

(18) The acid stability determined (bioassay) for bicyclomyacin belies the inherent instability of its eight-membered hemiaminal ring.<sup>1</sup> Cf. E. J. Corey, D. J. Brunelle, and K. C. Nicolaou, *J. Am. Chem. Soc.*, **99**, 7359 (1977).

Hans Maag,\* John F. Blount, David L. Coffen  
Thomas V. Steppe, Frederick Wong

Chemical Research Department, Hoffmann-La Roche Inc.  
Nutley, New Jersey 07110

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### Elusive Carbenes. Olefinic Capture of Cyclopropylchlorocarbene and Related Species

Sir:

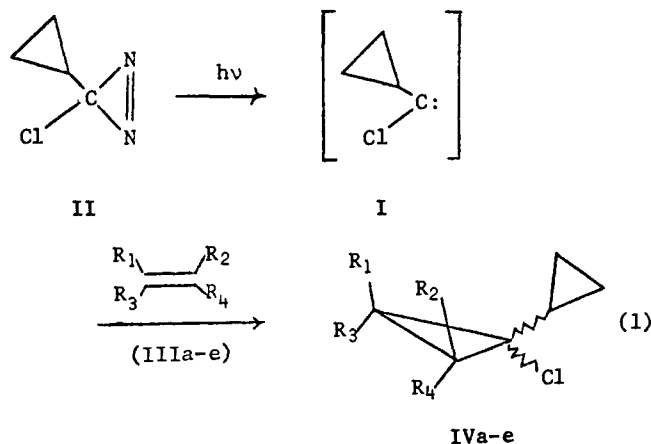
Rules are often honored by exceptions. Consider the proposition: "if a singlet carbene has an internal insertion or cycloaddition available, it will not be possible to trap it efficiently with an external reagent".<sup>1</sup> Cyclopropylcarbene, for example, readily ring expands to cyclobutene<sup>2</sup> or fragments to ethylene and acetylene;<sup>2a,c,3</sup> external traps, alkenes in particular, should be hard pressed to compete with these facile intramolecular modes of escape. One way to augment intermolecular carbene capture at the expense of intramolecular immolation is to selectively generate the triplet carbene, which appears to have a lower tendency toward rearrangement than its singlet counterpart. Indeed, *triplet* cyclopropylcarbomethoxycarbene adds to isobutene (but not to *cis*-butene) in up to 33% yield.<sup>2c,4</sup>

An alternative way to circumvent intramolecular rearrangement would be to stabilize the *singlet* cyclopropylcarbene, prolong its lifetime, and permit intermolecular capture to compete. Cyclopropylchlorocarbene (I) is of immediate interest because chlorine substitution appears to stabilize adjacent singlet carbene centers;<sup>5</sup> note that dichlorocarbene is one of the more selective carbenes in addition to alkenes.<sup>6</sup> The recent literature, however, reports that thermolysis of cyclopropylchlorodiazirine in cyclohexene affords only the intramolecular hydride shift product, chloromethylenecyclopropane.<sup>7</sup>

Nevertheless, we now report that (a) cyclopropylchlorocarbene may be readily generated by photolysis (or thermolysis) of the requisite diazirine and added to a variety of alkenes (including cyclohexene); (b) the principal intramolecular rearrangement of I leads to 1-chlorocyclobutene by ring expansion, and not to chloromethylenecyclopropane by hydride shift; (c) even the parent cyclopropylcarbene can be trapped by isobutene (albeit in low yield); and (d) the intermolecular addition of I is not an isolated phenomenon—*tert*-butylchlorocarbene, another species for which olefinic interception has been vainly sought,<sup>8</sup> also adds to simple alkenes.

3-Cyclopropyl-3-chlorodiazirine (II) was generated<sup>9</sup> from cyclopropylmethylammonium chloride<sup>10</sup> and condensed into

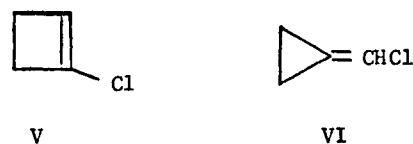
various alkenes (IIIa-e) at -78 °C. Olefinic solutions of II (0.2-1.5 M) were photolyzed in Pyrex vessels at -20 °C with a focussed Osram 200W XE mercury lamp; the decomposition of 3-7 mmol of II, monitored by nitrogen evolution, required 2-4 h. Removal of excess olefin and GC purification provided the product chlorobicyclopropyls IVa-e; cf. eq 1 and Table I.



Identities of the addition products were established by structurally consistent IR and <sup>1</sup>H NMR spectra<sup>11</sup> and by exact mass spectrometric analyses ( $\pm 5$  mmu on M<sup>+</sup>). Additions of I to *cis*- or *trans*-butene were stereospecific within the limits of GC detection. Moreover, additions to *cis*-butene or cyclohexene were stereoselective (cf. Table I), although the isomeric cyclopropanes formed in each case have not yet been configurationally differentiated.<sup>12a</sup>

Although photolytic generation of I is more convenient, thermal decomposition of II in refluxing cyclohexene (~16 h) also afforded adducts IVe in 26% yield (isomer ratio, 3.3).<sup>12b</sup>

Accompanying adducts IV was a minor product, V,<sup>13</sup> which became the major product obtained upon photolysis of II in pentane<sup>14</sup> and the sole product resulting from thermolysis of II in CCl<sub>4</sub> at 100 °C (sealed tube, 2 h). By NMR,<sup>15</sup> V was identical with the unimolecular rearrangement product of I, isolated by Liu and Chien and assigned structure VI.<sup>7</sup> The chlorocyclobutene assignment, V, is preferable, however, be-



cause of the facile thermal rearrangement of V to chloroprene. Indeed, at least three prior assignments of structure V to the cyclopropylchlorodiazirine unimolecular decomposition product already exist in the literature.<sup>16-18</sup> The thermal rearrangement of V to chloroprene<sup>17,18</sup> (which we have inde-

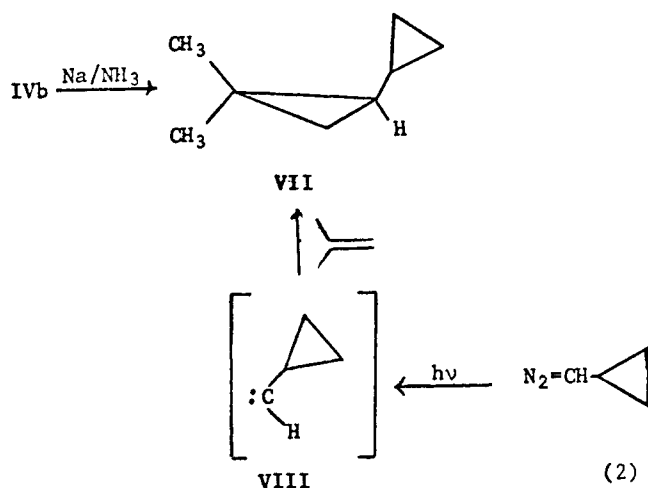
Table I. The Addition of Cyclopropylchlorocarbene to Alkenes

alkene	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Col <sup>b</sup>	GC condn <sup>a</sup>		yield of IV, % <sup>c</sup>
						temp, °C	ret time, min.	
IIIa	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	A'	100	22	78
IIIb	CH <sub>3</sub>	H	CH <sub>3</sub>	H	A	110	16	47
IIIc	CH <sub>3</sub>	H	H	CH <sub>3</sub>	A	100	25	33
IIId	CH <sub>3</sub>	CH <sub>3</sub>	H	H	B	100	23, 25 <sup>d</sup>	37 <sup>e</sup>
IIIe	-(CH <sub>2</sub> ) <sub>4</sub> -		H	H	C	100	36, 41 <sup>f</sup>	44 <sup>e</sup>

<sup>a</sup> Gas chromatographic conditions for isolation of IV; He gas flow 60 mL/min. <sup>b</sup> Columns: A, 13 ft × 0.25 in, 14% SF-96 on 80/100 Chromosorb W (A', 3 ft × 0.25 in, 14% SF-96 on 90/100 Anakrom); B, 15 ft × 0.25 in, 20% QF-1 on 45/60 Gas-Chrom R; C, 10 ft × 0.25 in 10% FFAP on 60/80 Chromosorb W. <sup>c</sup> Yields are based on decomposed II (nitrogen evolution), IV was quantitatively determined in crude photolysis residues by NMR spectroscopy against an internal CHCl<sub>3</sub> standard. <sup>d</sup> Two isomers were obtained in 8:1 distribution; the major isomer eluted first. <sup>e</sup> Overall yield. <sup>f</sup> Two isomers were obtained in 3.5:1 distribution; the major isomer eluted first.

pendently verified) is reasonably attributable only to 1-chlorocyclobutene, especially because of the nearly identical Arrhenius parameters which characterize the gas phase thermal rearrangements of both V (derived from II) to chloroprene and of 1-bromocyclobutene (derived from 1,2-dibromocyclobutane) to bromoprene.<sup>17</sup> In harmony with the behavior of other cyclopropylcarbenes,<sup>2a</sup> the principal unimolecular fate of I is ring expansion.<sup>16</sup>

Reaction 1 is clearly a facile entry to the 1-chlorobicyclopropyls, the parent of which has been of interest in solvolytic studies.<sup>19</sup> Reductive dechlorination of IV should also afford bicyclopropyls.<sup>20</sup> Indeed, IVb was reduced with sodium in ammonia ( $-78\text{ }^{\circ}\text{C}$ , 3 h, 40% yield) to bicyclopropyl VII<sup>21</sup> (eq 2).

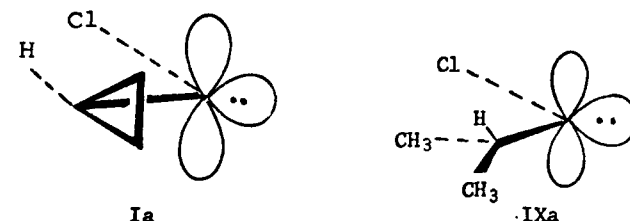


Of special note is our observation that the photolysis of cyclopropyldiazomethane<sup>22</sup> in isobutene ( $-20\text{ }^{\circ}\text{C}$ , 2 h) afforded 9.7% adduct VII, identical by GC coinjection and NMR spectrum<sup>21</sup> with authentic VII prepared by the reduction of IVb. This is most reasonably attributed to the capture by isobutene of photolytically generated cyclopropylcarbene (VIII); cf. eq 2. In a parallel control experiment, cyclopropyldiazomethane was stirred with isobutene in the dark ( $-20\text{ }^{\circ}\text{C}$ , 2 h, no nitrogen evolution). The diazoalkane was then quenched with benzaldehyde,<sup>22</sup> and the resulting solution was photolyzed for 2 h. GC investigation revealed no VII, indicating that a pyrazoline (thermally formed from isobutene and cyclopropyldiazomethane) was neither a thermal nor a photochemical precursor of VII. Whereas the stereospecificity displayed in additions of I is suggestive of a singlet carbene intermediate, cyclopropylcarbene may well be adding to isobutene as a *triplet*.<sup>2c</sup> This question and the scope of cyclopropylcarbene addition reactions are under study.

We note that the intermolecular additions of I are not an isolated phenomenon among alkylchlorocarbenes. Thus *tert*-butylchlorocarbene adds to isobutene in 49% yield (based on the nitrogen evolution accompanying the photolysis of 3-chloro-3-*tert*-butyldiazirine).<sup>23</sup> Isopropylchlorocarbene (IX), on the other hand, affords at best only a modest yield (8%) of an adduct with isobutene; intramolecular hydride shift to 1-chloro-2-methylpropene is strongly dominant (70%).<sup>23</sup>

In conclusion, we briefly speculate on the comparatively efficient intermolecular capture of I, relative to either VIII or IX. Singlet cyclopropylchlorocarbene probably prefers the energetically favorable "bisected" conformation (Ia), in which stabilizing factors include the dual interactions of a chlorine lone pair<sup>5,6</sup> and of the "bent"  $\sigma$  bonds of the cyclopropyl group<sup>5,24</sup> with the vacant p orbital at the carbenic center. In conformation Ia, hydride migration is stereoelectronically disfavored,<sup>25</sup> and ring expansion to V is probably slowed (relative to the analogous process in VIII) by  $\text{Cl} \rightarrow \text{p}$  electron

donation<sup>26</sup> (absent in VIII). The solution lifetime of I is therefore enhanced, relative to VIII, facilitating intermolecular



capture. Cyclopropyl stabilization<sup>24</sup> is unavailable to isopropylchlorocarbene, however, making conformations such as IXa accessible at relatively low energy cost. Facile hydride shift and concomitant difficulty of intermolecular capture result.

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## References and Notes

- W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. I, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, 1973, p 20.
- (a) For a review of the intramolecular chemistry of cyclopropylcarbenes, see ref 1, pp 32-36; (b) S. Kammula and P. B. Shevlin, *J. Am. Chem. Soc.*, **96**, 7830 (1974); (c) R. R. Gallucci and M. Jones, Jr., *ibid.*, **98**, 7704 (1976).
- S. S. Olin and R. M. Venable, *J. Chem. Soc., Chem. Commun.*, 104, 273 (1974); T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *J. Org. Chem.*, **38**, 4095 (1973).
- M. B. Sohn and M. Jones, Jr., *J. Am. Chem. Soc.*, **94**, 8280 (1972).
- R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).
- R. A. Moss in ref 1, Chapter 2.
- M. T. H. Liu and D. H. T. Chien, *J. Chem. Soc., Perkin Trans. 2*, 937 (1974).
- H. M. Frey and M. T. H. Liu, *J. Chem. Soc. A*, 1916 (1970). In fairness, we note that the trap employed in these experiments was *gaseous ethylene*, surely most inappropriate for the intermolecular capture of a fugitive carbene.
- W. H. Graham, *J. Am. Chem. Soc.*, **87**, 4396 (1965).
- A. W. Dox and F. C. Whitmore, "Organic Syntheses", Collect. Vol. 1, Wiley, New York, 1941, p 5.
- For example, adduct IVb displayed ( $\delta$ ,  $\text{CCl}_4$ ) singlets at 1.31 and 1.17 (methyls) and a 6 H cyclopropyl multiplet at 0.81-0.14. The cyclopropyl methine proton appeared as a multiplet beneath the methyl singlets (total, 7 H). The IR spectra of adducts IV indicated the presence of cyclopropyl C-H bonds and the absence of C=C bonds.
- (a) We tentatively assign the *endo*-cyclopropyl configuration to the major IVe isomer on the basis of its higher field (shielded) cyclopropyl protons. (b) Formally, thermal decomposition of II in cyclohexene could lead to adducts IVe via thermally unstable pyrazoline intermediates. This is unlikely, however, because pyrazolines are seldom formed from unactivated alkenes, and because related diazirines (e.g., ethylchlorodiazirine) decompose thermally at similar rates in cyclohexene and in a wide variety of polar, saturated solvents; cf. M. T. H. Liu and D. H. T. Chien, *Can. J. Chem.*, **52**, 246 (1974).
- Isolable by GC from the crude reaction mixtures obtained from the low-boiling alkenes IIIb, IIIc, and IIId; yields of V ranged from 5 to 10%.
- About 80% V was formed in this experiment; a second, unidentified component (20%) was also present.
- NMR ( $\delta$ ,  $\text{CCl}_4$ ): 2.4 (m, 2 H), 2.8 (t, 2 H), 5.8 (br s, 1 H).
- I. D. R. Stevens, H. M. Frey, and C. L. Bird, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968); private communication from Dr. Stevens, University of Southampton.
- D. Dickens, H. M. Frey, and J. Metcalfe, *Trans. Faraday Soc.*, **67**, 2328 (1971).
- W. J. Engelbrecht and S. W. J. van der Merwe, *J. S. Afr. Chem. Inst.*, **28**, 144, 148, 158 (1975).
- J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **89**, 2505 (1967); **90**, 395 (1968). J. A. Landgrebe and R. A. Martin, *J. Org. Chem.*, **37**, 1996 (1972). V. L. Fitjer and J.-M. Conia, *Angew. Chem., Int. Ed. Engl.*, **12**, 332 (1973).
- Also obtainable by the bis addition of carbenes to 1,3-dienes; see, for example, C. Romming and L. K. Sydes, *Acta Chem. Scand., Ser. B*, **30**, 963 (1976).
- Compound VII was purified by GC at  $100\text{ }^{\circ}\text{C}$  on column A (Table I) and displayed NMR absorptions ( $\delta$ ,  $\text{CCl}_4$ ) at 1.00 (s, 3 H,  $\text{CH}_3$ ), 0.87 (s, 3 H,  $\text{CH}_3$ ), and 0.57-0.29 (m, 8 H, cyclopropyl). A satisfactory elemental analysis was obtained.
- R. A. Moss and F. C. Shulman, *Chem. Commun.*, 372 (1966); *Tetrahedron*, **24**, 2881 (1968).
- R. A. Moss and R. C. Munjal, *J. Chem. Soc., Chem. Commun.*, in press. 1,1-dimethyl-2-chlorocyclopropane (2%) was formed intramolecularly

- in the  $t\text{-C}_4\text{H}_9\text{CCl}$  reaction.
- (24) For reviews of the structures of the isoelectronic cyclopropylcarbinylium cations, see (a) H. G. Richey, Jr., in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, 1972, pp 1216 ff; and (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, ref 24a, pp 1295 ff.
- (25) Facile 1,2-hydride migrations are generally believed to require a near  $-90^\circ$  dihedral angle between the carbenic p orbital and the adjacent C-H bond: A. Nickon, F.-c. Huang, R. Weglein, K. Matsuo, and H. Yagi, *J. Am. Chem. Soc.*, **96**, 5264 (1974). See, however, E. P. Kyba and C. W. Hudson, *ibid.*, **98**, 5696 (1976); E. P. Kyba and A. M. John, *ibid.*, **99**, 8329 (1977); and E. P. Kyba, *ibid.*, **99**, 8330 (1977).
- (26)  $\pi$ -p donation from a phenyl substituent to the carbenic center is apparently less effective; cyclopropylphenylcarbene, in contrast to 1, rearranges to 1-phenylcyclobutene more rapidly than it can be trapped with alkenes: P. C. Petrellis, G. W. Griffin, M. E. Hendrick, and M. Jones, Jr., *J. Chem. Soc., Chem. Commun.*, 1002 (1972).

Robert A. Moss,\* Mary E. Fantina

Wright and Rieman Laboratories, Department of Chemistry  
Rutgers, The State University of New Jersey  
New Brunswick, New Jersey 08903

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## "Water Splitting" by Titanium Exchanged Zeolite A

Sir:

Nonpolluting, hydrogen burning automobile engines<sup>1</sup> provide one of many practical motivations for seeking cheaper hydrogen. The possibility that solar illuminated inorganic complexes economically effect "water splitting" has inspired reviews<sup>2-4</sup> and experiments.<sup>5-9</sup> One subscheme<sup>10,11</sup> involves visible illumination of transition metal ion exchanged zeolites. Production of oxygen or hydrogen by such exchanged zeolites immersed in water and exposed to visible light can be demonstrated, but economical restoration of the transition metal in the zeolite to the oxidation state required for repetition of the gas production step is difficult. We have investigated properties of titanium(III) exchanged zeolite A (Linde 3A) which when bathed in water under visible illumination yields hydrogen.

Titanium(III) exchanged zeolite A is difficult to prepare using aqueous titanous chloride solution (Fisher Scientific Co. 20%, pH  $\sim$ 0).  $\text{TiCl}_3$  (aqueous) is unstable in nonacidic media (precipitating as  $\text{Ti}(\text{OH})_3$ ), whereas zeolite A is unstable under acidic conditions. In a conventional ion exchange procedure wherein solution and zeolite are combined in proportions of 1 L:  $\sim$ 20 g, stirring several days produces an amorphous gel. This may be circumvented by a high zeolite to solution ratio that capitalizes on a buffering capacity of the zeolite 3A (unit cell composition:<sup>12</sup>  $\text{K}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ). ESCA (Hewlett-Packard Model 5950B) peak areas indicate that 75% of the potassium cations is replaced by titanium cations on the surface of  $1/16$ -in.-diameter Linde 3A extrudate by letting 25 g of zeolite A stand in 50 mL of unstirred 20%  $\text{TiCl}_3$  solution for an hour at ambient temperature. The cages probably remain intact under these conditions since little aluminum leaching ( $\sim$ 25%) is indicated by the ESCA profile of the top  $\sim$ 50 Å of these pellets. Absence of chlorine in the ESCA spectrum indicates that titanium cations exchange into the zeolite rather than merely occlude as titanous chloride from solution. When this now-purple (characteristic color of hexaquotitanium(III) ions) exchanged zeolite is washed with deionized water under air until no further  $\text{TiCl}_3$  is eluted and is then illuminated with visible light (of any wavelength including red), gas bubbles form after an induction period of a minute or less. (The action spectrum may be determinable by photoacoustic spectroscopy.<sup>13</sup>) The reaction can be repeatedly started and stopped by exposure to weak illumination ( $\leq$  80 ft-c). Direct exposure to strong illumination ( $\geq$  8000 ft-c) for  $>$  5 min causes gas evolution for  $\sim$ 45 min without continued illumination, resulting

in the production of  $\sim$ 0.4 mL/g extrudate. The gas is 40% hydrogen by chromatographic analysis,<sup>14</sup> the remainder being  $\text{O}_2$  and  $\text{N}_2$  in the normal air ratio. Mass spectrometry confirms the presence of significant amounts of hydrogen. Titanium exchanged zeolites X and Y do not evolve detectable  $\text{H}_2$  under the above conditions.

Titanium(III) in zeolite A has an ESR spectrum (Varian E-3 EPR spectrometer) virtually identical with that observed by Ono et al.<sup>15</sup> for titanium(III) in zeolite Y. The line width in both cases is  $\sim$ 35 Oe with an isotropic peak confirmed in the present work to have a  $g = 1.950$  in Y-type zeolites and centered at 1.952 in the A type. Such a sample of vacuum-dehydrated titanium(III) in zeolite A exposed to oxygen in a light-tight ESR tube (i.d. 5 mm) retains the full intensity of the ESR signal just described. This contrasts with the observation of Ono et al.<sup>15</sup> and our own finding that a peroxide (denoted as  $\text{Ti-O-O}^-$ ) forms in Y-type zeolites exposed to oxygen. Illumination of the oxygen exposed zeolite A produces an intense, isotropic ESR signal at  $g = 2.0090$  with a line width of 7 Oe. This latter spectrum we attribute to a titanium(IV)-oxygen complex in which four oxygen atoms surround the titanium atom in a perfect tetrahedron with the unpaired electron shared equally by the oxygen atoms. ESCA data support the  $\text{TiO}_4$  stoichiometry. If the material is dehydrated ("activated") under vacuum at 200 °C, the radical persists indefinitely. However, admission of moisture promptly produces hydrogen gas and concomitant loss of the ESR signal with the rate of loss proportional to the amount of water (vapor or liquid) admitted. Thus it is this photoformed radical which is the precursor of  $\text{H}_2$  formation in water submerged titanium-zeolite A. An analogous sequence of procedures using  $\text{SO}_2$  in lieu of  $\text{O}_2$  produces an identical ESR spectrum with noticeable yellowing of the material, presumably caused by elemental sulfur formation. In this case, the free radical again disappears with gas bubbling on admission of moisture.

Cations in zeolites may be thermally restored to an oxidation state that gives rise to either thermolysis or photolysis of water.<sup>10,11,16</sup> Thermolysis has been demonstrated for chromium and indium in Y zeolites,<sup>16</sup> whereas photolysis has been observed in silver exchanged Y- and A-type zeolites.<sup>10,11</sup> In the present case of titanium exchanged zeolite A the radical oxygenated complex may be thermally regenerated (275 °C at  $3 \times 10^{-2}$  Torr) yielding an ESR signal over half as large after 4 h as the initial intensity. Oxygen could conceivably evolve during the thermolysis but is not detectable chromatographically (since the process occurs under vacuum.) Heating above 400 °C, rather than regenerating more of the desired free radical, produces an unidentified radical species with an anisotropic peak centered at  $g = 1.974$ .

Thus a means other than heating must be found to achieve a closed photochemical cycle that harnesses visible solar energy in the production of molecular hydrogen. The titanium exchanged zeolite A does, however, lend itself to a thermolysis of water described previously.<sup>16</sup>

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**Supplementary Material Available:** ESCA spectra and discussion (20 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) In one hydrogen fueled automotive engine (Billings Corp., Provo, Utah) 0.79 kg of  $\text{H}_2$  is equivalent to 1.0 gal of gasoline. Electrolysis units sold with these engines consume 131 kWh of electrical power per kilogram of  $\text{H}_2$  produced. Even neglecting capital costs of electrolysis units and  $\text{H}_2$  storage tanks,  $\text{H}_2$  is thus an economically disadvantageous fuel at prevailing prices of electricity and gasoline by a factor of  $\sim$ 7.