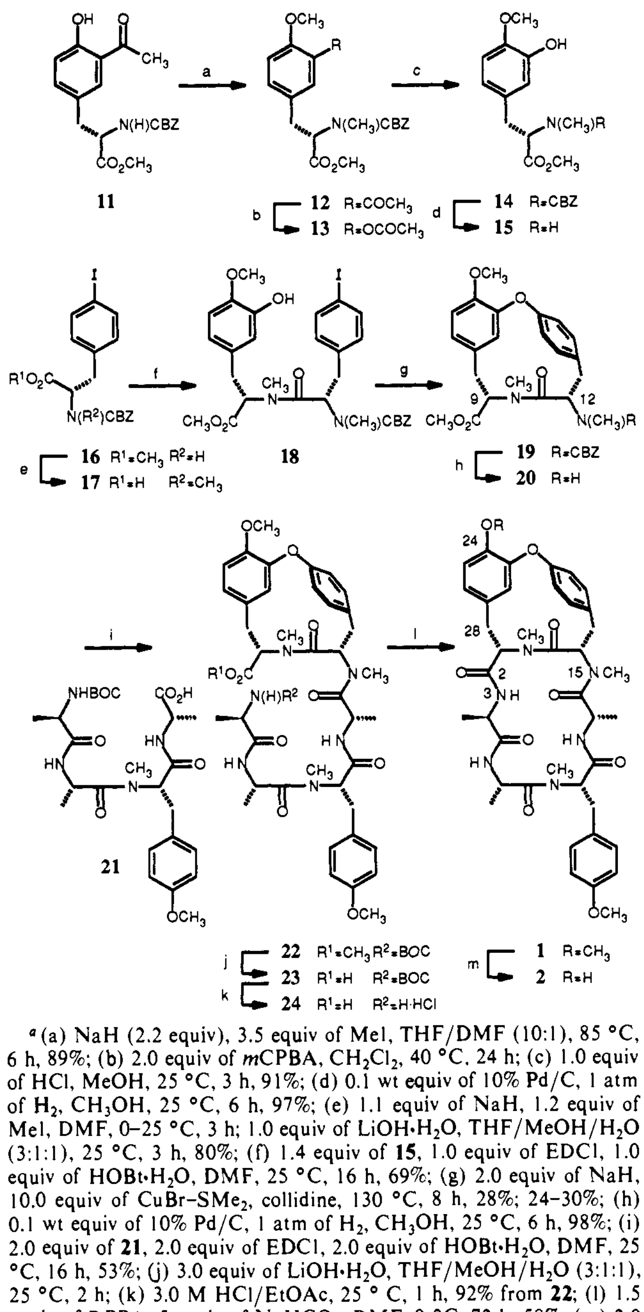
Scheme I



[a] (a) NaH (2.2 equiv), 3.5 equiv of MeI, THF/DMF (10:1), 85 °C, 6 h, 89%; (b) 2.0 equiv of *m*CPBA, CH_2Cl_2, 40 °C, 24 h; (c) 1.0 equiv of HCl, MeOH, 25 °C, 3 h, 91%; (d) 0.1 wt equiv of 10% Pd/C, 1 atm of H_2, CH_3OH, 25 °C, 6 h, 97%; (e) 1.1 equiv of NaH, 1.2 equiv of MeI, DMF, 0–25 °C, 3 h; 1.0 equiv of $LiOH{\cdot}H_2O$, THF/MeOH/H_2O (3:1:1), 25 °C, 3 h, 80%; (f) 1.4 equiv of **15**, 1.0 equiv of EDCI, 1.0 equiv of $HOBt{\cdot}H_2O$, DMF, 25 °C, 16 h, 69%; (g) 2.0 equiv of NaH, 10.0 equiv of $CuBr{-}SMe_2$, collidine, 130 °C, 8 h, 28%; 24–30%; (h) 0.1 wt equiv of 10% Pd/C, 1 atm of H_2, CH_3OH, 25 °C, 6 h, 98%; (i) 2.0 equiv of **21**, 2.0 equiv of EDCI, 2.0 equiv of $HOBt{\cdot}H_2O$, DMF, 25 °C, 16 h, 53%; (j) 3.0 equiv of $LiOH{\cdot}H_2O$, THF/MeOH/H_2O (3:1:1), 25 °C, 2 h; (k) 3.0 M HCl/EtOAc, 25 ° C, 1 h, 92% from **22**; (l) 1.5 equiv of DPPA, 5 equiv of $NaHCO_3$, DMF, 0 °C, 72 h, 58%; (m) 2.0 equiv of BBr_3, CH_2Cl_2, −78 to 0 °C, 3 h, 57%.

NMR, IR, EIMS, $[\alpha]^{21}_D$ −225° (c = 0.3, $CHCl_3$)[3]].

The successful implementation of the Ullmann macrocyclization reaction for direct formation of the elusive 14-membered diaryl ether representative of that found in **1–8** has been achieved.[24] Efforts to improve the macrocyclization procedure and its application in the preparation of conformational analogues of the natural products are in progress.

Acknowledgment. This work was assisted financially by the National Institutes of Health (CA41101) and a Purdue University Cancer Center fellowship (D.Y. 1988–1989). We thank Dr. T. Inaba for a generous sample of RA-VII, Professor R. B. Bates for providing photocopies of the ^{1}H NMR of deoxybouvardin (250 MHz, $CDCl_3$), Professor J. Hoffmann for an authentic sample of deoxybouvardin, and Professor H. Itokawa for an authentic sample of RA-VII.

(24) Efforts to close the 14-membered ring with C^{11}–N^{10} amide bond formation employing conventional macrolactamization techniques, efforts to close the 14-membered ring with diaryl ether formation through use of the reversed intramolecular Ullmann reaction (O^2–C^3 versus O^2–C^1 bond formation), or oxidative phenolic coupling on *O-seco*-deoxybouvardin[8] have not yet proven successful.

Supplementary Material Available: A general procedure for conduct of the Ullmann macrocyclization and full spectroscopic and physical characterization of **10a–f**, **12**, **14**, **17–19**, **22**, **1**, and **2** (11 pages). Ordering information is given on any current masthead page.

Novel Dimetal Complex Containing M(VI) and M(II) Centers United by a Short Metal–Metal Bond: $O_3ReReCl_2(Me_2PCH_2PMe_2)_2$

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The ability of multiply bonded dimetal complexes[1] to undergo *intramolecular disproportionation* reactions to yield products in which a multiple bond is retained offers some fascinating prospects for further developments in the chemistry of this class of compounds. However, very few such systems have been encountered to date, noteworthy examples being $(RO)_2X_2ReReX_2(PPh_3)_2$ (X = Cl, Br; R = Me, Et, *n*-Pr, *i*-Pr),[2] $Cl_4ReReCl(dth)_2$ (dth = $Me_2SCH_2CH_2SMe_2$),[3] $(Me_3SiCH_2)_2Mo[\mu\text{-}(CH_2)_2SiMe_2]Mo(PMe_3)_3$,[4] and $(i\text{-PrO})_4MoMo(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[5] In these cases the M–M bond orders can be considered to be 4, 3.5, 3, and 3, respectively, and the *formal* oxidation states are Re(IV)Re(II), Re(IV)Re(I), Mo(III)Mo(I), and Mo(IV)Mo(0).[6] We now report the isolation and structural characterization of the dirhenium(VI,II) complex $O_3ReReCl_2(dmpm)_2$ (**4**) (dmpm = $Me_2PCH_2PMe_2$) that has not only a disparity in metal oxidation states equal to that in $(i\text{-PrO})_4MoMo(dmpe)_2$[5] but also a difference in coordination numbers (4 and 7) that is unprecedented in the chemistry of metal–metal-bonded dimetal species.

This complex was obtained as one of three products from the reaction of *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (**1**) with a solution of dmpm in toluene (1.3 M). A quantity of **1** (0.20 g, 0.299 mmol) in 15 mL of ethanol was admixed with 0.46 mL of dmpm/toluene (0.598 mmol) and the mixture stirred at room temperature for 15 min. A quantity of brown insoluble $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-}dmpm)_2$ (**2**) was filtered off [0.09 g (36%) after recrystallization],[7,8] the filtrate evaporated to dryness, and the residue treated

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(2) (a) Chakravarty, A. R.; Cotton, F. A.; Cutler, A. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 4795. (b) Chakravarty, A. R.; Cotton, F. A.; Cutler, A. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3619.

(3) (a) Bennett, M. J.; Cotton, F. A.; Walton, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3866. (b) Bennett, M. J.; Cotton, F. A.; Walton, R. A. *Proc. R. Soc. London, A* **1968**, *303*, 175.

(4) Anderson, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

(5) Chisholm, M. H.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 2514.

(6) For a further discussion on the formulation of such complexes, see: Walton, R. A. In *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Jr., Ed.; Plenum: New York, 1990; pp 7–17. Note that the high bond orders are in accord with the experimentally observed very short M–M distances.

(7) This product was recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{12}H_{31}Cl_4O_2P_4Re_2$: C, 17.04; H, 3.67. Found: C, 16.76; H, 3.65. The identity of this paramagnetic complex is supported by the similarity of its ESR spectrum and electrochemical properties to those of its structurally characterized dppm analogue $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$).[8]

(8) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 5024.

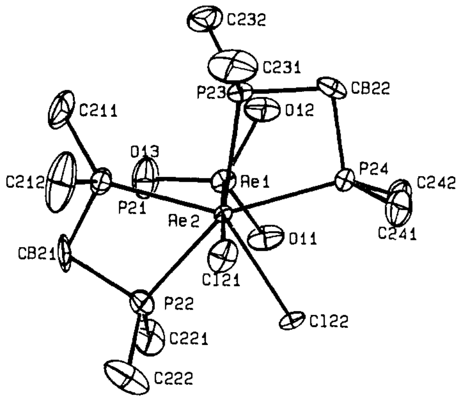
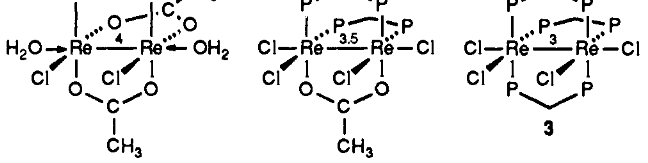


Figure 1. ORTEP view of one of the crystallographically independent molecules of $O_3ReReCl_2(dmpm)_2$ with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level. Some important representative bond distances (Å) and angles (deg) for this molecule are as follows: Re(1)–Re(2) = 2.4705 (5), Re(1)–O(11) = 1.716 (7), Re(1)–O(12) = 1.717 (7), Re(1)–O(13) = 1.729 (7), Re(2)–Cl(21) = 2.553 (2), Re(2)–Cl(22) = 2.483 (2), Re(2)–P(21) = 2.449 (3), Re(2)–P(22) = 2.422 (3), Re(2)–P(23) = 2.459 (2), Re(2)–P(24) = 2.427 (2); Re(2)–Re(1)–O(11) = 107.2 (2), O(11)–Re(1)–O(12) = 110.1 (4), Re(1)–Re(2)–Cl(21) = 178.95 (6), Re(1)–Re(2)–Cl(22) = 95.69 (6), Re(1)–Re(2)–P(23) = 90.37 (6), Re(1)–Re(2)–P(24) = 90.44 (6), Cl(21)–Re(2)–Cl(22) = 83.43 (8), Cl(21)–Re(2)–P(23) = 90.68 (8), Cl(22)–Re(2)–P(24) = 73.93 (8), P(23)–Re(2)–P(24) = 66.02 (8), P(21)–Re(2)–P(23) = 80.89 (9).

with a small volume of acetone to yield an orange-red solid that proved to be a mixture of the known complex $Re_2Cl_4(\mu\text{-dmpm})_3$ (3) (0.05 g, 18%)[9] and 4 (0.03 g, 13%). The mixture was dissolved in dichloromethane, and the components were separated by column chromatography.[10]



1 2 3

The X-ray crystal structure of 4 was determined on a crystal grown by slow evaporation of a CH_2Cl_2/acetone solution (ca. 1:3 by volume).[11-13] The important features of this structure are shown in Figure 1. There are two independent molecules in the asymmetric unit. These are structurally indistinguishable so that the structural parameters of only one of them will be discussed. The molecule consists of two Re atoms in quite different environments, namely, tetrahedral 4-coordinate and pentagonal-bipyramidal 7-coordinate, that are joined by a very short unsupported Re–Re bond (2.4705 (5) Å). While the molecule possesses no crystallographically imposed symmetry, it has virtual C_s symmetry with the mirror plane encompassing the two Re and two Cl atoms as well as O(11) of the ReO_3 fragment.[14] In accord with this, the Cl(21)–Re(2)–Re(1) angle is essentially linear (178.95 (6)°) and the Cl(22)–Re(2)–Re(1)–O(11) torsional angle is 0.1 (3)°. The Re–O bond lengths and O–Re–O angles associated with the ReO_3 unit are similar to those reported for other $(L)ReO_3$ species (where L represents a *single* donor atom such as F, Cl, O, or N from a monoanionic ligand),[15-17] although the angles (110.1 (4)–112.3 (4)°) are at the higher end of the range reported previously.

Formally, the compound consists of Re(VI) and Re(II) centers, so that while it bears a close relationship to Herrmann's half-sandwich complexes $(\eta^5\text{-}C_5R_5)ReO_3$,[18,19] the trioxorhenium unit is best considered to contain Re(VI) rather than Re(VII). The Re–Re interaction can then be viewed in its simplest terms as arising from the coupling of d^1 and d^5 fragments to give a strong σ bond, although the actual Re–Re bond order could be greater than 1. Not only is this the first time that the ReO_3 unit has been found to partake in direct metal–metal bonding, but the ability of a 6-coordinate Re(II) species of the type $ReCl_2(PR_3)_4$ to form such a bond is unexpected and unprecedented. Complexes such as *trans*-$ReX_2[R_2P(CH_2)_2PR_2]_2$, and related ones that also contain a *two*-carbon fragment between the phosphorus atoms as well as their one-electron-oxidized congeners,[20] are stable species that have not previously been found[21] to undergo reactions in which the metal stereochemistry deviates from pseudooctahedral. It may be that the smaller bite associated with the chelating $Me_2PCH_2PMe_2$ ligand permits an expansion of the metal coordination number from 6 to 7 and hence the formation of a Re–Re bond. Additional studies are underway to explore this point further.

The oxygen in the ReO_3 fragment probably originates from the water molecules that are present in **1**. Thus, when the pyridine adduct $Re_2(O_2CCH_3)_2Cl_4(py)_2$ is used as the starting material, reaction with dmpm affords **2** as the only identified product (80% yield) after 12 h. When the reaction between **1** and dmpm was carried out under an atmosphere of air rather than dinitrogen, a small quantity of **3** was identified but there was no evidence for the formation of any **4**.

Further studies are underway to examine the reactivity of the novel complex **4** and to devise synthetic strategies that can be used to prepare other complexes of this unusual type.

Acknowledgment. Support from the National Science Foundation, through Grant No. CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVax II computer and diffractometer, is gratefully acknowledged. One of us (I.A.) thanks the Spanish Ministerio de Educacion y Ciencia for a

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(10) A silica gel (230–400 mesh) column (length 10 cm and diameter 1.5 cm) was used with CH_2Cl_2/acetone (ca. 1:3 by volume) as eluent. A red-pink band of 3 eluted first, followed by a yellow-orange band of 4.

(11) Red crystals of 4 are monoclinic, space group $P2_1/c$, with a = 15.033 (2) Å, b = 18.707 (2) Å, c = 14.790 (2) Å, β = 100.833 (8)°, V = 4085 (2) Å^3, Z = 8, and d_{calcd} = 2.483 g/cm^3. X-ray data were collected at 20° on a 0.57 × 0.50 × 0.44 mm crystal for 5542 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius diffractometer using graphite-crystal-monochromated Mo Kα radiation (λ = 0.71073 Å). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. Hydrogen atoms of the dmpm ligands were included at fixed positions. An empirical absorption correction was applied,[12] but no correction for extinction was made. The non-hydrogen atoms of the dirhenium complex were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[13] The final residuals were R = 0.033 (R_w = 0.043) for 4561 data with $I > 3\sigma(I)$.

(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

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(14) The FAB mass spectrum of 4 showed a peak at m/z 765 as the most abundant molecular ion; this corresponds to $(M + H)^+$. The ^1H NMR spectrum of 4 (room temperature in $CDCl_3$) revealed multiplets at δ +4.8 and +3.6 (CH_2 of dmpm) and four doublets of doublets at δ +2.13, +2.03, +1.93, and +1.91 (CH_3 of dmpm, J(P–H) ≃ 5.5 Hz), while the $^{31}P\{^1H\}$ spectrum was an AA′BB′ pattern with the most intense components at δ −59.3 and −66.6.

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(20) For recent examples of such complexes, see: (a) Bakir, M.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1987**, *6*, 907. (b) Esjornson, D.; Bakir, M.; Fanwick, P. E.; Jones, K. S.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 2055.

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Fulbright Fellowship. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 87-14258) for funds for the purchase of the NMR spectrometers.

Supplementary Material Available: A listing of atomic positional parameters for the structure of $O_3ReReCl_2(dmpm)_2$ (Tables S1 and S2) (6 pages). Ordering information is given on any current masthead page.

Substituent Effects on Amine Cation Radical Acidity. Regiocontrol of β-(Aminoethyl)cyclohexenone Photocyclizations

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Ion radicals serve as key intermediates in a variety of SET photochemical, electrochemical, and biochemical redox processes. A number of recent studies[1-7] have focused on synthetic and mechanistic problems related to the chemistry of amine cation radicals. One of the more interesting issues has been the acidity of these reactive intermediates.[1-5] The rates of α-deprotonation[4,5,8] and pK_a values[4,5] of amine cation radicals have been measured. Lewis and his co-workers[1] in their study of SET-promoted, tertiary amine photoadditions to stilbene have probed the effects of substituents on the kinetic acidity of these ion radical intermediates. Lewis's efforts led to an interesting relative acidity scale in which the rates of α-deprotonation appear to be governed by stereoelectronic/steric factors.[1]

Our efforts focusing on the development of synthetically useful SET photochemical reactions of amine–enone systems have provided us with an opportunity to investigate the problem of amine cation radical acidity. Our efforts in this area were designed to determine the factors affecting the chemo- and regioselectivities of photocyclization reactions of β-(aminoethyl)cyclohexenones of general structure **1** (Scheme I). More importantly, the distribution of products obtained from photocyclization of **1**, which proceeds via the intermediacy of zwitterionic diradical **2**, will reflect the effects of substituents (R_1 vs R_2) on the kinetic acidity of amine cation radicals. In this communication, we report the results of these efforts, which suggest that factors in addition to those discussed earlier by Lewis[1] are also influential in determining the effect of substituents on the acidities of amine cation radicals.

The β-(aminoethyl)cyclohexenones **1** used in this study were prepared by use of routes beginning with 3-(2′-aminoethyl)anisole and involving sequential Birch reduction, N-alkylations, and hydrolysis.[9] Photocyclization reactions of these substances were promoted by direct irradiation (λ > 320 nm) of CH_3OH and CH_3CN solutions. Photoproducts (Table I) were separated by column chromatography and characterized via spectroscopic methods.[9] To insure that the ratios of products in each case were both accurately determined and reflective of the relative efficiencies for product formation, NMR[10] and GLC methods were used (both in selected cases) to assay crude photolysates produced by both low- and high-conversion irradiations.

Scheme I

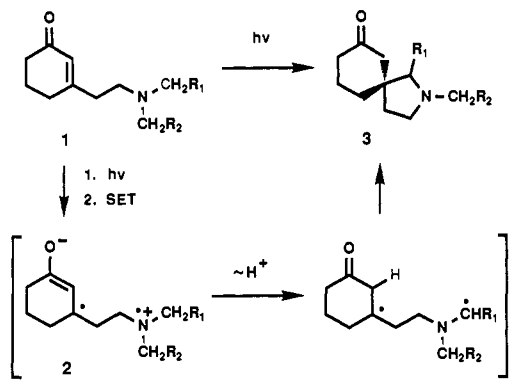

Table I. Product Distributions from Photoreactions of Silyl Amino Cyclohexenones **1** in MeCN and MeOH

reactant (1)		product (3)		% yield[a]
R_1	R_2	R_1	R_2	MeCN (MeOH)
H	CH_3	H	CH_3	24 (17)
		CH_3	H	34 (17)[b]
Ph	CH=CH$_2$	Ph	CH=CH$_2$	12 (22)[b]
		CH=CH$_2$	Ph	25 (66)[b]
Ph	C≡CH	Ph	C≡CH	6 (19)[b]
		C≡CH	Ph	24 (38)[b]
Ph	CO_2CH_3	Ph	CO_2CH_3	23 (44)[b]
		CO_2CH_3	Ph	12 (28)[b]
Ph	$Si(CH_3)_3$	Ph	$Si(CH_3)_3$	65 (0)[b]
		H	Ph	0 (71)
H	$Si(CH_3)_3$	H	H	0 (72)
		$Si(CH_3)_3$	H	76 (0)[b]
H	CH=CH$_2$	CH=CH$_2$	H	69 (79)[b]
H	C≡CH	C≡CH	H	59 (79)[b]

[a] Yields based on recovered starting cyclohexenone. [b] Mixture of α-R_1 and β-R_1 stereoisomers.

The data accumulated in Table I reveal several interesting trends. Firstly, products lacking the TMS group are formed exclusively in photoreactions of the *N*-(trimethylsilyl)methyl-substituted amino enones in CH_3OH. This chemoselectivity, observed in our earlier studies,[2b,d] is due to the decreased basicity of enone radical anions in protic solvents owing to H-bonding interactions and the rapid rate of cation radical desilylation. Secondly, deuterium isotope effects, measured by internal comparisons with the *N*-CH_3-*N*-CD_3 and the *N*-CD_2Ph-*N*-$CH_2CO_2CH_3$ analogues of **1**, show a marked solvent dependence (e.g., k_D/k_H for **1**-(CD_3,CH_3) is 5.1 in CH_3CN and 2.4 in CH_3OH and for **1**-(CD_2Ph,$CH_2CO_2CH_3$) is 6.5 in CH_3CN and 2.2 in CH_3OH).[11]

The third and most significant observation relates to substituent effects on kinetic acidities of amine cation radicals. The relative rates of proton transfer between the cation and anion radical centers in intermediate **2** govern the spirocyclic ketone product distributions from reactions of **1**. Consequently, product ratios can be transformed into per-hydrogen relative kinetic acidities. These are listed in Table II along with data derived by Lewis[1] from studies of amine–stilbene photoadditions. Significant differences exist between these series. For example, alkyl substitution decreases the rate of proton transfer in the amine–stilbene ion

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(9) The synthetic sequences used in this work as well as the spectroscopic and physical data for all new substances and pure photoproducts will be reported in a full paper on this subject.
(10) The NONOE technique was used to maximize the accuracy of ^{13}C NMR integrations for product analysis.
(11) The CH_3CN values are consistent with those found by Dinnocenzo (ref 4) in quinuclidine deprotonations of di-*p*-anisylmethylaminium hexafluoroarsenate deprotonations (k_D/k_H = 6–7.7 in CH_3CN at 15.1 °C). The magnitude of the isotope effect was found in that work to be directly proportional to the base strength of the quinuclidines.

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