J. Org. Chem. 1992, *57*, 4185–4188 4185

Alkylidenecarbenes from 1-Diazo-1-alkenes: Their Electrophilicity and Stereochemistry of [2 + 2]-Cycloaddition[1]

John C. Gilbert* and David H. Giamalva

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

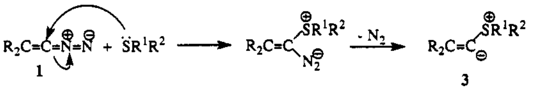
Received April 6, 1992

Determination of the ρ value for the [2 + 2]-cycloaddition of the alkylidenecarbene derived from 1-diazo-2-methyl-1-propene shows that the carbene has an electrophilicity comparable to that of the species derived from α-elimination of the corresponding vinyl triflate. Measurements of ρ as a function of solvent indicate that the carbene is free of encumbrance with solvent molecules, at least in the sense that the latter are functioning as Lewis bases. The observed stereochemistry of the [2 + 2]-cycloaddition is consistent with the alkylidenecarbene being produced in a singlet electronic state.

One of the more challenging aspects in the characterization of carbenes is determination of whether the reactive intermediate is free or complexed, i.e., is a carbenoid. Several mechanistic probes have been used for the evaluation of the carbene/carbenoid question, including (a) measurement of the relative reactivities of alkenes in the [2 + 2]-cycloaddition reaction as a function either of various chemical precursors of the putative carbene or of the mode of decomposition of a single progenitor of the carbene[2] and (b) assessment of various stereochemical factors associated with reaction of the carbenic species.[2,3] In the present paper we describe the application of the first type of probe to define the nature of the alkylidenecarbenes, **2**,[4,5] derived from 1-diazoethenes, **1**, themselves prepared by a modified Wittig reaction between diethyl (diazomethyl)phosphonate (DAMP) and carbonyl compounds (eq 1),[6,7] and explore the multiplicity of these species.

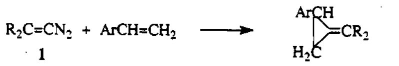
$$\mathrm{R_2C{=}O} + \underset{\mathrm{DAMP}}{\mathrm{(RO)_2P(O)CHN_2}} \xrightarrow[\mathrm{THF}]{\mathrm{Base}} \underset{\mathbf{1}}{\mathrm{R_2C{=}CN_2}} \xrightarrow{-\mathrm{N_2}} \underset{\mathbf{2}}{\mathrm{R_2C{=}C{:}}} \qquad (1)$$

There is good evidence to support the intervention of **1** in the olefination process.[7e,8] However, the unexpected instability of these species in tetrahydrofuran at −78 °C,[7d,9] and the nature of some of the reaction products arising from the postulated carbene **2** in this as well as other nucleophilic solvents,[7c,d,f] indicated that the solvent (R^1R^2S, eq 2) might be promoting the loss of dinitrogen from the diazoalkene **1** to give the ylide **3** as a key intermediate.



(2)

The ylide could be viewed as one extreme of a continuum of representations having at least some amount of covalency in the bond between the nucleophilic solvent and the carbenic center. Each of these species could be classified as a carbenoid and might account for all the known chemistry ascribed to alkylidenecarbenes. Definition of the character of the divalent species arising from **1** is thus of interest, and a Hammett study of [2 + 2]-cycloaddition that occurs upon generation of **1** in the presence of alkenes (eq 3) was undertaken to provide this.



(3)

The results of such a study, in which acetone was used as the precursor to 1-diazo-2-methyl-1-propene (**1**, R = CH_3), are collected in Table I. The table also contains the ρ values for 2-methyl-1-propylidene (**2**, R = CH_3), the divalent reactive intermediate we believe to arise from **1** (R = CH_3), but derived from precursors **4**–**9**. It is clear that the ρ value for our system (eqs 1 and 3) is similar to those derived by use of substrates **4**–**6**, but very different from those obtained with **7**–**9**. Experimental data provided

Table I. ρ Values for 2-Methylpropenylidene Generated from Various Precursors

carbene precursor	reaction conditions	ρ^a	r^2	std dev
$R_2C{=}CN_2$ (1, R = CH_3)[b]	−78 °C/THF/ KOBu^t	−0.64	0.995	0.019
$(CH_3)_2C{=}CHOSO_2CF_3$ (4)[c]	−20 °C/KOBu^t	−0.75[d]	0.994	
$(CH_3)_2C{=}C(OSO_2CF_3)Si(CH_3)_3$ (5)[e]	0 °C, $R_4N^+F^-$	−0.44	0.952	
$(CH_3)_2C{=}CHN{=}NTs$ (6)[e]	0 °C	−0.71	0.999	
$(CH_3)_2C{=}CHBr$ (7)[f]	−10 °C/KOBu^t	−4.2 (σ^+)	1.000	
$(CH_3)_2C{=}CBr_2$ (8)[f]	−40 °C/CH_3Li	−4.3 (σ^+)	1.000	
N-nitrosooxazolidone (9)[g]	+40 °C, $LiOCH_2CH_2OEt$	−3.5 (σ^+)	1.000	

[a] Obtained using σ values for substituents unless otherwise noted. [b] This work. [c] Reference 10. [d] We have obtained this same value in a repetition of the published study; see Experimental Section. [e] Derived from data taken from Table I, ref 4a. [f] Patrick, T. B.; Haynie, E. C.; Probst, W. J. *J. Org. Chem.* 1972, *37*, 1553–1556. [g] Reference cited in footnote 22.

---

[1] Taken in part from the dissertation of D.H.G., submitted in partial fulfillment of requirements for the Ph.D. degree.

[2] Review: Moss, R. A. In *Carbenes*; Jones, M. J., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1973; Vol. I.

[3] For example, see: Curtin, D. Y.; Flynn, E. W.; Nystrom, R. F. *J. Am. Chem. Soc.* 1958, *80*, 4599–4601. Stang, P. J.; Fox, D. P. *J. Org. Chem.* 1975, *43*, 364–365.

[4] Reviews: (a) Stang, P. *Chem. Rev.* 1978, *78*, 383–405. (b) Stang, P. *Acc. Chem. Res.* 1982, *15*, 348–354. (c) Hartzler, H. D. In *Carbenes*; Moss, R. A., Jones, M. J., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II.

[5] Recent leading references on the generation and chemistry of alkylidenecarbenes (oids): (a) Lewis, R. T.; Motherwell, W. B. *Tetrahedron* 1992, *48*, 1465–1484. (b) Kunishima, M.; Hioki, K.; Ohara, T.; Tani, S. *J. Chem. Soc., Chem. Commun.* 1992, 219–220. (c) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* 1991, *113*, 3135–3142. (d) Baird, M. S.; Baxter, A. G. W.; Hoorfar, A.; Jefferies, I. *J. Chem. Soc. Perkin Trans. 1* 1991, 2575–2581.

[6] Review: Boutagy, J.; Thomas, R. *Chem. Rev.* 1974, *74*, 87–99.

[7] Other papers in this series: (a) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* 1979, *44*, 4997–4998. (b) Gilbert, J. C.; Weerasooriya, U.; Giamalva, D. H. *Tetrahedron Lett.* 1979, *20*, 4619–4922. (c) Gilbert, J. C.; Weerasooriya, U. *Ibid.* 1980, *21*, 2041–2044. (d) Gilbert, J. C.; Weerasooriya, U.; Wiechman, B. E.; Ho, L. *Ibid.* 1980, *21*, 5003–5006. (e) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* 1982, *44*, 1837–1850. (f) Gilbert, J. C.; Weerasooriya, U. *Ibid.* 1983, *48*, 448–453. (g) Gilbert, J. C.; Weerasooriya, U.; Giamalva, D. H. *Ibid.* 1983, *48*, 5251–5256. (h) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* 1983, *105*, 664–665. (i) Gilbert, J. C.; Blackburn, B. K. *Tetrahedron Lett.* 1984, *25*, 4067–4070. (j) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* 1984, *106*, 1885. (k) Gilbert, J. C.; Giamalva, D. H.; Baze, M. *J. Org. Chem.* 1985, *50*, 2557–2563. (l) Gilbert, J. C.; Giamalva, D. H. *Ibid.* 1985, *50*, 2586–2587. (m) Gilbert, J. C.; Blackburn, B. K. *Ibid.* 1986, *51*, 3656–3663. (n) Gilbert, J. C.; Blackburn, B. K. *Ibid.* 1986, *51*, 4087–4089. (o) Gilbert, J. C.; Blackburn, B. K. *Tetrahedron Lett.* 1990, *31*, 4727–4730.

[8] Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* 1981, *103*, 7011–7012.

[9] Attempts to generate and characterize 1 at lower temperatures have been unsuccessful.

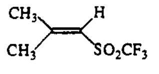
0022-3263/92/1957-4185$03.00/0 © 1992 American Chemical Society

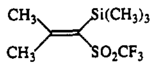
Table II. Solvent Parameters and ρ Values as a Function of Solvent

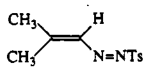
solvent	ρ	r^2	σ	π^{*a}	β^a	D (20 °C)
CH_3CN	−0.83	0.996	0.01	0.75	0.31	37.5
THF	−0.64	0.995	0.02	0.58	0.55	7.6
Et_2O	−0.45	0.999	0.01	0.27	0.47	4.34
CH_2Cl_2	−0.51	0.993	0.14	0.82	0.0	9.08
C_6H_6	−0.43	0.999	0.01	0.59	0.10	2.28
C_6H_6 + 18-crown-6	−0.43	0.997	0.01			

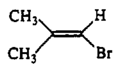
[a] See text for discussion of this parameter.

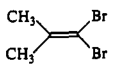
by Stang et al. show that neither potassium nor triflate ion is associated with the divalent intermediate produced by reaction of 4 with potassium *tert*-butoxide, and they have concluded that this method generates *unencumbered* 2 (R = CH_3).[10] By analogy, we were tempted to conclude that the base-promoted reaction of ketones and, presumably, aldehydes with a (diazomethyl)phosphonate not only affords alkylidenecarbenes, most likely by loss of dinitrogen from the corresponding 1-diazoalkenes (eqs 1 and 3), but also generates these species in a "free" state.

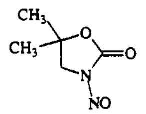

4


5


6

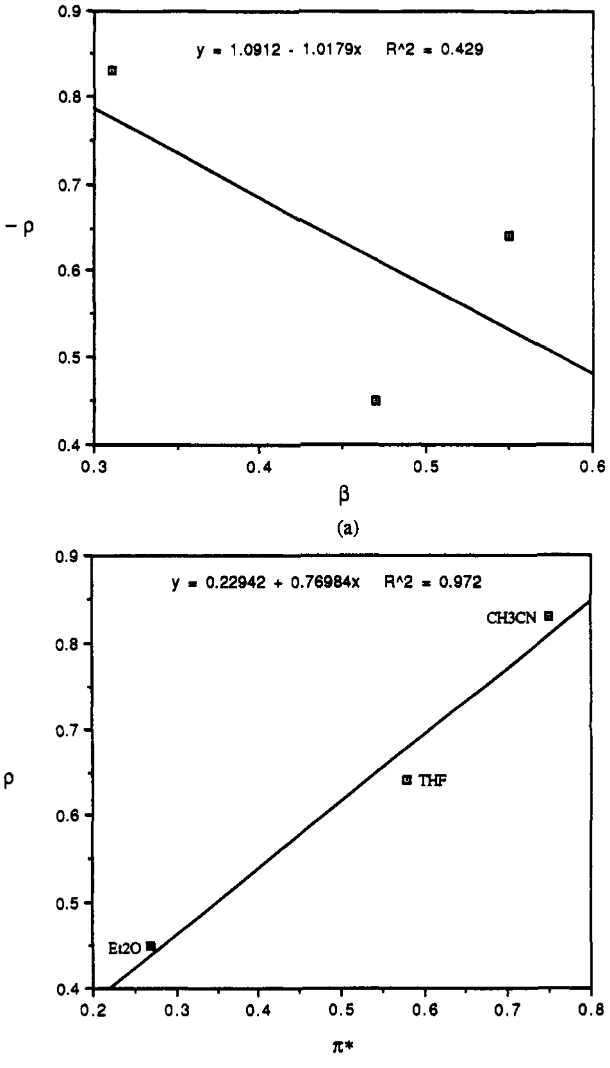

7


8


9

Two factors initially caused us to question the conclusion that alkylidenecarbenes 2 derived from diazoalkenes 1 were entirely unencumbered. First of all our ρ value is less negative, in a statistically significant amount, than that for the carbenes formed from precursor 4. This difference might signal the intervention of a solvent–carbene complex like 3 (eq 2) in our system, whereas no solvent other than substrate alkene was present in the studies performed with 4.[10] Retention of some bond character between the carbenic center and the oxygen atom of THF at the transition state of [2 + 2]-cycloaddition would presumably make the alkylidenecarbene from 1 *less* electrophilic than the truly free species. Secondly, the logic that the ρ value derived from use of 4 as the source of the carbene is that of the unencumbered entity may be flawed: the *tert*-butyl alcohol formed in the reaction may itself form a complex, e.g., 3 (R^1R^2S = $HOBu^t$), which would have an electrophilicity different from that of the free carbene.[11]

In an effort to identify the possible role of solvent on the properties of 2, we extended our Hammett studies to two additional solvents, acetonitrile and diethyl ether. The results are compiled in Table II and represent averages of at least two experimental runs on each substrate. Our working hypothesis in performing this series of experiments was that if complexation of a nucleophilic solvent with the alkylidenecarbene is modifying its reactivity, the ρ values should correlate with parameters that measure the ability of a solvent to donate an electron pair. However, attempts to fit the data using Guttman's "donor numbers"[12] and the "β" scale of Taft et al.[13] failed utterly, the latter giving a correlation coefficient, r^2, of only 0.429 (see Figure 1a).[14] We believe that this result militates strongly against *direct* complexation of the electrophilic carbenic carbon atom with solvent molecules.



(a)

(b)

Figure 1. Plots of ρ vs β and π^*.

An alternate description of the role of solvent would involve its intrinsic polarity and/or polarizability. The solvatochromic expression developed by Taft et al. (eq 4)

$$\rho = \rho_0 + s\pi^* \qquad (4)$$

incorporates such factors and is known to correlate well with a number of other solvent polarity scales.[15a] In this expression, ρ_0 is the ρ value in cyclohexane, s is the susceptibility to polarity effects, and π^* is a composite measure of the dipolarity and polarizability of a solvent and is believed to assay the characteristic ability of a solvent "to stabilize a charge or a dipole by virtue of its dielectric effect".[15c] The plot of ρ versus π^* (Figure 1b) provides a

---

[10] Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 6478–6481.

[11] This possibility was recognized by Stang et al. in footnote 69 of ref 4a.

[12] Gutmann, V. *CHEMTECH* 1977, 255–263. Gutmann, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1972; Chapter 2. Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979.

[13] (a) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377–383. (b) Taft, R. W.; Kamlet, M. J. *Ibid.* **1976**, *98*, 2886–2894. (c) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* **1981**, *46*, 661–667.

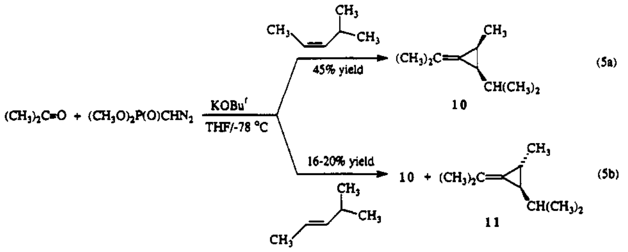
[14] Not surprisingly, the solvent acidity-related "α" scale of Taft and Kamlet[12b] also gives no correlation of the data in Table II.

[15] (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038. (b) Abboud, J.-L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8325–8327. (c) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Ibid.* **1981**, *103*, 1080–1086. (d) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887.

correlation coefficient of 0.974, a dramatic improvement over that obtained using β.[16]

This result provides a compelling argument that bulk properties of the solvent, not complexation, are responsible for the observed variation in ρ as a function of solvent. We therefore conclude that the synthetic methodology described by eq 1 affords alkylidenecarbenes unencumbered with solvent molecule(s). Whether or not the same conclusion can be drawn for the carbenes derived from **4–6** remains an open question, but what is clear from our approach to alkylidenecarbenes as well as those used by Stang et al. is that these carbenes are mildly electrophilic, a result that contrasts sharply with those obtained when **7–9** serve as precursors to these reactive intermediates.[17]

We next studied the stereochemistry of the [2 + 2]-cycloaddition reaction. Theory predicts that vinylidene (**2**, R = H) strongly favors the singlet electronic ground state, the triplet manifold lying some 40–50 kcal/mol higher in energy;[18] the cycloaddition should therefore occur with retention of the stereochemistry of the alkene. Indeed, Stang et al. have previously shown that this is the outcome when **4** serves as the source of the carbenic species.[19] The similarity of ρ in our system to that involving **4** made it likely that the same result would attend our studies, but the possible difference in degree of encumbrance in the two systems, as discussed above, made experimental demonstration of this expectation a necessity. In fact, base-promoted reaction of acetone with DAMP in the presence of *cis*-4-methyl-2-pentene gave the cis adduct **10** in 45% yield (eq 5a); none of the trans isomer **11** could be detected under GC conditions that would have revealed as little as 0.5% of it. This result supported a mechanism in which singlet dinitrogen is lost from the diazoalkene **1** (R = CH_3) to afford singlet 2-methyl-1-propenylidene (**2**, R = CH_3).

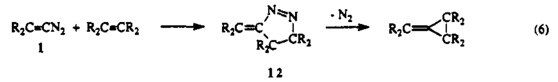


(5a)

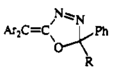
(5b)

We sought confirmation of this conclusion by use of *trans*-4-methyl-2-pentene in the reaction, but in this case the results were initially perplexing (eq 5b). The cycloaddition reaction afforded only a 15–20% yield of methylenecyclopropanes, and the adducts were found by GC analysis to be a 5.9:1 mixture of trans and cis isomers. The possibility that the formation of the cis adduct was the result of a stepwise process seemed unlikely, given that stereorandomization should be at least as great, if not greater, if the cycloaddition is not concerted and the *cis*-alkene is used as substrate.[20] We believe that the explanation for the observed sterorandomization is based on the fact that capillary GC analysis showed the *trans*-4-methyl-2-pentene to be contaminated with 0.9 ± 0.2% of the cis isomer. Our argument is then as follows: Twenty equivalents of the "*trans*"-alkene were used in the experiments, and given the observed ratio and overall yield of **10** and **11**, this means that at least 5 equiv of the *cis*-alkene were present relative to the amount of **11** that was formed; combining this information with the fact that the relative rate of the cycloaddition reaction of *cis*- and *trans*-disubstituted alkenes with alkylidenecarbenes is expected to be at least 5.3[21] at −78 °C, the temperature for our reaction, it is possible to attribute the formation of **10** to the contamination of the *trans*-alkene by its cis diastereomer.[22]

Thus we believe that [2 + 2]-cycloaddition using our system is completely stereoselective within experimental error. This result is entirely consistent with the intervention of singlet **2**. It also speaks against the intervention of pyrazolines, **12**, derived from reaction between alkenes and the diazo compound **1**, as these would be expected to decompose to cyclopropanes in a nonstereospecific manner (eq 6).[23] Further evidence against the intermediacy of the pyrazoline in the process is the negative value of ρ that we observe, whereas pyrazoline formation is normally characterized by positive ρ values.[24] Finally, the fact that we obtain [2 + 2]-cycloaddition products at −78 °C is also inconsistent with the formation of pyrazolines, since rather close analogs to them, viz. **13** (R = Ph, CH_3, or C_2H_5), are stable above room temperature.[25,26]



(6)



R = Ph, CH_3, or C_2H_5

13

In conclusion, by determination of its ρ value we have shown that the reactive species formed from the base-prompted reaction of DAMP with acetone has an electrophilicity comparable to that of the alkylidenecarbene

---

(16) The value of ρ was also determined in dichloromethane ($r^2 = -0.51$) and benzene ($r^2 = -0.43$). Inclusion of these data in Figure 1a would have lowere r^2 to 0.087. There is no valid way of incorporating these values in Figure 1b since the modified version of eq 4[15] shown below must be used where aromatic and polychlorinated solvents are concerned. Although the factor d has been set at 1.0, 0.5, and 0.0 for aromatic, polychlorinated aliphatic, and nonchlorinated aliphatic solvents, respectively, estimation of the value of d requires studies of the reaction of interest in a number of different such solvents: see footnote 14 of ref 13b.

$$\rho = \rho_0 + s(\pi^* + d\delta)$$

(17) The nature of the highly electrophilic species derived from **7–9** remains unclear.

(18) Kenney, J. W.; Simons, J.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6930–6936.

(19) Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 1459–1464.

(20) See, for example, Ring, D. F.; Rabinovitch, B. S. *J. Phys. Chem.* **1968**, *72*, 191–198. Gale, D. M.; Middleton, W. J.; Krespan, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 3617–3623. Jones, M., Jr.; Ando, W.; Kulczycki, A., Jr. *Tetrahedron Lett.* **1967**, 1391–1396.

(21) This is the value of k_{cis}/k_{trans} for the 2-butenes at −20 °C: Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1802–1804. The selectivity should increase at still lower temperatures and with increased steric requirements of the substituents on the double bond.

(22) A similar conclusion can be reached using the k_{cis}/k_{trans} value of 7.1 reported for reaction of the 4-methyl-2-pentenes with the carbenic species derived from *N*-nitrosooxazolidone **9** at 40 °C: Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 6461–6464. However, the ρ value of −3.4 reported by these workers for their system makes extrapolation of their results to our system questionable.

(23) Crawford, R. J.; Ali, L. H. *J. Am. Chem. Soc.* **1967**, *89*, 3908–3909. Firestone, R. A. *Tetrahedron Lett.* **1980**, *21*, 2209–2212.

(24) For example, see: Kadaba, P. K.; Colturi, T. F. *J. Heterocycl. Chem.* **1969**, *6*, 829–834. Murahasi, S.-I.; Okumura, K.; Naota, T.; Nagase, S. *J. Am. Chem. Soc.* **1982**, *104*, 2466–2475.

(25) Capuano, L.; Zander, R.; Zenner, P. *Chem. Ber.* **1979**, *112*, 3753–3758.

(26) The comparability of our value for ρ with that reported by Stang et al.[10] for the alkylidenecarbene obtained from **4** is evidence against pyrazoline formation, of course.

derived from α-elimination of the precursors **4–6**. This supports formation of an alkylidenecarbene **2** by way of the sequence shown in eq 1. We have also measured ρ for our system as a function of solvent and believe that the results support the proposition that the carbene is free of encumbrance with solvent molecules, at least in the sense that the latter are functioning as Lewis bases, as shown by correlation of the ρ values with π^* rather than β.[27] The observed stereochemistry of the [2 + 2]-cycloaddition of the alkylidenecarbene is consistent with its being produced in a singlet electronic state.

Experimental Section

IR spectra were recorded on a Beckman AccuLab spectrophotometer and were calibrated against the absorption of polystyrene at 1601 cm^{-1}. ^{1}H-NMR spectra were obtained with a Varian EM-390 spectrometer on solutions containing tetramethylsilane as internal standard. GC/MS data were measured on a Finnigan 4023 instrument using an INCOS data system.

Preparative GC of the styrene adducts was performed with a Varian A90-P chromatograph fitted with a 1.3-m × 0.6-cm column packed with 20% SF-96 on 60–80-mesh Chromosorb G; that of the methylenecyclopropanes derived from the 4-methyl-2-pentenes was done on a 2-m × 0.6-cm column packed with 6% SE-30 on 60–80-mesh Chromosorb P (acid washed). Analytical GC data were obtained with a Varian 7200 instrument equipped with a thermal conductivity detector and interfaced with a Vidar 6300 digital integrator; either a 2-m × 0.6-cm column packed with 10% SE-30 on 30–60-mesh Chromosorb W or a 4-m × 0.6-cm column packed with 15% FFAP on 60–80-mesh Chromosorb P (acid washed) was used to effect separation.

Competition Experiments. A dry 25-mL round-bottom flask equipped for magnetic stirring was charged with 0.6–1.1 mmol of potassium *tert*-butoxide, and 2.0 mL of a mixture of the substrate styrenes[28] and 3.0 mL of dry THF (freshly distilled from benzophenone ketyl) was added. The flask was sealed with a rubber septum and placed in a bath held at −20 ± 3 °C (dry ice–carbon tetrachloride or ice–methanol). A solution of diethyl (diazomethyl)phosphonate (DAMP)[29] and acetone (2–3 mmol) in 1.0 mL of dry THF was then added dropwise to the stirred reaction mixture over ca. 2 min. Stirring was continued at −20 °C for an additional 30–60 min, during which time gas was evolved; consequently, a needle was periodically inserted through the septum to equalize pressure.

The reaction was quenched by addition of 3 mL each of water and pentane, and the mixture that resulted was brought to room temperature. After separation of the layers, the organic portion was dried (Na_2SO_4), filtered, and concentrated to a volume of ca. 2 mL by simple distillation. The residue was subjected to analysis by GC. The product methylenecyclopropanes were identified by isolation and comparison of their spectra (IR, ^{1}H NMR, MS) with those reported in the literature.[10,30]

All reactions were performed at least twice, and the product mixtures were analyzed in triplicate.

The study reported by Stang and Mangum[10] in which trifluoromethyl 2-methyl-1-propenesulfonate (**4**) was the source of the alkylidenecarbene **2** (R = CH_3) was repeated. Workup and analysis of the reaction mixtures were as described above. The same ρ value was obtained.

***cis*- and *trans*-1-(1-Methylethylidene)-2-isopropyl-3-methylcyclopropane (10 and 11).** A solution of 2.0 g of the *cis*- or *trans*-4-methyl-2-pentene in 2.0 mL of dry THF was added to 0.4 g (3.6 mmol) of potassium *tert*-butoxide contained in a 50-mL round-bottom flask equipped with a magnetic stirring bar. The flask was sealed with a rubber septum fitted so that the contents of the flask constantly could be held under an atmosphere of dry nitrogen. The flask was cooled to −78 °C, and a mixture of DAMP (2.9 mmol) and 1.0 mL of dry THF was added dropwise to the stirred solution over a 5-min period. After an additional 5 min, acetone (3.0 mmol) in 1.0 mL of dry THF was added in the same manner. The homogeneous solution that resulted was stirred at −78 °C for 12 h and then was brought to room temperature. Pentane (5.0 mL) was added, and the organic mixture was washed with water (3 × 5 mL), dried (Na_2SO_4), filtered, and concentrated (rotary evaporator).

The concentrate produced in the reaction with *cis*-4-methyl-2-pentene was chromatographed over 40 times its weight of neutral alumina (80–200 mesh), using pentane as the eluent. The desired cyclopropane **10** was isolated in 48% yield from the first two column volumes of eluent. Its IR, ^{1}H-NMR, and mass spectra were identical to those reported.[29a] Analysis by GC–MS showed the sample to be uncontaminated with the trans isomer **11**, which would have coeluted with the cis isomer under the column chromatographic protocol that was used.

The concentrate from the reaction involving *trans*-4-methyl-2-pentene was chromatographed in the same manner as just described, and the eluate, isolated in ca. 20% yield, was found to be a mixture of **10** and **11** by GC–MS analysis. The amount of **10** was 14.5 ± 1.0% (average of four analytical runs). Pure trans adduct **11** was obtained by preparative GC techniques. Its IR, ^{1}H-NMR, and mass spectra were identical to those previously reported.[29]

Analysis of *trans*-4-Methyl-2-pentene. The *trans*-4-methyl-2-pentene (Phillips Petroleum Co.) was fractionally distilled and analyzed by GC–MS, in which the GC column was cooled to 16 °C. The fraction that was subsequently used as the substrate for the addition reaction contained 0.9 ± 0.2% of the cis isomer (average of three different analytical runs, with each GC peak for the alkenes being integrated in triplicate across the entire band).

Acknowledgment. The partial support of this research by the Robert A. Welch Foundation (Grant F-815) is gratefully noted.

Registry No. 1 (R = Me), 110785-02-9; 2 (R = Me), 26265-75-8; **10**, 24524-52-5; **11**, 24524-51-4; DAMP, 25411-73-8; acetone, 67-64-1; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0.

---

[27] To our knowledge, this is the first application of the solvatochromic approach for the assessment of the nature of encumbrance of carbenes.

[28] *p*-Methyl- and *p*-methoxystyrene was prepared by the method of Nishida et al.: Nishida, S.; Moritani, I.; Sato, T. *J. Am. Chem. Soc.* 1967, *89*, 6885–6889. Styrene and *p*-chlorostyrene were purchased from Aldrich Chemical Co.

[29] Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* 1977, 869–874.

[30] See the reference cited in footnote 21.