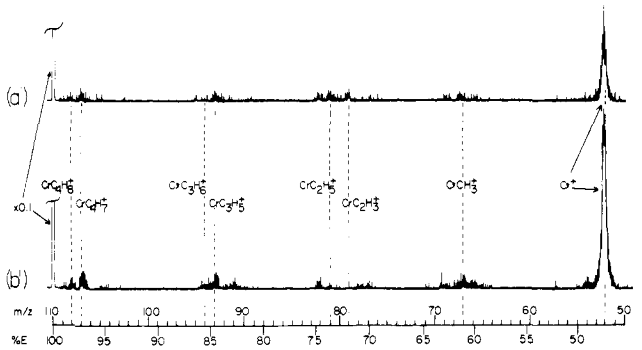

Figure 2. The collision-induced decomposition spectrum of $CrC_4H_{10}^+$ (*m/z* 114) formed in the ion source by reaction of $CrCO^+$ with *n*-butane (a′) and isobutane (b′). The accelerating voltage was 6 kV, and the collision gas was He. The small *m/z* 82 peak is $^{54}CrCO^+$ originating from $^{54}Cr(CO)_2^+$, which is a small fraction of the *m/z* 110 primary beam.

to **3** and **6**, which might be formed by insertion into a C–H bond followed by a β H-atom shift. Note that small amounts of $FeCH_3^+$ and $FeC_2H_5^+$ are observed, suggesting the occurrence of **1** in the isobutane case and **4** and **5** in the *n*-butane case. If we assume that $FeCH_3^+$ in the isobutane spectrum is formed from structure **1**, the absence of isopropyl cation from the spectrum suggests that $IP(FeCH_3) < IP(i\text{-}C_3H_7) = 7.36$ eV.[9] This in turn implies that $D(Fe^+\text{–}CH_3) - D(Fe\text{–}CH_3) > 11.8$ kcal/mol.

The striking feature of the CID spectra of the Cr^+–butane complexes shown in Figure 2 is the dominance of the Cr^+ fragment. This suggests that the Cr^+ is only loosely bound to the butane and that the butane tends to retain its integrity in the complex. This is consistent with the lesser extent of reactivity of Cr^+ with the butanes. Other fragments do appear in the CID spectrum, but they are mostly Cr^+–alkyl radical clusters rather than Cr^+–olefin clusters. These fragments suggest that there is some degree of incipient metal–carbon bond formation in the Cr^+–butane complexes but that β H-atom shift and reductive elimination do not proceed readily in the complexes. The lowest energy forms of the Cr^+–butane complexes are therefore very different from the lowest energy forms of the Fe^+–butane complexes.

Note Added in Proof: The reaction of Cr^+ with *n*-butane may result from the presence of ions in a long-lived excited state among the Cr^+ ions formed by electron impact on $Cr(CO)_6$. We observe Cr^+ from $Cr(CO)_6$ to react with CH_4 with a rate constant of ca. 10^{-10} cm³ molecule s⁻¹ to form $CrCH_2^+$. This reaction is almost certainly endothermic for ground state species. (See A. E. Stevens and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 6449 (1979), for data on $D(M^+\text{–}CH_2)$.) We also observe, using ion trapping techniques, that the kinetics of the reaction of Cr^+ with $Cr(CO)_6$ suggest two states of Cr^+ which react with different rates. The abundance of the slowly reacting state is roughly twice that of the rapidly reacting state. We have obtained no evidence that the reactions of Co^+, Fe^+, and Ni^+ with the butanes are affected by excited states.

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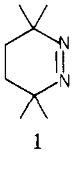
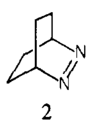
Facile Liquid-Phase Denitrogenation of "Reluctant" Azoalkanes on Photolysis with 185-nm Radiation

Sir:

While it is a well-established fact that cyclic azoalkanes, which contain the –N=N– linkage within a six-membered ring, resist denitrogenation (ϕ_r <0.05) on irradiation at 350 nm ($n_- \rightarrow \pi^*$ excitation),[1] we now report that at 185 nm ($n_+ \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ excitations) such "reluctant" azoalkanes can be smoothly and effectively denitrogenated into their corresponding hydrocarbons. Although it was suggested[2] that shorter wavelength radiation should promote denitrogenation, to the best of our knowledge the liquid phase 185-nm photochemistry of azoalkanes had not been previously investigated. The rich and abundant $\pi \rightarrow \pi^*$ photochemistry of cycloalkenes on 185-nm excitation[3] stimulated our interest in exploring the fate of the "reluctant" azoalkanes **1–3** on exposure to such "high-energy" radiation. As the quantum yields show, 185-nm radiation causes a dramatic increase [especially for the diazabasketene (**3**)] in the photodenitrogenation efficiency of such "reluctant" azoalkanes, thus confirming our expectation that $n_+ \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ excitation should be effective for such purposes.



1



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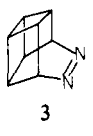

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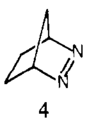

4

	1	2	3	4
ϕ_{350}	0.008	0.011	0.00006	1.0
ϕ_{185}	0.22	0.50	0.20	1.0
ϕ_{185}/ϕ_{350}	~30	~50	~3000	1

The 185-nm photolysis of the azoalkanes, prepared according to literature procedures,[4] was performed in Baker-Photrex pentane (0.01 M solution). A 50-W hot cathode mercury resonance lamp was used as the irradiation source; this was accommodated in a Suprasil immersion well and suspended into an outer vessel which contained the azoalkane solution.[5] The 254- and 350-nm (broad excitation band covering the range 310–420 nm) photolyses were performed in a Rayonet photoreactor under the same conditions as the 185-nm photolysis. Product analyses were made by vapor phase chromatography on a Perkin-Elmer Model 900 instrument equipped with a Perkin-Elmer Model II electronic integrator. The product composition, percent product formation, and quantum yields are reported in Table I.

Photodenitrogenation of azoalkane **4** and the cis–trans isomerization of cyclooctene were used as actinometers. The latter was previously used for 185-nm actinometry.[6] Consequently, the azoalkane **4**, which photodenitrogenates with essentially unit efficiency,[7] was first calibrated against the cyclooctene standard. An independent check confirmed gratifyingly that azoalkane **4**

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[6] The reported 3a value of $\phi_{c\rightarrow t}$ = 0.95 was corrected to be 0.35 (Srinivasan, R., private communication).

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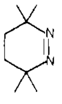
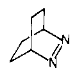
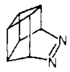
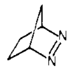
Table I. Photolysis Conditions, Product Composition, % Product Formation, and Quantum Yields of the Photodenitrogenation of Azoalkanes 1–4

azoalkane	photolysis conditions λ, nm	photolysis conditions t, s	product composition[a, b]	% product formation	quantum yield, ϕ	VPC conditions[c]
 1	185	900	22% IB + 12% TMCB	34	0.22[d,e]	A
	254	69 900	no products detected			
	350	58 500	70% IB + 18% TMCB	88	0.0083[f]	
 2	185	300	18% HD + 9% BCH	27	0.50[d,e]	B
	254	21 600	12% HD + 6% BCH	18	(0.0046)[g]	
	350	9 000	10% HD + 8% BCH	18	0.011[h]	
 3	185	900	27% COT + 4% benzene[i]	31	0.20[d,e]	C
	254	25 200	18% COT + 5% benzene	23	(0.005)[j]	
	350	67 500	0.7% COT (no benzene)	0.7	0.00006	
 4	185	300	54% BCP	54	1.02[d]	B
	254	28 800	67% BCP	67	(0.013)[g]	
	350	300	54% BCP	54	1.00[k]	

[a] IB = isobutylene; TMCB = 1,1,2,2-tetramethylcyclobutane; HD = 1,5-hexadiene; BCH = bicyclo[2.2.0]hexane; COT = cyclooctatetraene; BCP = bicyclo[2.1.0]pentane; ~5% error in the product percentages; ϕ values refer to product formation. [b] All products were characterized by comparison of VPC retention times with authentic materials. [c] A = 6 ft × 1/8 in. stainless steel column packed with 10% SE-30 on Chromosorb P (80–100 mesh); column and injector temperatures 78 and 90 °C, respectively. B = 8 ft × 1/8 in. stainless steel column packed with 10% β,β-oxydipropionitrile on Chromosorb P (80–100 mesh); column and injector temperatures 70 and 100 °C, respectively. C = 10 ft × 1/8 in. stainless steel column packed with 10% Carbowax 20 M on Chromosorb W (60–80 mesh); column and injector temperatures 80 and 140 °C, respectively. [d] When the cis–trans isomerization of cyclooctene is used as actinometer, $\phi_{c \rightarrow t} = 0.35$ (Srinivasan, R., private communication). [e] When azoalkane 4 is used as actinometer, $\phi_r = 1.00$ [ref 7(d)]. [f] Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* 1978, *100*, 1876. [g] 254-nm radiation contains ~2% 365-nm radiation, which is responsible for product formation. [h] Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* 1971, *93*, 6347, report $\phi_r = 0.022$. [i] Traces of acetylene were detected; the yields are optimized absolute yields which have been determined by quantitative VPC and have not been corrected for % consumption of the azoalkane; if corrected, ~80% COT is formed since ~35% azoalkane has been consumed; control experiments show that prolonged photolysis at 185 nm leads to destruction of the COT. [j] Control experiment showed that at 254-nm benzene sensitizes, although inefficiently, the photodenitrogenation of the diazabasketene. [k] Reference 7d.

photoeliminates nitrogen with unit efficiency at 185 nm. Within experimental errors (~10%), the same quantum yields of denitrogenation at 185 nm were obtained with both the azoalkane **4** and cyclooctene actinometers. At 350 nm the azoalkane **4** served as actinometer.

The quantum yield data of Table I clearly confirm that 185-nm photolysis is much more effective in the photodenitrogenation of the "reluctant" azoalkanes **1–3** than the 350-nm photolysis. Since the 185-nm source also radiates appreciable amounts of 254-nm radiation, as control experiments we investigated the 254-nm photochemistry of these azoalkanes. For example, azoalkane **4** gave $\phi_r = 0.013$. However, the 254-nm source emits ~2% 365-nm radiation, and consequently the low but measurable quantum yields of denitrogenation at 254 nm are due to this long wavelength impurity. Furthermore, in the case of diazabasketene (**3**), control experiments revealed that at 254-nm benzene sensitized the photoelimination of nitrogen. Consequently, we can conclude that 185-nm photolysis is an effective means of enhancing the denitrogenation of "reluctant" azoalkanes. The effect (3000-fold enhancement) is impressive for diazabasketene (**3**).

Although our initial hope to complete the elegant synthetic strategy[8] of preparing cubane via photodenitrogenation of diazabasketene by employing 185-nm radiation has again faltered, at least we have succeeded in extruding the nitrogen molecule smoothly, efficiently affording the cyclooctatetraene (see footnote *i* in Table I). The small amount of benzene is the consequence of secondary photolysis of cyclooctatetraene at 185 nm, as confirmed by control experiments. Whether cubane was formed in the 185-nm photolysis, but did not survive this high-energy radiation, could not be tested since no authentic cubane was available.

At present, very little is known about the spectroscopy of azoalkanes below 200 nm, but it is clear that the 185-nm radiation must engage $\pi \rightarrow \pi^*$ and/or $n_+ \rightarrow \pi^*$ excitations.[9] Therefore, besides inducing the photodenitrogenation of "reluctant" azoalkanes at 350 nm ($n_- \rightarrow \pi^*$ excitation) by employing elevated temperatures,[2,10–13] introducing radical stabilizing substituents[12] and ring strain,[12,14] or utilizing vapor-phase conditions,[2,10] the 185-nm photochemistry of these interesting molecules seems promising for mechanistic and synthetic exploration.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant No. 78-12621), and the National Institutes of Health (Grant No. GM-00141-04 and RR-8.02-07) for finanacial support. We are particularly grateful to Dr. R. Srinivasan (IBM) for getting us interested in and started on 185-nm photochemistry. We thank Professor F. D. Greene (MIT) for supplying us with a sample of azoalkane **1** and Professor P. S. Engel (Rice University) for a sample of azoalkane **2**. It is a pleasure to acknowledge the dedicated technical assistance of Miss Carmen Doris Santos.

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(15) NIH Career Awardee (1975-80); present address: Institute of Organic Chemistry, University of Würzburg, D-8700 Würzburg/am Hubland, West Germany.