

**Figure 1.** Absorption spectra in methanol of crown **2** in the presence and absence of added salts: A, crown **2**; B, crown **2** and LiCl; C, crown **2** and NaCl; D, crown **2** and KCl. Curves E and F are the spectra of 4-methoxyacetophenone and 3-methoxyacetophenone for comparison. The concentration of ketone (or crown) was  $1.0 \times 10^{-4}$  M in all cases, and the concentration of added salt was  $5 \times 10^{-3}$  M.

**Table II.** Effects of Alkali Metal Salts on the Photoelimination Quantum Yields of Valerophenone Derivatives in Methanol

Ketone <sup>a</sup>	Salt <sup>b</sup>	$\phi_{rel}$ <sup>c</sup>	$\lambda_{max}$ , nm ( $\epsilon$ ) <sup>d</sup>
Crown <b>2</b>		1	303 (8300)
Crown <b>2</b>	LiOAc	1.4	303 (8200)
Crown <b>2</b>	LiCl	1.2	303 (8200)
Crown <b>2</b>	NaOAc	5.0	300 (7700)
Crown <b>2</b>	NaCl	4.3	300 (7700)
Crown <b>2</b>	KOAc	8.8	299 (7600)
Crown <b>2</b>	KCl	10.8	299 (7600)
3,4-Dimethoxyvalerophenone		1.2	
3,4-Dimethoxyvalerophenone	KOAc	1.0	
3,4-Dimethoxyvalerophenone	KCl	1.1	

<sup>a</sup> Deoxygenated solutions containing  $1.0 \times 10^{-3}$  M ketone were photolyzed with 313-nm light in a conventional merry-go-round apparatus. <sup>b</sup>  $1.0 \times 10^{-3}$  M. <sup>c</sup> Relative quantum yields for the formation of propene; conversions were  $<10\%$ ; the conversion of valerophenone to acetophenone and propene ( $\phi = 0.33$ ) in benzene was used as an actinometer. <sup>d</sup> As described in Figure 1.

presence and absence of equimolar quantities of various alkali metal salts were photolyzed using conventional procedures. We found it convenient to analyze for the formation of propene (eq 1) by gas chromatography.<sup>10</sup> The results of these studies are presented in Table II. Control experiments for 3,4-dimethoxyvalerophenone studied in the presence and absence of potassium salts are also included. The presence of sodium salts enhances the efficiency of photoelimination by a factor of 5 and that of potassium salts by a factor of 10. The corresponding lithium salts exhibit only a small increase. The potassium salts, as expected, have no effect on the corresponding photochemistry of 3,4-dimethoxyvalerophenone. Furthermore we have found that UV spectral shifts for crown **2** parallel the photochemical effects (Figure 1 and Table II). Both the shift to shorter wavelength and the reduction in extinction coefficient are in the direction expected if complexation reduced the electronic interaction of the "alkoxy" substituents with the aryl ketone chromophore (spectra of the mono alkoxy ketones are included for comparison).

In principle, it should be possible to ascertain whether the "catalytic" effect of complexation serves to increase the hydrogen abstraction rate constant ( $k_r$ ) or to decrease the competing radiationless decay ( $k_d$ ) of the excited state, or both. Measurement of the excited-state lifetime,  $(k_r + k_d)^{-1}$ , by conventional triplet quenching experiments should yield a larger value for the excited-state lifetime if the effect involves

decrease in  $k_d$  or a smaller (perhaps imperceptibly so) value if the effect is to increase  $k_r$ . These experiments have unfortunately been very problematic, and we have been unable to draw definitive conclusion. In addition to considerable scatter in the Stern-Vollmer plots, no more than 50% (in the case of crown **2** complexed with potassium acetate) or 70% (in the case of crown **2** alone) of the photochemistry is quenchable with high concentrations ( $\sim 2$  M) of typical triplet quenchers such as 1,3-pentadiene.<sup>11</sup> The latter observation implies that a portion of the observed photochemistry occurs from the singlet state.

In conclusion, we have observed a substantial "catalytic" effect of alkali metal cations on the efficiency of a photochemical reaction. It is moderately specific for potassium ion. Studies are in progress to assess the potential magnitude and specificity of the effect.

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## References and Notes

- (1) (a) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (b) D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974); (c) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
- (2) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
- (3) L. R. Sousa and J. M. Larson, *J. Am. Chem. Soc.*, **99**, 307 (1977).
- (4) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
- (5) P. J. Wagner, M. J. Thomas, and E. Harris, *J. Am. Chem. Soc.*, **98**, 7675 (1976), and references therein.
- (6) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Am. Chem. Soc.*, **95**, 5604 (1973).
- (7) D. F. Evans, S. L. Wellington, J. A. Nadis, and E. L. Cussler, *J. Solution Chem.*, **1**, 499 (1972).
- (8) Under the conditions described for the photochemical experiments, 50% of the crown is complexed with KOAc and 47% of the crown is complexed with NaOAc.
- (9) Spectral data and elemental analysis are consistent with the proposed structure.
- (10) Photolyses were carried out in sealed Pyrex tubes and were analyzed immediately upon opening. The reliability and reproducibility of the propene analysis were exhaustively tested using valerophenone and 3,4-dimethoxyvalerophenone. The efficiencies for production of propene were found to be identical with those for production of the corresponding methyl ketones.
- (11) It should be noted that identical complications with quenching are also observed with 3,4-dimethoxyvalerophenone and do not arise from features of the crown per se.

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## Preparation and Rearrangements of Some 8,8-Dimethylhomotropylium Cations<sup>1</sup>

Sir:

While the migration of C<sub>8</sub> and its attendant substituents around the periphery of the "seven-membered" ring of a homotropylium cation can be induced photochemically,<sup>2</sup> no comparable thermal rearrangement has yet been detected.<sup>3</sup> The barrier of such a thermally initiated rearrangement is expected to be dependent on the substitution pattern at the migrating carbon.<sup>4</sup> Indeed, on the basis of molecular orbital calculations, Hehre has suggested that, in contrast to the unsubstituted ion, circumambulatory rearrangements of the 8,8-dimethylhomotropylium cation should be facile.<sup>5</sup> We report here the preparation of several 8,8-dimethyl substituted homotropylium cations and show that these species undergo a variety of molecular rearrangements, including circumambulation.

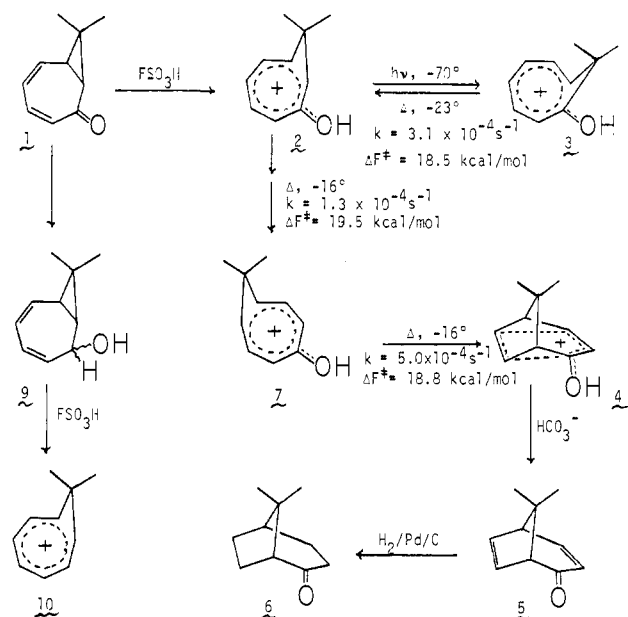
The dimethylhomotropone **1**, prepared by the procedure of Franck-Neumann,<sup>6</sup> was dissolved in FSO<sub>3</sub>H at  $-78$  °C to give the cation **2**. Irradiation of **2** ( $-70$  °C,  $\lambda > 360$  nm) caused it

Table I.  $^1\text{H}$  Chemical shifts<sup>a</sup>

Compd	Chemical shifts, ppm							
	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	CH <sub>3</sub>
<b>1</b>	2.06 (d)		5.90 (d)	6.22 (q)	5.78 (t)	6.40 (q)	1.60 (t)	1.03, 1.36
<b>2</b>	3.23 (d)		7.10 (d)	7.69 (q)	6.99 (t)	7.52 (q)	3.42 (t)	0.68, 1.92
<b>3</b>				8.35–7.25 (m)			5.53 (d)	0.15, 2.10
<b>8</b>	1.63 (q)	6.30 (hd)	5.85 (d)		5.85 (d)	6.30 (hd)	1.63 (q)	0.83, 1.32
<b>7</b>	3.33 (d)	8.00 (t)	7.11 (d)		7.11 (d)	8.00 (t)	3.33 (d)	0.41, 2.03
<b>5</b>	2.66 (m)		5.30 (se)	6.94 (dd)	2.66 (m)	6.50 (dd) <sup>b</sup>	5.83 (dd) <sup>b</sup>	1.20, 1.20
<b>4</b>	3.63 (m)		6.57 (q)	8.78 (q)	3.63 (m)	6.48 (dd) <sup>b</sup>	7.22 (t) <sup>b</sup>	1.42, 1.54
<b>9</b>	1.98 (dd)	4.70 (d)		5.72 (m)		6.10 (m)	1.52 (dd)	1.00, 1.22
<b>10</b>	5.26 (br s)			8.37 (br s)			5.26 (br s)	-0.48, 2.36

<sup>a</sup> Neutral compounds in CS<sub>2</sub>; cations in FSO<sub>3</sub>H (CH<sub>2</sub>Cl<sub>2</sub> internal standard,  $\delta$  5.30); d, doublet; t, triplet; q, quartet; se, sextet; hd, hexadecet; signals assigned by decoupling experiments. <sup>b</sup> Assignment could be reversed.

Scheme I



to isomerize to **3**, the structure of which was established by comparison of its  $^1\text{H}$  NMR spectrum with other closely related 1-hydroxyhomotropylium cations.<sup>2</sup> The cation **3** quantitatively reverted to **2** when solutions of it were warmed to temperatures above  $-30^\circ\text{C}$ . The thermal instability of 1-hydroxyhomotropylium cations is well known, but in all other reported cases ring contraction reactions occur to give benzenoid materials.<sup>2,7</sup>

The cation **2** was also thermally unstable and at  $-20^\circ\text{C}$  rearranged to give **4**. Neutralization of the acid solution of **4** yielded the ketone **5**.<sup>8</sup> These structural assignments were confirmed by reduction of **5** ( $\text{H}_2/\text{Pd}/\text{C}$ ) to the saturated ketone **6**, which was shown to be identical in every respect with an authentic sample.<sup>9</sup>

NMR spectra obtained during the course of the isomerization of **2** to **4** showed that a further cation was present. The relative concentration of this cation reached a maximum of some 16% when the concentration of **2** had dropped to  $\sim 50\%$  of its initial value and thereafter steadily decreased as the reaction proceeded. The  $^1\text{H}$  NMR spectrum of this intermediate, obtained using spectral subtraction techniques, suggested that it was the symmetrical cation **7** (Table I).

Three products were obtained when a FSO<sub>3</sub>H solution of **2** was quenched after it had been allowed to partially rearrange. These products were separated by preparative GLC and identified as **1**, **5**, and 8,8-dimethylbicyclo[5.1.0]octa-2,5-dien-4-one (**8**). The properties of **8** were entirely consistent with the assigned structure. The cation **7** was regenerated when **8** was dissolved in FSO<sub>3</sub>H at  $-78^\circ\text{C}$  and, on warming the so-

lution above  $-20^\circ\text{C}$ , **7** isomerized to give **4** (no **2** was formed). First-order rate constants for these isomerizations were obtained by computer matching of the time/concentration plots and are shown in Scheme I.

Reduction of **1** with diisobutylaluminum hydride<sup>10</sup> gave the alcohol **9** which dissolved in FSO<sub>3</sub>H/SO<sub>2</sub> at  $-78^\circ\text{C}$  to give **10**. The  $^1\text{H}$  NMR spectrum of **10** was fully consistent with its assigned structure. There was no evidence in the NMR spectra of **10** of any averaging of the ring proton resonances at temperatures up to  $-50^\circ\text{C}$ , indicating that degenerate rearrangement of **10**, if occurring, is slow on the NMR time scale ( $\Delta F^\ddagger > 12$  kcal/mol). At  $-50^\circ\text{C}$ , **10** isomerized irreversibly to give the isopropyltropylium cation.<sup>5</sup>

Several points emerge from these results. First, it is clear with the hydroxy substituted systems that the introduction of two methyl groups on C<sub>8</sub> has permitted circumambulatory rearrangements to take place.<sup>11</sup> No such thermal isomerizations have been detected in less highly substituted protonated homotropones.<sup>2</sup> As **4** is stable under the reaction conditions, its intermediacy in the rearrangements of **3** to **2** and **2** to **7** is precluded and it would seem likely that these rearrangements proceed by stepwise migration of C<sub>8</sub> around the periphery of the homotropylium cations.

The substantial downfield shifts of the methine and vinyl proton resonances of **1**, **8**, and **5** on protonation (Table I) show that extensive delocalization of the positive charge is occurring in these hydroxy cations. Using the difference in chemical shift of the *exo*- and *endo*-methyl groups as an indication of an induced ring current, it can be seen that, while this difference is attenuated on the introduction of a hydroxy group into the various positions of the dimethylhomotropylium cation, it is still large compared with that of the neutral ketones.<sup>12</sup> Thus it would appear on the basis of magnetic criteria that the cations **2**, **3**, and **7** can be classified as being homoaromatic.<sup>12</sup> It is particularly intriguing, therefore, that **4**, which has been considered to be an "antibishomoaromatic" system,<sup>13</sup> is thermodynamically more stable than any of these hydroxyhomotropylium cations.

## References and Notes

- (1) Research supported by a grant from the National Research Council of Canada.
- (2) R. F. Childs and Carol V. Rogerson, *J. Am. Chem. Soc.*, **98**, 6391 (1976).
- (3) J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8907 (1972).
- (4) R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6409 (1974); I. Pikullik and R. F. Childs, *Can. J. Chem.*, **53**, 1818 (1975).
- (5) W. J. Ehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974).
- (6) M. Franck-Neumann and D. Martina, *Tetrahedron Lett.*, 1759 (1975).
- (7) M. Brookhart, M. Ogillaruso, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1965 (1967); M. S. Brookhart and M. A. M. Atwater, *Tetrahedron Lett.*, 4399 (1972).
- (8) All new compounds have satisfactory elemental analyses and spectroscopic properties.
- (9) G. Komppa and A. Bergström, *Chem. Ber.*, **75**, 1607 (1942). The route used to prepare **6** involved reaction of 7,7-dimethylbicyclo[2.2.1]heptane-2,3-dione, obtained by SeO<sub>2</sub> oxidation of 7,7-dimethylbicyclo[2.2.1]-

heptan-2-one, with  $\text{CH}_2\text{N}_2$  to give 8,8-dimethyl-4-methoxybicyclo[3.2.1]-oct-3-en-2-one. Reduction of this latter compound with  $\text{LiAlH}_4$  and then  $\text{H}_2/\text{Pd/C}$  gave **6**.

- (10) K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970).
- (11) Preliminary results obtained with labeled derivatives of **10** and its iron tricarbonyl complex indicate that circumambulatory rearrangements also occur in these cations.
- (12) S. Winstein, *Quart. Rev. Chem. Soc.*, **23**, 141 (1969); P. J. Garratt, "Aromaticity", McGraw Hill, London, 1971, p 176.
- (13) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **98**, 1545 and 1551 (1976); A. F. Diaz, M. Sakai, and S. Winstein, *ibid.*, **92**, 7477 (1970).

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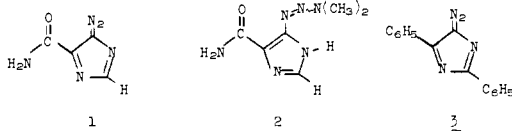
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### Insertion Reactions of 4H-Imidazolylidenes into C-H Bonds of Alcohols

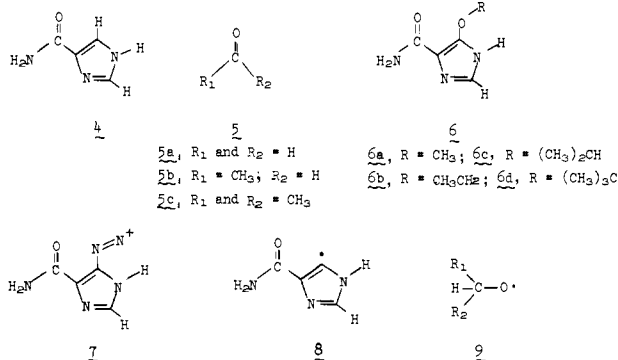
Sir:

4-Diazoimidazole-5-carboxamide<sup>1a,b</sup> (**1**, DZC), a diazo compound with antineoplastic activity in experimental tumors, an antibacterial agent,<sup>1c</sup> and a potent electrophile with nucleic acids,<sup>1d</sup> is converted by dimethylamine to 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide (**2**, DIC, DCTIC,



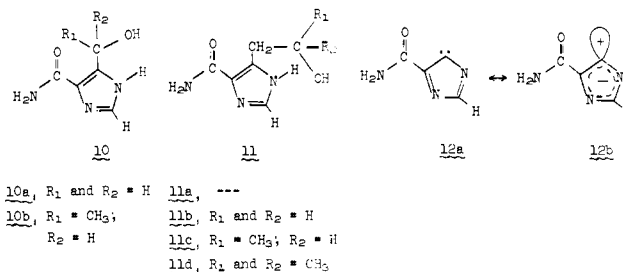
NSC-45388),<sup>1b,e,f</sup> as yet the most effective antitumor agent against malignant melanoma.<sup>1g</sup> The principal chemistry of **1** and **2** that has been described follows: (1) **1** isomerizes to 2-azahypoxanthine in the presence of acids or bases<sup>1a</sup> and couples with various amines, thiols, and aromatics to give triazenes,<sup>1b</sup> azo thioethers,<sup>1h</sup> and arylazo<sup>1b</sup> derivatives, respectively, and (2) **2** is thermally unstable, light sensitive, and dissociates in part to **1** and dimethylamine. We should now like to summarize certain efficient thermal and/or photolytic reactions of **1**, **2**, and 5-diazo-2,4-diphenylimidazole (**3**), respectively, in various environments. These studies are of note in that they reveal the ability of 4H-imidazolyl carbenes as generated in solution at 10 to 60 °C to insert preparatively into the C-H bonds of alcohols.<sup>2,3</sup> These results also lead to further definition of the kinds of carbenes, alcohols, and experimental conditions which allow intermolecular C-H insertion.

Thermolysis of **1** occurs efficiently (~100%) at 60 °C in primary and secondary alcohols with loss of nitrogen to form (1) imidazole-4(5)-carboxamide (**4**)<sup>5</sup> and aldehydes or ketones (**5**) as major oxidation-reduction products and (2) 5(4)-alkoxyimidazole-4(5)-carboxamides (**6**)<sup>4d</sup> by addition of the



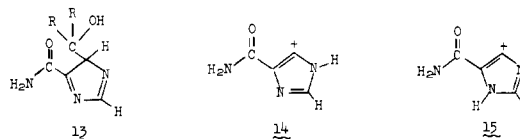
alcohols. Thus **1** is converted by methanol to **4** (71%), **5a**, and **6a** (29%), by ethanol to **4** (75%), **5b**, and **6b** (25%), and by 2-propanol to **4** (78%), **5c**, and **6c** (22%). The behavior of **1** in primary and secondary alcohols is similar to that of aryldiazonium salts in these environments<sup>6a</sup> and possibly involves conversion of **1** to alkyl 4(5)-carboxamido-5(4)-imidazolyl-diazonium ions (**7**) and to 4(5)-carboxamido-5(4)-imidazolyl (**8**) and alkoxy (such as **9**) radicals. Reactions of **7** with alcohols with loss of nitrogen and deprotonation will give **6** and chain reactions involving **7**, **8**, **9** and alcohols and/or hydride transfer from alcohols by **7** will account for **4** and **5**.<sup>6b</sup>

Photolysis of **1** in alcohols at 10–20 °C<sup>7</sup> differs significantly from thermolysis in that nitrogen is expelled rapidly and 5(4)-(hydroxyalkyl)imidazole-4(5)-carboxamides (**10** and **11**),<sup>4d</sup> products of insertion into the various C-H bonds of the alcohols, are formed along with ethers (**6**). Oxidation-reduction to **4** and **5** also occurs in the presence of alcohols which undergo  $\alpha$ -dehydrogenation. Thus irradiation of **1** in methanol yields **10a** (20%) along with **4** (14%), **5a**, and **6a** (66%).<sup>7,8</sup> Of even greater interest is that **1** photolyzes in ethanol to give **10b** (2%) and **11b** (27%) as  $\alpha$ - and  $\beta$ -C-H insertion products<sup>8</sup> and



**4** (32%), **5b**, and **6b** (39%). Analogously, photolysis of **1** in 2-propanol results in **11c** (43%),<sup>8</sup> **4** (30%), **5c**, and **6c** (27%). The ability of **1** to effect efficient photolytic insertion into the C-H bonds of alcohols is illustrated further by reaction with 2-methyl-2-propanol to yield **11d** (80%) along with **6d** (20%).

C-H insertion into alcohols upon photolysis of **1** appears to involve reactions of singlet 5-carboxamido-4H-imidazolylidene (**12a–12b**) and isomerization of the initial insertion products (**13**) to **10** and **11** by hydrogen migration.<sup>9</sup> These results are of significance in that carbenes are usually expected to react efficiently with alcohols to give ethers upon protonation to carbonium ions and then solvolytic exchange.<sup>10</sup> Alternative but less well established processes include direct carbenic insertion into the O-H bonds or/and ylidic attack on oxygen of the alcohols with protic rearrangement.<sup>10,11</sup> The present effective C-H insertions are rationalizable, however, on the basis that (1) **1** is not decomposed rapidly by alcohols in the absence of light and then can be converted effectively to **12a–12b** by photolysis in such environments, (2) protonation of **12a–12b** and then conversion to **6a–d** will be resisted because of the kinetic hurdles in formation of energetic cations **14** and **15**,<sup>12a</sup>



and (3) **12a–12b** is anticipated to be a highly electrophilic carbene<sup>12b</sup> as a singlet. A further point is that C-H bonds are weaker than O-H bonds and, in the absence of mechanistic complications, alcohols should undergo effective carbenic C-H insertion.

Conversions of **1** by alcohols to ethers (**6**) and to oxidation-reduction products (**4** and **5**) differ relatively in that **6** are formed predominantly or competitively upon irradiation whereas thermolysis leads principally to **4** and **5**. These results