9 Hz, 2 H), 8.25 (d, J = 9 Hz, 2 H); IR (mineral oil mull) 1510 (s), 1335 (s), 825 (s) cm^{-1}.

(h) Coupling of (2,4,6-Trimethylphenyl)boronic Acid with 2-Bromonitrobenzene. Following the general procedure, 2-bromonitrobenzene (505 mg, 2.50 mmol) was reacted for 48 h with (2,4,6-trimethylphenyl)boronic acid[9] (451 mg, 2.75 mmol). The crude product was purified on a basic alumina (grade III) column eluting with pentane/dichloromethane (50/50) to give 2-nitro-2′,4′,6′-trimethylbiphenyl (532 mg, 88% yield): mp (ethanol/water) 63–64 °C [lit.[12] 55–56 °C]; NMR ($CDCl_3$) δ 1.96 (s, 6 H), 2.31 (s, 3 H), 6.92 (s, 2 H), 7.14–7.80 (m, 3 H), 8.00 (d of d, J = 7.5 Hz, 3.0 Hz, 1 H); IR (melt) 1530 (s), 1355 (s), 860 (s), 790 (m) 760 (s), 710 (m) cm^{-1}; high-resolution mass spectrum, m/e calcd for $C_{15}H_{15}NO_2$ 241.1103, found 241.1127.

(i) Coupling of (2,4,6-Trimethylphenyl)boronic Acid with 3-Bromonitrobenzene. Following the general procedure, 3-bromonitrobenzene (1.01 g, 5 mmol) was reacted for 48 h with (2,4,6-trimethylphenyl)boronic acid[9] (902 mg, 5.5 mmol). The crude product was purified on a basic alumina column (grade III) eluting with pentane/dichloromethane (50/50) to give 3-nitro-2′,4′,6′-trimethylbiphenyl (1.15 g, 95% yield): mp (pentane) 82–83 °C [lit.[13] 83–84 °C]; NMR ($CDCl_3$) δ 2.00 (s, 6 H), 2.33 (s, 3 H), 6.98 (s, 2 H), 7.37–7.72 (m, 2 H), 8.00–8.13 (m, 1 H), 8.22 (t of d, J = 7.5 Hz, 2.2 Hz, 1 H); IR (mineral oil mull) 1525 (s), 1345 (s), 855 (m), 810 (m), 750 (m), 730 (s), 695 (s) cm^{-1}.

Table II. (a) Coupling of (3-Nitrophenyl)boronic Acid with Bromobenzene. Following the general procedure, bromobenzene (196 mg, 1.25 mmol) was reacted for 6 h with (3-nitrophenyl)boronic acid[14] (230 mg, 1.38 mmol) to give 3-nitrobiphenyl (237 mg, 95% yield). The product obtained by this route was identical with that obtained by coupling phenylboronic acid with 3-bromonitrobenzene.

(b) Coupling of (3-Nitrophenyl)boronic Acid with 2-Bromotoluene. Following the general procedure, 2-bromotoluene (214 mg, 1.25 mmol) was reacted for 9 h with (3-nitrophenyl)boronic acid[14] (230 mg, 1.38 mmol) to give 2-methyl-3′-nitrobiphenyl (260 mg, 98% yield). The product obtained by this route was identical with that obtained by coupling (2-methylphenyl)boronic acid with 3-bromonitrobenzene.

(c) Coupling of (3-Nitrophenyl)boronic Acid with 2-Bromomesitylene. Following the general procedure, 2-bromomesitylene (250 mg, 1.26 mmol) was reacted for 48 h with (3-nitrophenyl)boronic acid[14] (230 mg, 1.38 mmol) to give 3-nitro-2′,4′,6′-trimethylbiphenyl (302 mg, 99% yield). The product obtained by this route was identical with that obtained by coupling (2,4,6-trimethylphenyl)boronic acid with 3-bromonitrobenzene.

Acknowledgment. We thank the Cancer Research Coordinating Committee, University of California and the Committee on Research, University of California, Davis, for partial support of this work.

Registry No. $(Ph_3P)_4Pd$, 14221-01-3; 2-nitrobiphenyl, 86-00-0; 3-nitrobiphenyl, 2113-58-8; 2-methyl-2′-nitrobiphenyl, 67992-12-5; 2-methyl-3′-nitrobiphenyl, 51264-60-9; 4-methyl-2′-nitrobiphenyl, 70680-21-6; 4-methyl-3′-nitrobiphenyl, 53812-68-3; 4-methyl-4′-nitrobiphenyl, 2143-88-6; 2,4,6-trimethyl-2′-nitrobiphenyl, 14872-62-9; 2,4,6-trimethyl-3′-nitrobiphenyl, 39117-69-6; phenylboronic acid, 98-80-6; (2-methylphenyl)boronic acid, 16419-60-6; (4-methylphenyl)boronic acid, 5720-05-8; (2,4,6-trimethylphenyl)boronic acid, 5980-97-2; (3-nitrophenyl)boronic acid, 13331-27-6; 2-nitrobromobenzene, 577-19-5; 3-nitrobromobenzene, 585-79-5; 4-nitrobromobenzene, 586-78-7; bromobenzene, 108-86-1; 2-methylbromobenzene, 95-46-5; 2,4,6-trimethylbromobenzene, 576-83-0.

---

[12] Cadogan, J. I. G.; Todd, M. J. *J. Chem. Soc. C* **1969**, 2808.

[13] Vink, A. J.; Verheijdt, P. L.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1972**, *28*, 5081.

[14] Seaman, W.; Johnson, J. R. *J. Am. Chem. Soc.* **1931**, *53*, 711.

Photolytic Reaction of Chromium Carbene Complexes with Azobenzenes. Azo Metathesis

Louis S. Hegedus* and Andreas Kramer

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received April 9, 1984

Photolysis of solutions of azobenzenes and chromium carbene complexes in hexane solvent produces mixtures of 1,2- and 1,3-diazetidinones and imino ethers. Electron-rich azobenzenes such as p-methoxy- and p-(dimethylamino)azobenzene are very reactive, while p-nitroazobenzene is virtually inert. The reaction is thought to proceed by a photolytic cycloaddition of the azobenzene to the chromium carbene, followed by insertion/reductive elimination, or by metathesis to give an imino ether and a chromium "nitrene" complex.

Introduction

The inorganic chemistry of heteroatom-stabilized chromium carbene complexes has been extensively developed over the last 20 years.[1] It is only recently that this class of complexes has found application in organic synthesis.[2] Most notable is their use in the cyclopropanation of olefins[2,3] and their reactions with alkynes to produce naphthol or naphthoquinone derivatives.[4] We recently reported the photolytic reaction of chromium carbene complexes with

---

[1] For reviews on group 6 heteroatom-stabilized carbene complexes see: (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139. (c) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (d) Fischer, E. O. *Rev. Pure Appl. Chem.* **1970**, *24*, 407. (e) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487.

[2] (a) Brown, J. F. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Casey, C. P. *React. Intermed.* **1981**, *2*, 135. (c) Casey, C. P. In: "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 189.

[3] Fischer, E. O.; Dotz, K. H. *Chem. Ber.* **1972**, *105*, 1356, 3966.

[4] (a) Dotz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689 and references cited therein. (b) Wulff, W. D.; Tang, P. C.; McCullum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677. (c) Semmelhack, M. F.; Bozell, J. J.; Sado, T.; Wulff, W.; Speiss, E.; Zask, A. *Ibid.* **1982**, *104*, 5850.

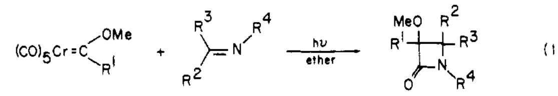
0276-7333/84/2303-1263$01.50/0

Table I. Photolytic Reaction of Azobenzenes with Complex 1

azobenzene				imino ether, %		diazetidinone,[c]	ratio[d]
Ar	Ar′	$h\nu$	T, °C	Ar	Ar′	%	1,2:1,3
Ph	Ph	a	30	65	0	10	1:1
		a	0	40	0	31	1:1
		b	0	35	0	34	15:85
Ph	*p*-MeOPh	a	30	20[e]	5	10	1:1
		a	0	35	0	30	1:2
		b	0	25	0	45	0:100
Ph	*p*-Me_2NPh	a	30	60	5	8	0:100
		b	0	45	0	29	0:100
Ph	*p*-NO_2Ph	a	30	~2	10	3	100:1
		b	0	no reaction			

[a] Full sunlight, July-December, 5000 ft altitude, Fort Collins, CO. [b] Six 20-Wt Vitalite fluorescent tubes. [c] Yield of isolated purified product. [d] Ratio estimated from NMR spectra of the pure mixture, before separation. [e] This material partially decomposed upon isolation. A substantially higher crude yield was obtained.

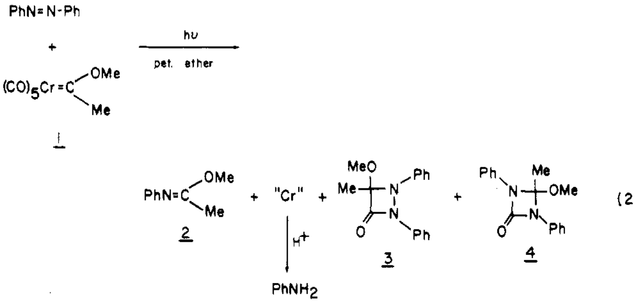
imines to produce β-lactams (eq 1).[5] Herein we report the results of this same reaction using azobenzenes as substrates.



(1)

Results and Discussion

Sunlight irradiation of a petroleum ether solution of azobenzene and (methylmethoxycarbene)pentacarbonylchromium(0) (1) at 30 °C produced a dark, heterogeneous mixture from which two organic components and a dark, chromium-containing residue could be separated (eq 2).



(2)

By far the major product was imino ether 2 (65%),[6] containing the carbene carbon and half of the azobenzene. Treatment of the chromium residue with aqueous hydrochloric acid, followed by neutralization, produced aniline in amounts comparable to the imino ether. The minor organic product (10% total) consisted of a 1:1 mixture of two different diazetidinones, ultimately shown to be the 1,2-diazetidinone 3 and the 1,3-diazetidinone 4. Crystallization of this mixture from petroleum ether led to isolation of pure 3, the structure of which was assigned from spectral data. In addition to the parent ion, a major peak in the mass spectrum corresponded to azobenzene (m/e 182), a fragment *only* possible from the 1,2-diazetidinone 3 and not the 1,3-diazetidinone 4. In the ^{13}C NMR spectrum, the carbonyl carbon appeared at δ 165.8, in the range of carbonyls reported for the 1,2-diazetidinones.[7] In addition, seven of the eight nonequivalent aromatic carbons were detected. The ^1H NMR spectrum had a singlet at δ 1.28 and one at δ 3.52, corresponding to the methyl and methoxy groups, respectively, and the C=O band in the infrared spectrum appeared at 1785 cm^{-1}.

The 1,3-diazetidinone 4 could never be entirely freed of traces of 3, and thus the mass spectrum was of little use in structure assignment. The ^1H NMR spectrum was substantially different from that of 3, with singlets at δ 1.92 and 3.38, and the infrared CO stretching absorption appeared at 1795 cm^{-1}. The ^{13}C NMR was most diagnostic. The signal from the carbonyl carbon was at δ 148.5, well upfield from that of the 1,2-isomer, and only four aryl carbonyl signals were observed, as expected for two equivalent aryl groups. In addition, this compound had *no* ^{13}C resonances at δ 145, expected for the N-bearing aromatic carbon in aniline-like systems, but rather a single, strong peak at δ 136.7, characteristic of the N-bearing aromatic carbon in *N*-acylanilines. Finally, all spectroscopic data for 4 where strictly analogous with the substituted 1,3-diazetidinone 5, for which an X-ray crystal structure determination has been carried out.

The product distribution of this reaction was remarkably sensitive to reaction conditions (Table I). Irradiation at lower temperatures (0 °C) in sunlight led to a decrease in the yield of imino ether 2 (40%), and a corresponding increase in the yield of cyclic products 3 and 4 (31%, as a 1:1 mixture). When six 20-W Vitalite fluoresent bulbs (which approximate the spectral distribution of sunlight) were used as a source of irradiation rather than direct sunlight, the proportion of cyclic compounds increased slightly, but under these conditions involving lower intensity light, 1,3-diazetidinone 4 was by far the major cyclic product. Unsymmetrically substituted azobenzenes also underwent this reaction. Thus irradiation of 4-methoxyazobenzene and complex 1 at 0 °C in petroleum ether using Vitalite gave a 45% yield of *exclusively* the 1,3-diazetidinone 5. No 1,2 product was detected. Additionally, a 25% yield of imino ether containing only the *unsubstituted* phenyl portion of this azobenzene was obtained. The structure of this substituted 1,3-diazetidinone was unequivocally established by a single-crystal X-ray diffraction study.[8] Its ^1H and ^{13}C NMR spectra and its mass spectrum were strictly analogous to those of compound 4, confirming the assignment of 4 as the 1,3-diazetidinone. Particularly characteristic was the ^{13}C absorption for the carbonyl carbon, which appeared at δ 148.8, well upfield from that observed for the 1,2-diazetidinone. The char-

---

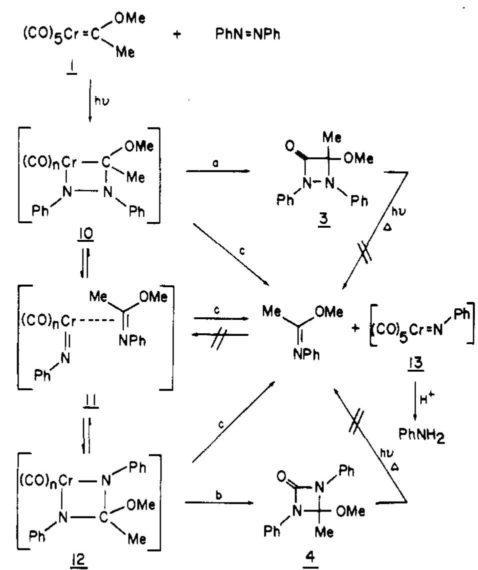
(5) (a) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *Ibid.* **1984**, *106*, 2680.

(6) Moodie, R. B.; Thomas, P. N.; Schofield, K. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1693.

(7) (a) Taylor, E. C.; Clemens, R. J.; Davies, H. M. L.; Haley, N. F. *J. Am. Chem. Soc.* **1981**, *103*, 7659. (b) Taylor, E. C.; Davies, H. M. L.; Clemens, R. J.; Yanagisawa, H.; Haley, N. F. *Ibid.* **1981**, *103*, 7660. (c) Taylor, E. C.; Haley, N. F.; Clemens, R. J. *Ibid.* **1981**, *103*, 7743. (d) Taylor, E. C.; Clemens, R. J.; Davies, H. M. L. *J. Org. Chem.* **1983**, *48*, 4567.

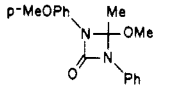
(8) This X-ray crystal structure was determined by Professor Oren P. Anderson, Department of Chemistry, Colorado State University. Full details will be published elsewhere.

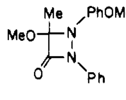
Scheme I

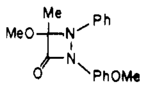


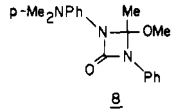
acteristic ^1H NMR peaks were singlets at δ 1.88 and 3.42 for the methyl and methoxy groups on the four-membered ring, and the infrared absorption of the carbonyl group appeared at 1785 cm^{-1}. The mass spectrum showed *no* fragment corresponding to methoxyazobenzene, a fragment available from the 1,2- but not the 1,3-diazetidinone.

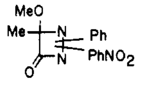
The product distribution of this reaction was also dependent upon both temperature and light intensity. Sunlight irradiation produced more imino ether and less of the diazetidinone. In addition, about one-third of the diazetidinone produced were the 1,2-isomers 6 and 7 easily distinguished by its ^1H NMR spectrum (singlets at δ 1.23 and 3.50 rather than δ 1.88 and 3.42). The 1,2-isomer appeared to be an inseparable mixture of both possible isomers, 6 and 7, since the ^1H NMR spectrum had singlets at δ 1.23 and 1.26, from the methyl groups of two different isomers. (The methoxy groups were magnetically equivalent.) In sunlight at 30 °C the yield of diazetidinone was even lower, and a small amount of iminoether containing the p-methoxyphenyl group[9] was detected.


5


6


7


8


9

Similarly, *p*-(dimethylamino)azobenzene and complex 1 combined to produce exclusively the 1,3-diazetidinone 8 having a characteristic ^1H NMR spectrum (singlets at δ 1.83 and 3.40 for methyl and methoxy groups). In addition, a high-resolution mass spectrum confirmed all expected fragments from the 1,3-adduct and, further, lacked a fragment corresponding to the azobenzene, expected for 1,2-adduct.

In contrast to electron-rich azobenzenes, the electron-deficient *p*-nitroazobenzene was relatively inert toward complex 1. Even after 4 days of sunlight irradiation, over 80% of the starting azobenzene remained. The only products isolated were a small amount of the nitro imino ether (~10%),[10] even less of 2 (~2%), and a very small (~3%) amount of diazetidinone. Its structure was assigned as the 1,2-diazetidinone 9 on the basis of its mass spectrum (strong *m/e* 227 fragment corresponding to 4-nitroazobenzene) and its ^1H NMR spectrum (methyl and methoxy peaks at δ 1.41 and 3.50, as is characteristic for the 1,2-system).

The formation of 1,3-diazetidinones and of imino ethers from the reaction of azobenzenes with chromium carbene complexes was unexpected. Scheme I details a reasonable sequence of steps by which all of the products observed in this reaction may be formed, but which awaits experimental verification. As with the related β-lactam-forming reaction (eq 1),[5] the reactions of azobenzenes requires irradiation. A reasonable first step is the photocycloaddition of the azobenzene to the chromium carbene complex to produce a diazametallacyclobutane 10. With high light intensity, CO insertion and reductive elimination to form the 1,2-diazetidinone 3 is favored (path a). Metathesis-like cleavage of 10 would produce unprecedented nitrene–imino ether complex 11. Readdition of the imino ether fragment in the opposite sense would produce metallacycle 12 that could insert CO and reductively eliminate 1,3-diazetidinone 4 (path b). This route is favored by low light intensity. Complexes 10, 11, or 12 could thermally fragment to produce imino ether and "nitrene" complex 13 (path c). Indeed higher temperatures favor production of imino ether over diazetidinone, and a corresponding amount of a dark, chromium residue that releases aniline upon acidification is obtained. Both diazetidinones 3 and 4 are stable to the reaction conditions and do *not* fragment to produce imino ether.

If the imino ether is a product of a metathesis reaction, the process could be reversible. To check this, the reaction in Scheme I was repeated by using azobenzene in which one aromatic ring was perdeuterated ($PhN{=}NPh\text{-}d_5$). Under both Vitalite and sunlight irradiation, recovered azobenzene and diazetidinones 3 and 4 contained only one perdeuterated phenyl group, indicating that no scrambling had occurred and path c, if operable, was irreversible. Attempts to trap the proposed "nitrene" complex, and to isolate the proposed metallacyclic intermediate are in progress, as are synthetic applications of this process.

Experimental Section

General Procedures. All melting points were obtained with a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4200 spectrometer. All 60-MHz ^1H NMR spectra were recorded on a Varian Model T-60 spectrometer using Me_4Si as an internal standard and are reported in δ. All ^{13}C NMR spectra were recorded on a JEOL JNM FX-100 Fourier transform spectrometer. Mass spectra were recorded on a V. G. Micromass 16F spectrometer. Exact mass spectra were obtained at Midwest Center for Mass Spectroscopy, University of Nebraska, Lincoln, NE.

All chromatographic isolations were accomplished by radial layer chromatography using a Chromatotron Model 7924 using aluminum oxide 60 GF (neutral) as adsorbent. Analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. All solvents were freshly distilled and stored under an argon atmosphere. Immediately before use they were degassed and saturated with argon. Diethyl ether (Fischer, Reagent Grade) was predried over $MgSO_4$, heated at reflux over Na with benzophenone, and distilled at atmospheric pressure under a N_2 atmosphere. Petroleum ether (Skelly solve F, petroleum naptha) was heated at reflux over CaH_2 and distilled at atmospheric pressure under a N_2 atmosphere. (Methylmethoxycarbene)-

---

[9] DeWolfe, R. H. *J. Org. Chem.* **1962**, *27*, 490.

[10] Martin, S. A.; Summers, P. G.; Upton, R. M. *J. Chem. Soc., Perkin Trans 1* **1973**, 2478.

pentacarbonylchromium(0) (1) was synthesized by literature procedure.[11,12] Azobenzene was purchased from Eastman. The azobenzene-d_5 was synthesized by literature procedure[13] from aniline-d_5 and nitrozobenzene purchased from Aldrich. The *p*-methoxyazobenzene and *p*-(dimethylamino)azobenzene were synthesized by literature procedures[14,15] from *p*-hydroxyazobenzene and *p*-aminoazobenzene purchased from Aldrich. The *p*-nitroazobenzene was synthesized by a selective nitration of azobenzene.[16]

General Procedure for the Photolytic Reaction of Azo Compounds with (Methoxymethylcarbene)pentacarbonylchromium(0) (1). Complex 1 (1 equiv) and the azo compound 1 equiv) were weighed into a Pyrex 125-mL Erlenmeyer flask that was then sealed with a rubber serum cap, evacuated, and filled with argon (three cycles). Distilled petroleum ether or diethyl ether (100 mL/mmol) was added by means of a cannula. The irradiation was performed as follows.

The Erlenmeyer flask was exposed to bright sunlight on the roof of the chemistry building for *x* h at 0 °C (placed in snow) or at ambient temperatures (25–35 °C). Alternatively, the Erlenmeyer flask was placed in a light box that contained six 20-W Vitalite fluorescent tubes and irradiated for *x* h. When the reaction was performed at 0 °C, the clear solution was transferred via cannula under argon into a modified Allihn condenser (the male joint was removed, the open end flame sealed, and the female joint was sealed with a rubber serum cap). The reaction mixture was cooled to 0 to −5 °C by circulating a methanol/water mixture, which was precooled in a constant temperature bath, through the condenser. The modified condenser was then placed in the Vitalite box.

During irradiation the original clear, yellow/orange solution rapidly darkened in color and deposited a black precipitate. The end point was determined to be when TLC (Al_2O_3, petroleum ether/ether) showed that all the azo compound was consumed. The reaction mixture was then filtered over "Celite" to yield a clear colored solution that was exposed to air in sunlight. After 2 h a great deal of precipitate was formed and the solution was clear and light yellow. Filtration and removal of the solvent in vacuo yielded a yellow oil. Purification was accomplished by chromatography on Al_2O_3.

Reaction of 1 with Azobenzene. 1,2-Diphenyl-4-methoxy-4-methyl-1,2-diazetidin-3-one (3). Carbene complex 1 (1 mmol, 250 mg) and azobenzene (1 mmol, 182 mg) were combined in the usual manner in a 125-mL Erlenmeyer flask, in petroleum ether (100 mL). The flask was placed in direct sunlight at 0 °C. After 6 h the mixture was dark brown and heterogeneous. Standard isolation and purification by Chromatotron (1-mm Al_2O_3 plate, petroleum ether/ether, 10:1) afforded two fractions. The product with the higher R_f (0.55), 60 mg (40%) of light yellow oil, was imino ether 2. All spectroscopic data were identical with the literature.[6] The lower R_f (0.35) fraction, 84 mg (31%) of clear oil, was confirmed by NMR to be a 1:1 mixture of the two isomers 3 and 4. By fractional crystallization from petroleum ether at −40 °C, the pure 1,2-diazetidinone 3 was precipitated as a white solid. Purification by recrystallization at −78 °C from petroleum ether gave white crystals: mp 128–129 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 1.28 (s, 3 H, CCH_3), 3.53 (s, 3 H, OCH_3), 6.8–7.3 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 165.8 (C=O); 144.8 (Ar*C*NR_2), 137.0 (Ar*C*N(R)C=O), 129.0 (Ph), 124.6 (Ph), 124.4 (Ph), 118.8 (Ph), 116.5 (Ph), 107.4 (*C*(CH_3)(OCH_3)), 53.2 (OCH_3), 18.7 (CH_3); mass spectrum, *m/e* 268 (parent), 240 (P − CO), 182 (PhN=NPh), 149 (PhN=C(CH_3)(OCH_3)), 119 (PhCNO), 91 (PhN), 86 (CO=C(CH_3)(OCH_3)), 77 (C_6H_5); IR (KBr) 1785 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.45; H, 5.89; N, 10.49.

By exactly the same procedure as indicated above, but irradiation in direct sunlight at 25–35 °C, the imino ether 2 was formed in 65% yield as main product. The diazetidinones 3 and 4, a 1:1 mixture confirmed by NMR, were formed in only 10%.

1,3-Diphenyl-4-methoxy-4-methyl-1,3-diazetidin-2-one (4). Carbene complex 1 (1 mmol, 250 mg) and azobenzene (1 mmol, 182 mg) were combined in the usual manner in a 125-mL Erlenmeyer flask in petroleum ether (100 mL). The clear orange reaction mixture was transferred into the modified Allihn condenser and irradiated with the Vitalite at 0 °C. After 48 h the mixture was dark brown and heterogeneous. Standard isolation and purification by Chromatotron afforded 91 mg (34%) of a 85:15 mixture of 1,3- and 1,2-diazetidinones 4 and 3, respectively, confirmed by NMR: ^1H NMR (60 MHz, $CDCl_3$) δ 1.92 (s, 3 H, CCH_3), 3.38 (s, 3 H, OCH_3), 6.8–7.3 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 148.5 (C=O), 136.7 (ArN(R)C=O), 129.3 (Ph), 122.7 (Ph), 115.4 (Ph), 100.5 (*C*(OCH_3)(CH_3)), 50.6 (OCH_3), 21.2 (CH_3) (these peaks were observed in addition to those previously reported for the 1,2-diazetidinone); IR (CCl_4) 1795 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.45; H, 5.89; N, 10.49.

Reaction of 1 with Monosubstituted Azobenzenes. 4-Methoxy-4-methyl-1-(4-methoxyphenyl)-3-phenyl-1,3-diazetidin-2-one (5). Carbene complex 1 (1 mmol, 250 mg) and 4-methoxyazobenzene (1 mmol, 212 mg) were combined in the usual manner in a 125-mL Erlenmeyer flask in petroleum ether (100 mL). The clear orange reaction mixture was transferred into the modified Allihn condenser and irradiated with Vitalite at 0 °C. After 24 h the mixture was dark brown and heterogeneous. Standard isolation and oxidation gave an oily solid that was purified by Chromatotron (1-mm Al_2O_3 plate, petroleum ether/ether, 10:2) to give 5 (135 mg, 45%) as a light yellow crystalline solid. Recrystallization at −20 °C from hexane gave white crystals: mp 95–96.5 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 1.88 (s, 3 H, CCH_3), 3.42 (s, 3 H, OCH_3), 3.78 (s, 3 H, $PhOCH_3$), 6.7–7.3 (m, 9 H, Ph); ^{13}C NMR ($CDCl_3$) δ 155.5 (Ar*C*OCH_3), 148.8 (C=O), 136.9 (Ar*C*N(R)C=O), 130.1 (CH_3OAr*C*N(R)C=O), 129.3 (Ph), 122.5 (Ph), 117.5 (Ph), 115.2 (Ph), 114.7 (Ph), 100.5 (*C*(OCH_3)(CH_3)), 55.5 ($ArOCH_3$), 50.5 (OCH_3), 21.1 (CH_3); mass spectrum, *m/e* 298 (parent), 179 [CH_3OPhN=C(OCH_3)(CH_3)], 149 [PhN=C(OCH_3)(CH_3) and CH_3OPhNCO], 119 (PhNCO), 107 (CH_3OPh), 91 (PhN), 77 (C_6H_5); IR (CCl_4) 1785 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.43; H, 5.98; N, 9.34.

When the reaction mixture, as described above, in a 125-mL Erlenmeyer flask was exposed to direct sunlight at 0 °C, the reaction was complete after 4 h. Standard isolation afforded 90 mg (30%) of a 1:2 mixture of 1,2- and 1,3-diazetidinones 6, 7, and 5, respectively, confirmed by NMR.

By the procedure as indicated above, but irradiation in direct sunlight at 25–30 °C, the following products were isolated: 30 mg (20%) of imino ether, 9 mg (5%) of methoxy imino ether, and 30 mg (10%) of a 1:1 mixture of 1,2- and 1,3-diazetidinones 6, 7, and 5, respectively, confirmed by NMR.

^1H NMR of 1,2-diazetidinone 6 and 7 (60 MHz, $CDCl_3$): δ 1.23 (s, 1.5 H, CCH_3), 1.26 (s, 1.5 H, CCH_3), 3.50 (s, 3 H, OCH_3), 3.77 (s, 3 H, $ArOCH_3$), 6.6–7.3 (m, 9 H, Ph). Anal. Calcd for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.43; H, 5.98; N, 9.34.

4-Methoxy-4-methyl-1-(4-(dimethylamino)phenyl)-3-phenyl-1,3-diazetidin-2-one (8). Carbene complex 1 (1 mmol, 250 mg) and *p*-(dimethylamino)azobenzene (1 mmol, 228 mg) were combined in the usual manner in a 125-mL Erlenmeyer flask in petroleum ether (100 mL). The clear solution was transferred into the modified Allihn condenser and irradiated with Vitalite at 0 °C. After 20 h the reaction mixture was dark brown and the reaction was complete. Standard isolation and oxidation gave a red brown oil, which was purified by Chromatotron (1-mm Al_2O_3 plate, petroleum ether/ether, 10:2) to give 8 (90 mg, 29%) as a light yellow crystalline solid. Recrystallization at −20 °C from petroleum ether gave light yellow crystals: mp 144–145 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 1.83 (s, 3 H, CCH_3), 2.92 (s, 6 H, N(CH_3)$_2$), 3.40 (s, 3 H, OCH_3), 6.6–7.3 (m, 9 H, Ph); exact mass calcd *m/e* 311.1635, found *m/e* 311.1663; mass spectrum, *m/e* 311 (parent), 192 [(CH_3)$_2$NPhN=C(OCH_3)(CH_3)], 162 [(CH_3)$_2$NPhNCO)], 161 [(CH_3)$_2$NPhN=C(CH_3)], 145 [PhN=C(OCH_3)(CH_3)], 119 (PhNCO), 91 (PhN), 77 (C_6H_5); IR (CCl_4) 1790 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.79; N,

---

[11] Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954.

[12] Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. T.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

[13] Gata, O. Y.; Takagi, U. Y. *J. Am. Chem. Soc.* **1958**, *80*, 3591.

[14] Woolfolk, E. O.; Donaldson, E.; Payne, M. *J. Org. Chem.* **1962**, *27*, 2653.

[15] Horner, L.; Muller, H. *Chem. Ber.* **1956**, *89*, 2756.

[16] Badger, G. M.; Lewis, G. E. *J. Chem. Soc.* **1953**, 2150.

13.45. Found: C, 69.64; H, 6.90; N, 13.37.

When the reaction mixture, as described above, in the 125-mL Erlenmeyer flask was exposed to direct sunlight at 25–35 °C, the reaction was complete after 4 h. Standard isolation provided 90 mg (60%) of imino ether **2**, 10 mg (5%) of (dimethylamino) imino ether, and 25 mg (8%) of 1,3-diazetidinone **8**.

4-Methoxy-4-methyl-1-(4-nitrophenyl)-2-phenyl-1,2-diazetidin-3-one (9). Carbene complex **1** (1.5 mmol, 375 mg) and 4-nitroazobenzene (1 mmol, 227 mg) were combined in the usual manner in a 125-mL Erlenmeyer flask, in ether (100 mL). The flask was placed in direct sunlight at 25–35 °C. After 4 days the reaction mixture was dark brown and heterogeneous. TLC showed still starting material; however, the reaction was worked up in the usual manner. Purification by Chromatotron (1-mm Al_2O_3 plate, hexane/ether, 10:1) afforded 20 mg (10%) of nitro imino ether and 9 mg (3%) of 1,2-diazetidinone **9** that was still contaminated with imino ether: ^1H NMR (60 MHz, CCl_4) δ 1.41 (s, 3 H, CCH_3), 3.50 (s, 3 H, OCH_3), 6.5–8.3 (m, 9 H, Ph); mass spectrum, m/e 313 (parent), 285 (P − CO), 227 ($NO_2PhN{=}NPh$); IR (CCl_4) 1805 (C=O) cm^{-1}. There was insufficient material to permit further purification and elemental analysis.

Azobenzene-d_5. The reaction with azobenzene-d_5 and the carbene complex **1** was carried out as described for azobenzene. The 85:15 mixture of 1,3-diazetidinone-d_5 **4** and 1,2-diazetidinone-d_5 **3**, synthesized by irradiation with Vitalite at 0 °C, gave a single parent peak at m/e 273 in the mass spectrum. No scrambling was observed. Purified azobenzene-d_5 recovered from an incomplete reaction (Vitalite, 25 °C, ~4 h), gave a single parent peak at m/e 187. Also the 1:1 mixture of **3**-d_5 and **4**-d_5 as well as pure 1,2-diazetidinone-d_5, synthesized by sunlight irradiation at 0 °C, gave no scrambling in the mass spectrum.

Acknowledgment. Support for this research under Grant No. 2R01GM21178-05 from the National Institutes of General Medical Sciences (PHS) is gratefully acknowledged. High-resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant No. CHE8211164). A.K. acknowledges the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung for partial financial support.

Registry No. **1**, 20540-69-6; **2**, 24433-81-6; **3**, 90742-54-4; d_5-**3**, 90742-52-2; **4**, 90742-55-5; d_5-**4**, 90742-56-6; **5**, 90742-57-7; **6**, 90742-58-8; **7**, 90742-59-9; **8**, 90742-60-2; **9**, 90742-53-3; PhN=NPh, 103-33-3; PhN=N(*p*-MeOPh), 2396-60-3; PhN=N(*p*-Me_2NPh), 60-11-7; PhN=N(*p*-NO_2PH), 2491-52-3; azobenzene-d_5, 90742-61-3.

Decomposition Channels of Chemically Activated Disilane. The π Bond Energy of Disilene and Its Derivatives

G. Olbrich,* P. Potzinger, and B. Reimann

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a. d. Ruhr, West Germany

R. Walsh*

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, United Kingdom

Received March 5, 1984

The Hg ($^3P_1$) sensitized photolysis of an H_2/SiH_4 mixture not only yields Si_2H_6 but also Si_3H_8 and Si_4H_{10}. The formation of the latter two products as well as parts of the Si_2H_6 yield is explained by the decomposition of chemically activated disilane, formed by the combination of two silyl radicals. The activated disilane decomposes mainly into $SiH_2 + SiH_4$ which finally reacts to Si_2H_6 and to a lesser extent into $H_2 + H_3SiSiH{:}$ and $H_2 + H_2SiSiH_2$. The silylsilylene inserts into SiH_4 yielding Si_3H_8, while disilene is thought to be scavenged successively by two SiH_3 radicals, the main reactive species under the given conditions. From the relative rate constants of the three decomposition channels, $\Delta H_f(H_3SiSiH{:}) = 273 \pm 11$ kJ/mol can be calculated. Also a lower bound to the π bond energy of disilene $B_\pi(H_2SiSiH_2) \geq 69 \pm 11$ kJ/mol is obtained. Ab initio CI calculations give $B_\pi(H_2SiSiH_2) = 93 \pm 8$ kJ/mol. A substituted disilene is shown to have a probable π bond energy of 108 ± 20 kJ/mol from a thermochemical analysis of literature data.

Introduction

In a previous publication we showed[1] that in the H atom induced decomposition of SiH_4 disilane is formed by two parallel pathways: (i) recombination of the primarily formed silyl radicals leading to a chemically activated disilane (eq 1) which is either stabilized or decomposes according to (eq 2); (ii) direct disproportionation of two silyl radicals leading also to silylene and silane (eq 3). Silylene inserts into SiH_4 yielding ultimately Si_2H_6.

$$2SiH_3 \rightarrow Si_2H_6(v) \tag{1}$$

$$Si_2H_6(v) \rightarrow SiH_2 + SiH_4 \tag{2}$$

$$2SiH_3 \rightarrow SiH_2 + SiH_4 \tag{3}$$

However, there must be other processes taking place as well. In their investigation of the 147-nm photolysis of SiH_4, Lampe and co-workers[2] observed Si_3H_8 also as a primary product. They proposed an additional decomposition channel for $Si_2H_6(v)$, namely, the decomposition to silylsilylene and hydrogen (eq 4). Silylsilylene will

$$Si_2H_6(v) \rightarrow H_3SiSiH{:} + H_2 \tag{4}$$

insert into SiH_4 yielding trisilane.[3] Hydrogen elimination from both silicon atoms under formation of disilene was also considered (eq 5), but volatile products that might

$$Si_2H_6(v) \rightarrow H_2SiSiH_2 + H_2 \tag{5}$$

---

[1] Reimann, B.; Matten, A.; Laupert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 500–504.

[2] Perkins, G. G. A.; Austin, E. R.; Lampe, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 1109–1115.

[3] Sefcik, M. D.; Ring, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 5168–5173.

0276-7333/84/2303-1267$01.50/0