis of their spectral properties (see Experimental Section). Since these isomers were separable only by use of capillary GLPC, the analyses consisted of a mass spectrum (MS) of each pure compound and IR and NMR spectra of mixture of the two. Identification of the major component as **9b** is based on the observation that the singlet in the ^1H NMR spectrum at δ 1.01 for the two methyl groups integrates to 6 times the area of the vinylic multiplet at δ 5.10, which in turn has ca. 9 times the area of the lower field vinylic multiplet.

The relative reactivity of a secondary benzylic vs. a secondary aliphatic C–H bond was defined by the use of **8c** as the carbonyl substrate. The product mixture, isolated in 95% yield, again contained two major components that accounted for 95.7% of the volatiles. In this case the ratio was 7.5:1, and spectral data (see Experimental Section) allowed their assignment as **9c** and **10c**, respectively. As with compounds **9b** and **10b**, these isomers were not readily separable, so the spectral analyses, with the exception of the mass spectra, were once more performed on mixtures. The ^1H NMR spectrum of the mixture again led to establishment of the major isomer present because of the two vinylic multiplets at δ 5.3 and 5.2; the latter is of greater area and itself has an integration one-third that of the triplet at δ 0.90 due to the methyl group of **9c**. Similarly, the other vinyl multiplet has an integration one-third that of the doublet at δ 1.00 assigned to the C-3 methyl group of **10c**.

A summary of the above data is contained in Table II along with the values of relative reactivity for C–H insertion of alkylidenecarbenes as reported by Dreiding et al.[5g] and Wolinsky et al.[5b] All three approaches to the carbene show the same general trend is selectivity as measured by rate ratios, i.e., primary < secondary < secondary (benzylic) < tertiary. Conversion of these ratios to values of $\Delta\Delta G^{\ddagger}$ provides data that suggest that 1,2 hydrogen or acyl shifts in ynones[5g] and decomposition of diazoethenes afford transient species having similar relative reactivities with respect to intramolecular insertion into C–H bonds. This is consistent with the intervention of an alkylidenecarbene, **1** (n = 0), as a common reactive intermediate.[18,20] On the other hand, α elimination of vinyl

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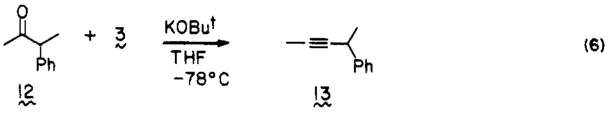
[15] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981.

[16] An isomer of the major product had a mass spectrum that closely matched that of 4-nonyne; this material constituted only 0.6% of the product mixture.

[17] Lord, R. C.; Walker, R. W. *J. Am. Chem. Soc.* **1954**, *76*, 2518.

bromides[5b] appears to provide a species that is more selective than that from the other two systems. This may signify generation of a carbenoid rather than a free carbene.

In closing, it should be noted that the diazoethene route to cyclopentenes has at least two major advantages relative to α elimination (eq 1) and flash vacuum pyrolysis (eq 2) with respect to potential synthetic applications. First, the lower temperature of the reaction results in a greater kinetic discrimination among the various types of C–H bonds present. Second, the method is not plagued by the formation of significant quantities of coupling products (eq 1)[5d] or alkynes,[5e] as in the case of α elimination. In fact, an attempt to force such a reaction from a dialkyl diazoethene, by use of **12** as the carbonyl substrate, gave the alkyne **13** in only 5% yield (eq 6). It will be necessary, of course, to demonstrate the applicability of our approach to the formation of more highly functionalized cyclopentenes before the synthetic promise of the method can be realized.[22]



(6)

Experimental Section

All IR spectra were recorded on a Beckman IR-5A or AccuLab 8 spectrophotometer, and the polystyrene absorption at 1601 cm^{-1} was used as a reference. Samples were run as liquid films between salt plates; only major absorptions are reported.

^{1}H NMR spectra were measured with a Varian Associates A-60 or EM-390 spectrometer, and all quantitative ^{1}H NMR analyses were repeated on a Nicolet NT-200 instrument. Integrations were the same within 5% in all cases. ^{13}C NMR spectra were recorded with either a Varian Associates FT-80A or a Bruker WH-90 spectrometer. Chemical shifts are reported in units of δ downfield of internal Me$_4$Si. Unless otherwise noted, chloroform-*d* was used as the solvent.

Mass spectra (MS) were obtained with a Du Pont 21-471 double-focusing mass spectrograph operating at 70 eV. High-resolution mass spectrometry for exact mass measurements was conducted with a Du Pont (CEC) 21-110 instrument. All GCMS spectra were recorded on a Finnigan GCMS with an INCOS data system operating at 70 eV. A 50-m fused silica capillary column, containing SP-2100 as the stationary phase, was used to separate volatiles.

Preparative GLPC was executed on a Varian A90-P chromatograph equipped with a thermal-conductivity detector. Helium was used as the carrier gas, and retention times are given relative to air. The following columns were used: A, 4 m × $^1/_4$ in., 6% SE-30 on 60/80-mesh silylated Chromosorb P-A; B, 3 m × $^1/_4$ in., 10% SE-30 on 30/60-mesh Chromosorb P-A; C, 0.6 m × $^1/_4$ in., 20% SF-96 on 60/80-mesh Chromosorb G; D, 4 m × $^1/_4$ in., 15% FFAP on 60/80-mesh Chromosorb P-A.

General Procedure for the Synthesis of Dialkyl Ketones. A 500-mL round-bottomed flask was equipped with a magnetic stirring bar, reflux condenser, addition funnel, and nitrogen inlet/outlet. Magnesium turnings (2.3 g, 0.1 mol) were added, the flask was flushed with nitrogen, and a 5-mL portion of a solution of 0.1 mol of an alkyl bromide in 100 mL of anhydrous diethyl ether was introduced. After initiation of the reaction, 25 mL of ether and the remainder of the solution of bromide were added, the latter at a rate such to maintain gentle reflux. The resulting mixture was heated at reflux an additional 15 min and then cooled to ca. 15 °C in an ice–water bath. Into this solution was introduced 0.12 mol of an aldehyde dissolved in 50 mL of diethyl ether in a dropwise fashion during a 20-min period. This mixture was stirred an additional 10 min before being poured into 200 mL of cold 10% aqueous H$_2$SO$_4$. The layers were separated, and the aqueous portion was extracted with ether (2 × 100 mL). The combined ethereal portions were washed sequentially with water (2 × 100 mL), saturated aqueous sodium bicarbonate (2 × 100 mL), water (100 mL), and brine (100 mL). The solution was dried (MgSO$_4$) and concentrated by rotary evaporation.

The crude alcohol was taken up in 100 mL of acetone in a 500-mL Erlenmeyer flask equipped with a magnetic stirring bar. To this solution was added 50 mL of a 3 N chromic acid solution during a period of 1 h. The reaction temperature was maintained below 45 °C with the aid of a water bath. After an additional 1 h, 2-propanol was introduced to destroy excess chromic acid, most of the acetone was removed by rotary evaporation, and 100 mL of water was added. The resulting mixture was extracted with ether (3 × 100 mL), and the extracts were washed with water (2 × 100 mL), saturated aqueous sodium bicarbonate (2 × 100 mL), and water (100 mL). The solution was dried (Na$_2$SO$_4$), the solvents were removed by rotary evaporation, and the residue was purified by distillation.

4-Octanone (8a). This material was either purchased from Aldrich Chemical Co. or prepared from 1-bromobutane and butanal in 48% overall yield. The IR and ^{1}H NMR spectra were identical with those of an authentic sample (Aldrich).

2-Methyl-5-nonanone (8b). Compound **8b** was prepared from 1-bromo-3-methylbutane and pentanal in 57% overall yield. The spectral data (IR, ^{1}H NMR, MS) were identical with those of an authentic sample.[23]

1-Phenyl-4-octanone (8c). This compound was prepared in the same manner as the other ketones: 77% yield; bp 100–105 °C (0.15 mmHg); ^{1}H NMR (CCl$_4$) δ 7.2 (m, 5 H, Ar H), 2.5 (t, J = 8 Hz, 2 H, PhCH$_2$), 2.2 (m, 4 H, CH$_2$-CO-CH$_2$), 2.0–1.0 (m, 6 H, methylenes), 0.9 (t, J = 6 Hz, 3 H, CH$_3$); IR 1700 cm^{-1}; MS, *m/e* (relative intensity) 204 (60), 147 (28), 104 (100), 91 (85), 85 (40); HRMS, calcd for C$_{14}$H$_{20}$O *m/e* 204.1514, found *m/e* 204.1509.

3-Phenyl-2-butanone (12). This compound was prepared from iodomethane and 2-phenylpropanal: 60% yield; bp 52–54 °C (0.4 mmHg) [lit.[24] mp 106–107 °C (22 mmHg)]; semicarbazone, mp 144.5–156 °C (lit.[25] mp 155 °C); ^{1}H NMR (CCl$_4$) δ 7.3 (m, 5 H, Ar H), 3.6 (q, J = 7 Hz, 1 H, PhCH), 1.9 (s, 3 H, COCH$_3$), 1.3 (d, J = 7 Hz, CHCH$_3$); IR 1710 cm^{-1} (lit.[24,26] 1750 cm^{-1}); MS, *m/e* 148 (M$^+$).

General Procedure for the Preparation of Cyclopentenes. Potassium *tert*-butoxide (1.12 g, 10 mmol) was dissolved in 30 mL of anhydrous THF contained in a 50-mL round-bottomed flask equipped with a magnetic stirring bar. The flask was purged with nitrogen, sealed with a rubber septum, and cooled to −78 °C (dry ice/2-propanol). A solution of DAMP (1.50 g, 10 mmol)[27] in 3 mL of THF was added via syringe over a 5-min period. After this mixture had been stirred for an additional 5 min, a solution of a ketone (5.0 mmol) in 3 mL of THF was added during the course of 5 min. Stirring was continued at −78 °C for 18 h, with occasional venting to relieve internal pressure.

The solution was allowed to warm to room temperature, and 50 mL of pentane was added. The resulting mixture was washed with water (5 × 100 mL) and dried (Na$_2$SO$_4$), and the solvent was removed by either rotary evaporation or simple distillation. The crude reaction mixture was chromatographed on neutral silica

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(18) Calculations have indicated that electron-withdrawing substituents should stabilize alkylidenecarbenes.[19] Such stabilization should lead to greater selectivities for the carbenes derived from ynones, in analogy to the relationship between selectivity and stability noted for saturated carbenes.[3] On the basis of the limited data given in Table II, this appears to be the case, although the trend is hardly dramatic, if indeed it is real.

(19) Apeloig, Y.; Schreiber, R. *Tetrahedron Lett.* **1978**, 4555.

(20) It is of interest that these carbenes appear to have a selectivity comparable to that of dicarbomethoxycarbene [(CH$_3$OCO)$_2$C:] generated photochemically from the corresponding diazo compound.[21]

(21) Doering, W. von E.; Knox, L. H. *J. Am. Chem. Soc.* **1961**, *83*, 1989. Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *Ibid.* **1972**, *94*, 7499.

(22) One fascinating example involving use of the diazoethene method to achieve insertion into the C–H bond of a methoxy group has recently been reported.[5k]

(23) We thank K and K Laboratories for providing the authentic sample.

(24) Guyon, R.; Villa, P. *Bull. Soc. Chim. Fr.* **1972**, 137S.

(25) "Tables for Identification of Organic Compounds"; CRC Press: Cleveland, OH, 1960.

(26) This value is suspected to be in error, as the frequency is far higher than would be expected for a dialkyl ketone.

(27) Seyferth, D.; Marmar, R. M.; Hilbert, P. H. *J. Org. Chem.* **1971**, *36*, 1379.

gel (pentane), all of the material eluting before the starting ketone being collected.

5-Nonanone (2a). Use of the general procedure afforded a 33% (^1H NMR) yield of 1-butyl-3-methylcyclopentene (**4a**) having ^1H NMR and IR spectra identical with those reported:[5e] MS, *m/e* (relative intensity) 138 (M^+, 12), 123 (14), 81 (100).

Repetition of the reaction, with the exception that 3 equiv of DAMP was used, raised the yield to 51%.

Another repetition of the original reaction, except that methanol was used as solvent, gave 2-butyl-1-methoxy-1-hexene (**5**) as the only detectable (GLPC, column D, 110 °C) product. As little as 1% of **4a** could have been detected under the analytical conditions: ^1H NMR (CCl_4) δ 0.90 (m, 6 H), 1.00–1.55 (m, 8 H), 1.60–2.20 (m, 4 H), 3.45 (s, 3 H), 5.65 (m, 1 H); IR 1685 cm^{-1}; MS, *m/e* (relative intensity) 170 (M^+), 127 C_3H_7 (85); HRMS, calcd for $C_{11}H_{22}O$ *m/e* 170.1671, found *m/e* 170.1668.

A final repetition of the original reaction, this time with a quench at −78 °C with methanol, gave only (^1H NMR) **4a** in 33% yield.

6-Undecanone (2b). The general procedure yielded 36% of 1-(1-pentyl)-3-ethylcyclopentene (**2b**): ^1H NMR (CCl_4) δ 0.90 (br t, 6 H), 1.10–1.75 (m, 8 H), 1.75–2.35 (m, 6 H), 2.50 (m, 1 H), 5.25 (m, 1 H); IR 1660 cm^{-1}; MS, *m/e* 166 (M^+, 20), 151 (0), 137 (86), 95 (81), 67 (100); HRMS, calcd for $C_{12}H_{22}$ *m/e* 166.1722, found *m/e* 166.1717.

4-Octanone (8a). The general procedure gave a colorless liquid in 22% yield, based on the formula C_9H_{16}. The crude reaction mixture contained an undetermined amount of starting material **8a**, but on exclusion of this, 96.6% of the remainder was determined to be 3-methyl-1-propylcyclopentene (**9a**) by GCMS: ^1H NMR δ 5.15 (m, 1 H, vinylic H), 2.6 (m, 1 H, tertiary allylic H), 2.2–1.1 (m, 8 H, methylenes), 0.9 (d, J = 7 Hz, 3 H, CH_3), 0.8 (t, J = 7 Hz, 3 H, CH_3); IR 3040 (C=CH), 1648 cm^{-1} (C=C); MS, *m/e* (relative intensity) 124 (M^+, 6), 81 (100); ^{13}C NMR δ 143.9, 129.8, 39.9, 34.8, 33.4, 32.7, 21.4, 21.1, 14.0; HRMS, calcd for C_9H_{16} *m/e* 124.1252, found *m/e* 124.1254.

One minor component, accounting for 0.55% of the product mixture, was identified as 4-nonyne by GCMS. No other minor peaks were identified.

2-Methyl-5-nonanone (8b). When **8b** was subjected to the conditions for cyclopentene formation, chromatography on silica gel (pentane) with a ratio of 35:1 of silica gel to substrate afforded a colorless liquid in 85% yield based on the formula $C_{11}H_{20}$. This mixture proved inseparable by GLPC (column A or B) but could be resolved, on a 50-m capillary column, into two major components, which accounted for 99.5% of the volatiles present. These were identified as 1-butyl-3,3-dimethylcyclopentene (**9b**, 89.8%) and 1-(3-methylbutyl)-3-methylcyclopentene (**10b**, 9.7%). The mass spectra were run on pure compounds (GCMS), and all other spectra were run on mixtures: HRMS, calcd *m/e* 152.1565 for $C_{11}H_{20}$, found *m/e* 152.1568.

1-Butyl-3,3-dimethylcyclopentene (9b): ^1H NMR δ 5.1 (m, 1 H, vinylic H), 2.25 (m, 2 H, CH_2), 2.00 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 1.45–1.15 (m, CH_2CH_2), 1.01 (s, 6 H, $(CH_3)_2$), 0.9 (m, 3 H, CH_3); IR 1650 (C=C), 1465 cm^{-1} (methyl groups); MS, *m/e* (relative intensity) 152 (M^+, 4.4), 137 (77), 95 (5) 81 (100); ^{13}C NMR δ 141.9, 134.4, 44.7, 39.5, 30.8, 30.0, 28.7, 24.2, 22.5, 13.9.

1-(3-Methylbutyl)-3-methylcyclopentene (10b): ^1H NMR δ 5.22 (m, 1 H, vinylic H), 2.70 (m, 1 H, tertiary allylic H), 2.3–1.2 (m, 9 H, methylenes and one methine), 1.0–0.8 (m, 9 H, 3 methyl groups); MS, *m/e* (relative intensity) 152 (M^+, 3), 137 (1), 95 (7), 81 (100).

1-Phenyl-4-octanone (8c). The general procedure produced a colorless liquid in 99% crude yield (based on the formula $C_{15}H_{20}$). The two major components were inseparable by preparative GLC (columns A, B, or C, various conditions) but did resolve on GCMS. These two components, accounting for 95.7% of the reaction mixture, were identified as 1-butyl-3-phenylcyclopentene (**9c**, 77.9%) and 3-methyl-1-(3-phenylpropyl)cyclopentene (**10c**, 17.8%). The spectra, with the exception of the mass spectra, were determined on mixtures. The ^{13}C NMR spectrum of only the major isomer, 18, was observed, and a single exact mass measurement was made on the mixture: HRMS, calcd for $C_{15}H_{20}$ *m/e* 200.1565, found *m/e* 200.1570.

1-Butyl-3-phenylcyclopentene (9c): ^1H NMR δ 7.2 (m, 5 H, Ar H), 5.3 (m, 1 H, vinylic H) 3.8 (m, 1 H, tertiary benzylic H), 2.7–1.2 (m, 10 H, methylenes), 0.9 (t, J = 7 Hz, CH_3); IR 1610, 1500, 1465 cm^{-1}; MS, *m/e* (relative in tensity) 200 (M^+, 6), 143 (100), 91 (19); ^{13}C NMR δ 147.2, 146.4, 128.3, 127.2, 125.9, 51.4, 35.1, 34.3, 30.8, 30.2, 22.7, 14.0.

3-Methyl-1-(3-phenylpropyl)cyclopentene (10c): ^1H NMR δ 7.2 (m, 5 H, Ar H), 5.2 (m, 1 H, vinylic H), 2.7–1.2 (m, 11 H, methylenes and methine), 1.0 (d, J = 7 Hz, 3 H, CH_3); MS, *m/e* (relative intensity) 200 (M^+, 1), 104 (83), 91 (21), 81 (100).

3-Phenyl-2-butanone (12). Use of the general procedure for formation of cyclopentenes afforded 0.6 g of a pale yellow liquid. Analysis of it by GCMS indicated the presence of six major volatile components, only two of which produced molecular ions at *m/e* 144. One of these had a retention time and mass spectrum identical with that of authentic 4-phenyl-2-pentyne (**13**). The yield of this product was ca. 5%. The other components of the mixture were not identified.

3-Phenyl-1-butyne. Into a dry 100-mL, round-bottomed, one-necked flask equipped with a magnetic stirring bar was placed a solution of 1.57 g (14.0 mmol) of potassium *tert*-butoxide in 50 mL of THF. The system was purged with nitrogen, sealed with a rubber septum, and cooled to −78 °C. A solution of DAMP (2.17 g, 14.5 mmol) in 2 mL of THF was added during a 5-min period, and this was followed by a similar addition of 2-phenylpropanal (1.60 g, 11.9 mmol) in 2 mL of THF. The resulting solution was stirred at −78 °C for 0.5 h and allowed to warm to room temperature. Water (50 mL) was added, and the resulting mixture was extracted with pentane (2 × 50 mL). The combined organic portions were washed with water (2 × 50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated by rotary evaporation. Distillation of the residue afforded 1.04 g (8.01 mmol, 67.2% yield) of 3-phenyl-1-butyne, which had spectra (IR, ^1H NMR, MS) that corresponded to those reported.[28]

4-Phenyl-2-pentyne (13). A 100-mL, one-necked, round-bottomed flask was equipped with a magnetic stirring bar, a rubber septum, and a nitrogen inlet/outlet. The system was purged with nitrogen, and 10 mL of THF was introduced. Methyllithium (8.8 mmol in 6 mL of diethyl ether) was added, followed by 0.98 g (7.5 mmol) of 3-phenyl-1-butyne. After this mixture had been stirred for 5 min, 2.3 g (16 mmol) of iodomethane was added, and the solution was allowed to warm to room temperature and stirred for 16 h. Pentane (25 mL) was added, and the mixture was then washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated by rotary evaporation. The pale yellow oil that resulted was purified by preparative GLPC (column B, 80 °C, flow rate = 54 mL/min) to give **13** (t_R = 12.7 min) and 4-methyl-4-phenyl-2-pentyne (t_R = 13.8 min).

4-Phenyl-2-pentyne: ^1H NMR δ 7.2 (m, 5 H, Ar H), 3.6 (m, 1 H, PhCH), 1.8 (d, J = 1.5 Hz, 3 H, acetylenic CH_3), 1.4 (d, J = 7 Hz, 3 H, aliphatic CH_3); IR 1450, 1375 cm^{-1}; HRMS, calcd for $C_{11}H_{12}$ *m/e* 144.0939, found *m/e* 144.0943.

4-Methyl-4-phenyl-2-pentyne: ^1H NMR δ 7.25 (m, 5 H, Ar H), 1.90 (s, 3 H, acetylenic CH_3), 1.50 (s, 6 H, *gem*-CH_3); IR 1390, 1370 cm^{-1}; HRMS, calcd for $C_{12}H_{14}$ 158.1096, found 158.1095.

1-Butylcyclopentene (10a). A 100-mL round-bottom flask was equipped with a magnetic stirring bar, an addition funnel, and a fractional distillation apparatus. A catalytic amount (0.5 g) of 2-naphthalene sulfonic acid was placed in the flask, the system was evacuated (12 mmHg), and the flask was heated to 140 °C (oil bath). 1-Butyl-1-pentanol[28] was added dropwise over 25 min, and the alkene and water that formed were flash distilled at 48–51 °C.

The distillate was taken up in pentane (10 mL), and the organic layer was separated and dried (Na_2SO_4). Evaporation of the solvent afforded 8.3 g (66.9 mmol, 76%) of crude alkene. Purification was effected by GLPC (column B, 55 °C, flow rate = 50 mL/min, t_R = 4.0 min). The ^{13}C NMR spectrum of the product was identical with that reported:[29] ^1H NMR δ 5.20 (m, 1 H, vinylic H), 2.30–1.10 (m, 12 H, CH_2), 0.85 (s, 3 H, CH_3); IR 1645 cm^{-1}.

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Registry No. **2a**, 502-56-7; **2b**, 927-49-1; **2c**, 123-05-7; **3** (R = Me), 27491-70-9; **4a**, 57497-24-2; **4b**, 87712-64-9; **5**, 73314-70-2; **6**, 55944-43-9; **8a**, 589-63-9; **8b**, 22287-02-1; **8c**, 78427-96-0; **9a**, 87712-65-0; **9b**, 87712-66-1; **9c**, 87712-67-2; **10a**, 2423-01-0; **10c**, 87712-68-3; **12**, 769-59-5; **13**, 87712-69-4; 3-phenyl-1-butyne, 4544-28-9; 4-methyl-4-phenyl-2-pentyne, 1007-91-6.

Mechanistic Aspects of 1,4-Dicyanonaphthalene-Sensitized Phototransformation of Aryl Glycopyranosides[1a]

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Steady-state irradiation of phenyl glycopyranosides under conditions of photosensitization (electron transfer) by 1,4-dicyanonaphthalene (DCN) leads to the formation of the corresponding monosaccharides (or their methyl derivatives, if methanol is present in the solvent). Mechanistic aspects of this photoreaction have been examined by steady-state fluorescence quenching measurements and 337.1-nm laser flash photolysis. Formation of the DCN radical anion (with yields of 0.18–0.35 δ_{ion}) as well as the DCN triplet (with yields of 0.14–0.27 δ_{T}) is observed as a result of the electron-transfer quenching of the DCN singlet by phenyl glycopyranosides in acetonitrile and a methanol–acetonitrile (1:10) mixture. Phenoxy radical is also shown to be a transient photoproduct in the latter solvent. Various features of the reaction scheme involving the fragmentation of electron-transfer-derived radical cations of phenyl glycopyranosides into the phenoxy radical and carbonium ions and possible roles of oxygen and methanol in enhancing or inhibiting the yields are discussed.

Under suitable conditions, excited-state-mediated charge-transfer interactions[2-4] of a donor or an acceptor with a substrate lead to the formation of radicals and radical ions that are labile enough to undergo chemical transformations before back electron transfer or charge neutralization may occur. In many cases, the donor or the acceptor, known as the sensitizer, is regenerated in its ground state and acts as the light-absorbing species that initiates photoreactions in a substrate while the substrate itself does not absorb the light. Cyanoaromatics have been popular as electron-transfer sensitizers (acceptors) for use in a variety of light-induced organic reactions such as photooxygenation,[5] photorearrangement/fragmentation,[6] and photoisomerization.[7]

In an earlier paper[8] we have reported on the results of a study concerning the irradiation of several aryl glycopyranosides in solutions in the presence of 1,4-dicyanonaphthalene (DCN) under conditions of photoinduced electron transfer. HPLC analyses of the products obtained under various conditions, namely, in acetonitrile and in acetonitrile/methanol (10:1) saturated with oxygen, air, or nitrogen show the formation of simple monosaccharides, their methyl derivatives, and phenol. A reaction scheme in terms of the fragmentation of electron-transfer-derived radical cations of phenyl glycopyranosides into phenoxy radical and carbonium ions (composed of carbohydrate rings) has been proposed. In this paper we are presenting the mechanistic details, namely, rate constants for DCN singlet quenching and efficiency of electron transfer, as revealed by steady-state fluorescence measurements and time-resolved laser flash photolysis. Interestingly, in addition to DCN radical anion generation, we also observe enhanced formation of the DCN triplet via the charge transfer interaction of the DCN singlet with phenyl glycopyranosides. We point out that the aryl glycopyranosides serve as reasonable models for lignocellulosic materials, and the present work is of potential significance in the field of solar energy and biomass conversion.

Experimental Section

The aryl glycopyranosides, purchased from Sigma, were used as received. The preparation of 1,4-dicyanonaphthalene (DCN) is described elsewhere.[6a,8] Phenol (Baker) was sublimed under

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