

Table I

Compound	Nmr absorptions ( $\tau$ ) <sup>a</sup>	Compound	Nmr absorptions ( $\tau$ ) <sup>a</sup>
W(benzene) <sub>2</sub>	5.00 s	Mo( <i>N,N</i> -dimethylaniline) <sub>2</sub>	5.42 m (5.02 H)
W(toluene) <sub>2</sub>	5.10 s (5.00 H)		7.76 s (5.97 H)
	8.03 s (3.00 H)	Mo(toluene) <sub>2</sub>	5.40 m (4.97 H)
W( <i>o</i> -xylene) <sub>2</sub>	5.18 br s (4.00 H)		8.11 s (3.00 H) <sup>b</sup>
	8.09 s (6.26 H)	Mo(benzene) <sub>2</sub>	5.40 s
W(anisole) <sub>2</sub>	4.71 d (2.00 H)	Mo(fluorobenzene) <sub>2</sub>	4.88 d (2.01 H)
	5.24 t (2.00 H)		5.62 t (2.06 H)
	5.72 m (0.93 H)		5.95 m (0.93 H)
	6.88 s (3.30 H)	Mo(chlorobenzene) <sub>2</sub>	4.92 d (2.01H)
W(fluorobenzene) <sub>2</sub>	4.50 d (1.75 H)		5.57 t (2.11H)
	5.38 t (2.00 H)		5.78 m (0.82H)
	6.00 m (1.00 H)	Mo(methylbenzoate) <sub>2</sub>	4.40 d (1.86 H)
Mo(anisole) <sub>2</sub>	5.04 d (2.00 H)		5.33 m (3.12 H)
	5.48 t (2.32 H)		6.44 s (3.02 H)
	5.77 m (1.03 H)		
	6.82 s (3.22 H)		

<sup>a</sup> In perdeuteriobenzene or toluene. <sup>b</sup> M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 301 (1973).

zene, 71% yield for molybdenum and 1.8% for tungsten. At best this method is applicable to benzene and alkyl benzenes.

A more versatile method is the interaction of the free metal atoms with the substrates. The recent report by Green<sup>2</sup> and coworkers of the reaction of molybdenum atoms with benzene, to produce dibenzenemolybdenum, prompts us to report our results in synthesizing a variety of sandwich compounds with both molybdenum and tungsten atoms.

Green and coworkers employed e-gun heating of a molybdenum target for vaporization. We had dropped that method in favor of a simpler, less costly, and cleaner method, vaporization by resistive heating of tungsten or molybdenum wires, an extension of the methods employed for carbon vaporizations.<sup>3</sup> The 5–7 kV electron beam employed in e-gun methods can be used for vaporizations, but the atom flux and secondary electron flux are coincident, and the latter is the source of significant independent chemistry.<sup>4</sup> A 30-mil tungsten or molybdenum wire is easily heated with currents of 30–50 A (11–20 V) to temperatures suitable for vaporizations into the 10<sup>-5</sup> Torr vacuum, at rates of 1–2 mmol/hr.

Cocondensation at –196° of the metal atoms with the chosen arenes (molar ratios 100) results in formation of brightly colored matrices. On warming to room temperature the solutions of products in excess arene are siphoned out of the reaction system and isolated by sublimation (after removing excess substrate) at temperatures of 50–80° at pressures less than 10<sup>-3</sup> Torr. From runs in which 200–250 mg of metal is vaporized, the pure products are isolated in yields of 30–50%. Some of the products are shown in Table I. With the exception of the red molybdenum methylbenzoate and dimethylaniline products, the others are green or yellow-green.

The mass spectra (with expected isotope patterns) and proton magnetic resonance spectra serve to identify these products. Electron impact ionization to P<sup>+</sup> is a dominant process; fragmentation to molybdenum-

containing ions occurs by loss of one or both arenes; no tungsten-containing fragments were observed.

The unique synthetic value of this method is illustrated by the preparation involving O, N, and halogen containing substituents.

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## Flash Cadmium Photosensitization Studies. II. Absolute Rate Constants for the Quenching of Cadmium(<sup>5</sup>P<sub>0,1</sub>) Atoms

Sir:

The quenching reactions of Cd(<sup>5</sup>P) atoms have been extensively investigated and absolute rate constants determined for a variety of quenchers using conventional fluorescence techniques.<sup>1,2</sup>

In a recent communication from this laboratory<sup>3</sup> we described a novel flash photolysis-kinetic absorption spectroscopic technique for the study of the room temperature quenching reactions of triplet cadmium atoms. It was shown that equilibration of the <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> states is facile and in fact it is not possible to study the reactions of either state separately. The measured value of the decay rate constant of Cd(<sup>3</sup>P<sub>0,1</sub>) atoms in the presence of ethylene was some two orders of magnitude smaller than the earlier value of the Cd(<sup>3</sup>P<sub>1</sub>) quenching rate constant and it was concluded that conventional fluorescence techniques are not applicable for the determination of absolute rate constants for the quenching of Cd(<sup>5</sup>P<sub>1</sub>) atoms. The discrepancy can be attributed primarily to the intervention of <sup>3</sup>P<sub>0</sub> atoms in the reaction and to some extent to the effect of imprisonment on the fluorescence lifetime in the conventional measurements. Also, the technique used for calibration of the photographic plates in the early conventional studies was not fully satisfactory.

(1) H. C. Lipson and C. G. Mitchell, *Phys. Rev.*, **48**, 625 (1935).

(2) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, **11**, 164 (1943).

(3) P. J. Young, G. Greig, and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 413 (1970).

(2) F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J. Chem. Soc., Chem. Commun.*, 866 (1973).

(3) (a) P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Accounts Chem. Res.*, **6**, 97 (1973); (b) P. S. Skell, L. D. Westcott, Jr., J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).


(4) P. S. Skell and P. W. Owen, *J. Amer. Chem. Soc.*, **94**, 5434 (1972).

The purpose of the present communication is to report absolute rate constants and Arrhenius parameters for the decay of  $\text{Cd}(^3\text{P}_{0,1})$  atoms in the presence of a representative set of quencher molecules and to derive values for the quenching rate constants.

As in the previous communication, cadmium atoms were produced by the flash photolysis of dimethyl cadmium in the presence of an inert coolant, methane. The ground-state atoms absorb light from the primary flash and are promoted to the  $5^1\text{P}_1$  level from which, by collision induced intersystem crossing, the lower lying triplet manifold is populated with the appearance of the absorption lines of the  $5^3\text{P}_0$ ,  $5^3\text{P}_1$ , and  $5^3\text{P}_2$  atoms at 3404, 3466, and 3611 Å, respectively. Relaxation of the  $^3\text{P}_2$  state and equilibration of the  $^3\text{P}_0$  and  $^3\text{P}_1$  states are rapid, and decay of the latter two states by fluorescence is very nearly parallel. The first-order decay rate constant of  $^3\text{P}_0$  atoms in the range of 200–650 Torr  $\text{CH}_4$  pressure and 27–110°, from 144 measurements, is  $3.3 (\pm 0.5) \times 10^4 \text{ sec}^{-1}$ , corresponding to a lifetime of  $3.0 \times 10^{-5} \text{ sec}$  and a fluorescence decay rate constant of the  $^3\text{P}_1$  atoms  $\leq 1.8 \times 10^5 \text{ sec}^{-1}$ .

In the presence of the  $\text{CH}_4$  diluent the  $^3\text{P}_1$  atom concentration is too small to allow accurate quantitative measurements. Therefore decay rate constants were determined at various pressures of the added quencher from the measured decay rates of  $^3\text{P}_0$  atoms at 27°. The data are presented in Table I. Each rate constant

**Table I.** Decay Rate Constants and Arrhenius Parameters for  $\text{Cd}(^3\text{P}_0)$  Atoms<sup>a</sup>

Quencher	— $k$ , l. mol <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>-7</sup> —		No. of measurements	$E_a$ , <sup>c</sup> kcal/mol	log $A$ , <sup>c</sup> l. mol <sup>-1</sup> sec <sup>-1</sup> units
	27°	275°			
$\text{H}_2$	$4.8 \pm 1.2^b$		61	5.4	11.6
$\text{CH}_3\text{OH}$	$1.0 \pm 0.2$		24		
$\text{CH}_3\text{Cl}$	$3.8 \pm 0.7$		39		
$\text{C}_2\text{H}_4$	$64 \pm 15$		57	2.4	10.6
$\text{C}_2\text{H}_2$	$62 \pm 13$		36	2.4	10.6
<i>cis</i> - $\text{C}_4\text{H}_8$ -2	$97 \pm 30$		54	1.8	10.3
$\text{C}_2\text{H}_3\text{F}$	$14 \pm 3$		53	4.0	11.1
$\text{C}_2\text{F}_4$	$2.3 \pm 1.1$		52	4.5	10.7
	<0.5		58		
$\text{CH}_3\text{SiH}_3$	$160 \pm 50$		52		

<sup>a</sup> 0.5 Torr  $(\text{CH}_3)_2\text{Cd}$  + 300 Torr  $\text{CH}_4$ . <sup>b</sup> Weighted average, using the reciprocal standard deviation as weight. Errors are standard deviations. <sup>c</sup> Estimated error limit is approximately  $\pm 1.0 \text{ kcal/mol}$  or  $\pm 0.7$  in log  $A$ .

is the average of at least 50 measurements with errors given in standard deviations.

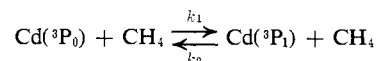
An Arrhenius-type temperature study was carried out on the ethylene reaction at four temperatures between 27 and 110° yielding from 200 measurements  $E_a = 2.3 \text{ kcal/mol}$  and log  $A = 10.6$  in l. mol<sup>-1</sup> sec<sup>-1</sup> units. From this it was possible to calculate the value of the rate constant at 275°, at which temperature relative rate constants for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and *cis*- $\text{C}_4\text{H}_8$ -2 have been reported by Tsunashima, Satoh, and Sato.<sup>4</sup> We also measured the relative quenching rates of fluoroethylenes at 275°. The Arrhenius parameters were then calculated using the values available at 25 and 275°.

(4) S. Tsunashima and S. Sato, *Bull. Chem. Soc. Jap.*, **40**, 2987 (1967); S. Tsunashima, S. Satoh, and S. Sato, *ibid.*, **43**, 2389 (1970).

The reported rate constants and Arrhenius parameters are for the observed decay of  $^3\text{P}_0$  atoms. The decay rates of  $^3\text{P}_1$  atoms were determined in two cases, with ethylene and hydrogen, and found to be 5 and 2% higher than those of  $^3\text{P}_0$  atoms, respectively. Now, it can be readily shown that the experimental decay rate constants are related to the quenching rate constants by the equation

$$\frac{k_1}{k_1 + k_2} k(^3\text{P}_1) + \frac{k_2}{k_1 + k_2} k(^3\text{P}_0) = k_{\text{exptl}}$$

where  $k_1$  and  $k_2$  refer to the reactions



Owing to the lower excitation energy of the  $^3\text{P}_0$  state,  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0) \leq k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$ . If  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0) = k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$ , then  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0) = k(^3\text{P}_1 \rightarrow ^1\text{S}_0) = k_{\text{exptl}}$ . Otherwise  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0)$  is higher and  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0)$  is lower than  $k_{\text{exptl}}$ . In the extreme when  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0)$  is assumed to be zero  $k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$  will be higher than  $k_{\text{exptl}}$  by a factor of

$$\leq \frac{k_1 + k_2}{k_1} = 5.4$$

Thus,  $k_{\text{exptl}}$  is an upper limit for  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0)$  and a lower limit for  $k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$ . For mercury, where the  $^3\text{P}_0 - ^3\text{P}_1$  splitting is 5 kcal/mol,  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0)$  is about 1.65 times smaller than  $k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$  for quenching by ethylene<sup>5,6</sup> and therefore for cadmium, where the splitting is only 1.55 kcal/mol, it is unlikely that the difference in the values of  $k_{\text{exptl}}$ ,  $k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$ , and  $k(^3\text{P}_0 \rightarrow ^1\text{S}_0)$  would exceed the experimental error. For the hydrogen abstraction reactions the situation is different. Here, even for mercury the  $^3\text{P}_1$  and  $^3\text{P}_0$  states show significant differences,<sup>5,6</sup> hence it is likely that  $k(^3\text{P}_1 \rightarrow ^1\text{S}_0)$  will be close to the upper limit,  $5.4k_{\text{exptl}}$ .

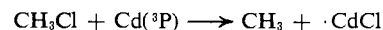
The rate constant values obtained in the present study are all 1 or 2 orders of magnitude smaller than those reported in the literature for the quenching of  $\text{Cd}(^3\text{P}_1)$  atoms and are more consistent with the low excitation energy of triplet cadmium atoms.

The hydrogen reaction features a substantial activation energy and an  $A$ -factor which is approximately equal to the gas kinetic collision frequency. The decay rate constants in the presence of paraffins are smaller and the activation energies involved are probably larger. As with the  $\text{Hg}(6^3\text{P}_1)\text{-H}_2$  quenching reaction this can be taken as evidence for an insertive rather than an abstractive type reaction<sup>7,8</sup>



The presence of  $\text{CdH}$  is evidenced by the appearance of the  $\text{CdH}$  spectrum in absorption.

The quenching by methyl chloride is *via* Cl-atom abstraction



(5) A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **41**, 1705 (1964).

(6) A. Callear and J. McGurk, *J. Chem. Soc., Faraday Trans. 2*, **69**, 97 (1973).

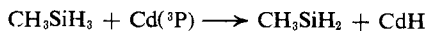
(7) H. E. Gunning, J. M. Campbell, H. S. Sandhu, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 746 (1973).

(8) W. H. Breckenridge and A. B. Callear, *Trans. Faraday Soc.*, **67**, 2009 (1971).

as indicated by the appearance of the CdCl spectrum in absorption.

The marked trend in the rates and activation energies of the olefins points to the electrophilic nature of the triplet cadmium atom by analogy with the behavior of the triplet mercury atom.<sup>9</sup> The generally lower rate constants with cadmium reflect the nonvertical nature of triplet energy transfer,  $\text{Cd}(^3\text{P}) + \text{olefin} \rightarrow \text{olefin}$  (nonvertical triplet). The activation energies are probably due to the presence of an energy barrier at the cross-over point of the potential energy surfaces correlating with the  $\text{Cd}(^3\text{P}) + \text{olefin}$  and  $\text{Cd} + \text{olefin}$  (triplet) states.

The quenching by methylsilane is *via* hydrogen abstraction from the silicon moiety



Silicon hydrides are excellent hydrogen donors, but the high value of the rate constant is somewhat surprising since it is considerably higher than the rate constant for hydrogen abstraction by hydrogen atoms,<sup>10</sup>  $3.1 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$ , while the enthalpy changes of the two reactions are approximately equal.

Further studies are in progress.

**Acknowledgments.** The authors are indebted to the National Research Council of Canada for financial assistance and Mr. R. Kadlec for helpful assistance in the construction of the apparatus.

(9) Y. Rousseau, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **39**, 962 (1963).

(10) K. Obi, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Phys. Chem.*, **76**, 3911 (1972).

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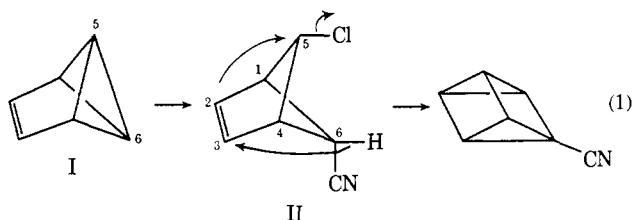
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## Additions of Chlorosulfonyl Isocyanate and Sulfonyl Halides to Benzvalene

Sir:

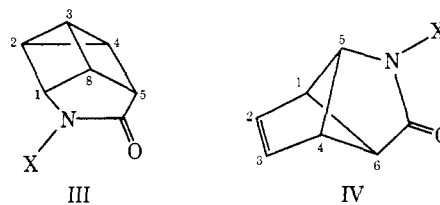
Benzvalene (I) has suddenly become so readily available<sup>1</sup> that if we knew how it behaved, it could become a very useful molecule in synthesis.<sup>2</sup> The reactions of benzvalene with two kinds of reagents, sulfonyl halides<sup>3</sup> and chlorosulfonyl isocyanate,<sup>4</sup> are reported here and result in syntheses of derivatives of benzvalene and of bicyclo[2.1.1]hexene, materials difficult to make otherwise. The study of sulfonyl halides and chlorosulfonyl isocyanate began with the idea that if benzvalene could be transformed into a material like II below and then further transformed as

indicated in eq 1, a simple synthesis for prismanes



would result. The first of these goals has been achieved but not the second.<sup>5</sup>

Chlorosulfonyl isocyanate (1.1 mol in  $\text{CH}_2\text{Cl}_2$ , initially  $-20^\circ$ , then 5 hr at  $25^\circ$ ) reacts with benzvalene in ether giving IIIa (6 parts), IVa (2 part), and another



a, X =  $\text{SO}_2\text{Cl}$   
b, X = H

adduct (2 parts),<sup>6</sup> which were not isolated but, upon further reaction with dimethylformamide at room temperature for 48 hr,<sup>7</sup> give II and an isomeric chloronitrile and with 4 N NaOH in acetone-water<sup>4d</sup> at  $0^\circ$  IIIb and IVb.<sup>8</sup> Both nitriles and lactams were isolated by chromatography on silica gel<sup>9</sup> and then crystallized.<sup>10,11</sup>

The proton nmr spectra provide the primary evidence for the structures: for II the similarity to the spectrum of the analogous dibromobicyclo[2.1.1]hexane;<sup>2a,12</sup> for IIIb the five chemical shifts<sup>14</sup> in the spectrum of the

(5) Reagents tried:  $\text{KOC}(\text{CH}_3)_3$  in THF,  $\text{MN}[\text{Si}(\text{CH}_3)_2]$  (M = Li, Na, K) in  $(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{LiN}(i\text{-C}_3\text{H}_7)_2$  in  $(\text{C}_2\text{H}_5)_2\text{O}$ , KH in  $(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{KNH}_2$  in  $\text{NH}_3$ .

(6) The three adducts were isolated by Dr. Nancy Acton, and their ratio in the reaction product analyzed by proton nmr. The third is incompletely characterized.

(7) The reaction is patterned on the conversion of *N*-chlorosulfonyl- $\beta$ -lactams into unsaturated nitriles: (a) K. Matterstock and G. Lohaus, DAS 1,253,704 (1964) mentioned in R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968); (b) E. J. Moriconi and C. C. Jalandoni, *J. Org. Chem.*, **35**, 3796 (1970).

(8) The expected third lactam has not yet been isolated.

(9) Using *n*-pentane-ether for the nitriles and  $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$  for the lactams.

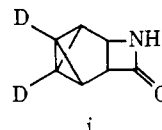
(10) For each new compound the analyses for all elements except oxygen were determined satisfactorily and the mass spectra exhibit the required parent peaks. Infrared absorptions characteristic of all functional groups were observed.

(11) Yields and melting points: II, 31%,  $26\text{--}27^\circ$  (from pentane); the isomer of II, 10%,  $40\text{--}41^\circ$  (from ether-pentane); IIIb, 21%,  $86\text{--}87^\circ$  (from  $\text{CHCl}_3$ -pentane); IVb, 5%,  $80\text{--}81^\circ$  (from ether-pentane).

(12) In  $\text{CDCl}_3$ :  $\tau$  3.07 (t, 1.97 H,  $\text{H}_2$ ,  $|J_{12}| = 2 \text{ Hz}$ ), 5.51 (t, 1.03 H,  $\text{H}_6$ ,  $|J_{16}| = 2 \text{ Hz}$ ), 5.68 (s, 0.99 H,  $\text{H}_5$ ), 6.92 (q 2.08 H,  $\text{H}_1$ ). The difference in the chemical shifts in the dibromo derivative and in II is larger for the triplets than for the singlets, indicating the location of Cl and CN.<sup>13</sup>

(13) (a) L. M. Jackman and S. J. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, table 3-2-10; (b) ref 2a, footnotes 12 and 13.

(14) If the structure had been i there would have been only four.



IIIb's resonances in  $\text{CDCl}_3$  are  $\tau$  2.73 (NH) and multiplets 5.62 ( $\text{H}_1$ ,  $|J_{18}| = 5.5 \text{ Hz}$ ,  $|J_{1\text{NH}}| = |J_{12}| = 2 \text{ Hz}$ ), 6.54 ( $\text{H}_5$ ), 7.17 ( $\text{H}_2$  and  $\text{H}_3$ ), 7.60 ( $\text{H}_2$ ), 7.83 ( $\text{H}_4$ ).  $\text{H}_5$  is split by NH into 1 Hz doublets.