heptan-2-one, with CH_2N_2 to give 8,8-dimethyl-4-methoxybicyclo[3.2.1]-oct-3-en-2-one. Reduction of this latter compound with $LiAlH_4$ and then H_2/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.

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

Sir:

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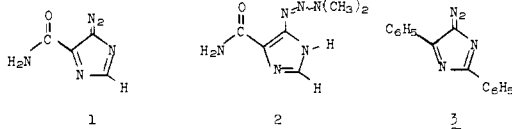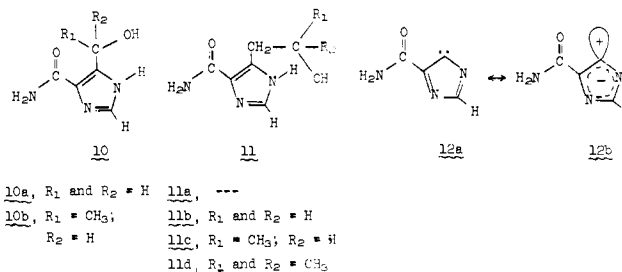

NSC-45388),[1b,e,f] as yet the most effective antitumor agent against malignant melanoma.[1g] The principal chemistry of **1** and **2** that has been described follows: (1) **1** isomerizes to 2-azahypoxanthine in the presence of acids or bases[1a] and couples with various amines, thiols, and aromatics to give triazenes,[1b] azo thioethers,[1h] and arylazo[1b] 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 4*H*-imidazolyl carbenes as generated in solution at 10 to 60 °C to insert preparatively into the C–H bonds of alcohols.[2,3] 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**[4] occurs efficiently ($\sim$100%) at 60 °C in primary and secondary alcohols with loss of nitrogen to form (1) imidazole-4(5)-carboxamide (**4**)[5] and aldehydes or ketones (**5**) as major oxidation–reduction products and (2) 5(4)-alkoxyimidazole-4(5)-carboxamides (**6**)[4d] by addition of the
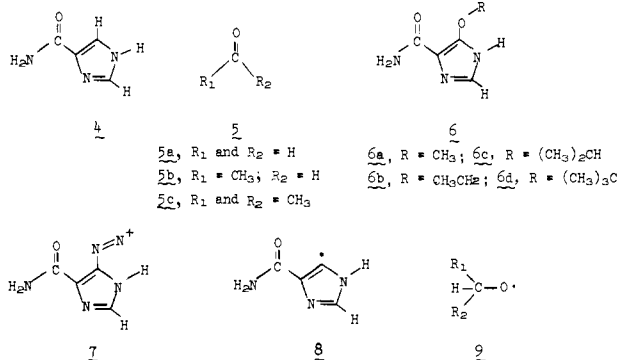

alcohols. Thus **1** is converted by methanol to **4** (71%), **5a,** and **6a** (29%), by ethanol to **4** (75%), **5b,** and **6b** (25%), and by 2-propanol to **4** (78%), **5c,** and **6c** (22%). The behavior of **1** in primary and secondary alcohols is similar to that of aryldiazonium salts in these environments[6a] and possibly involves conversion of **1** to alkyl 4(5)-carboxamido-5(4)-imidazolyldiazonium 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**.[6b]

Photolysis of **1** in alcohols at 10–20 °C[7] differs significantly from thermolysis in that nitrogen is expelled rapidly and 5(4)-(hydroxyalkyl)imidazole-4(5)-carboxamides (**10** and **11**),[4d] 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 α-dehydrogenation. Thus irradiation of **1** in methanol yields **10a** (20%) along with **4** (14%), **5a,** and **6a** (66%).[7,8] Of even greater interest is that **1** photolyzes in ethanol to give **10b** (2%) and **11b** (27%) as α- and β-C–H insertion products[8] and

10a, R_1 and R_2 = H 11a, ---
10b, R_1 = CH_3; 11b, R_1 and R_2 = H
    R_2 = H   11c, R_1 = CH_3; R_2 = H
                    11d, R_1 and R_2 = CH_3

4 (32%), **5b,** and **6b** (39%). Analogously, photolysis of **1** in 2-propanol results in **11c** (43%),[8] **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-4*H*-imidazolylidene (**12a–12b**) and isomerization of the initial insertion products (**13**) to **10** and **11** by hydrogen migration.[9] 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.[10] 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.[10,11] 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**,[12a]
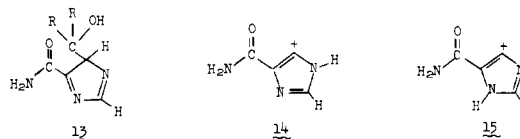

and (3) **12a–12b** is anticipated to be a highly electrophilic carbene[12b] as a singlet. A further point is that C–H bonds are weaker than O–H bonds and, in the absence of mechanistic complications, alcohols should undergo effective carbenic C–H insertion.

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

indicate clearly that photolytic conversions of **1** to **6** and to **4** and **5** can not involve total transformation to the intermediates (such as **7–9**) formed in thermolysis. Principal formation of **6** by photolysis may thus involve direct or ylidic attack of carbene **12a–12b**, cations **14** and **15**, or/and excited **1** on the hydroxyl groups of the alcohols. The photochemical oxidation–reduction products (**5** and **4**) are minor, and their origins, be they homolytic, cationic, and/or carbenic (singlet or triplet), are as yet totally speculative.

Decomposition of **2** also results in **12a–12b** which inserts in part into the C–H bonds of alcohols. Thus photolysis of **2** at 10–20 °C in ethanol gives **10b** (3%), **11b** (13%), **4** (60%), **5b**, and **6b** (39%). Further, irradiation of **2** in methanol yields **10a** (20%), **4**, **5a**, and **6a**. These results are of possible further significance in that they indicate that decomposition of appropriate triazenes with loss of nitrogen and amines may serve as convenient sources of carbenes.

2,5-Diphenyl-4*H*-imidazolylidene (**16**), generated thermally from **3** at 60 °C, behaves impressively in reactions with C–H bonds. Thus decomposition of **3** in cyclohexane and in benzene yields **17a** (60%) and **17b** (72%),[13] respectively. Of particular
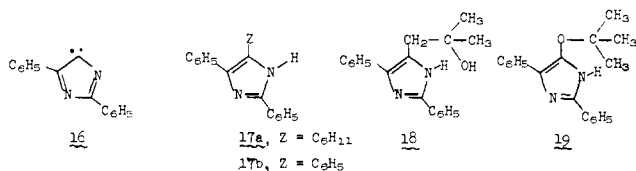
interest is that **3** is converted preparatively by 2-methyl-2-propanol to **18** (80%) and **19** (20%); formation of **18** is the first example of thermal decomposition of a diazo compound in an alcohol resulting in intermolecular C–H penetration. Insertion into the C–H bonds of alcohols by appropriate carbenes appears to be of considerable synthetic promise. It is likely that such reactions will be of advantage with carbenes (and diazo compounds) of limited nucleophilicities and with alcohols which are poor proton donors.

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(2) (a) Decomposition of diazomethane in 2-propanol in sunlight gives mainly methyl 2-propyl ether; 2-butanol and 2-methyl-2-propanol are minor products.[2d] (b) Photolyses of ethyl diazoacetate in methanol and in 2-propanol yield ethyl 3-hydroxypropanoate[2e] (trace) and ethyl 3-hydroxy-3-methylbutanoate (9%),[2f] respectively, along with Wolff rearrangement products. (c) In gas phase photolysis of diazomethane in *tert*-butyl alcohol, the reactivity of the O–H bond of the alcohol is 10.9 ± 0.5 times that of any of its single C–H bonds.[2g] (d) H. Meerwein, H. Rathjen, and H. Werner, *Chem. Ber.*, **75**, 1610 (1942). (e) H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *J. Am. Chem. Soc.*, **90**, 4088 (1968). (f) O. P. Strausz, T. DoMinh, and H. E. Gunning, *ibid.*, **91**, 1261 (1969). (g) J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 897 (1967).
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(4) (a) Diazoimidazoles **1** and **3** (1.0 g, respectively) were thermolyzed in the various solvents (550 mL) until nitrogen evolution was complete. (b) The products were separated and analyzed by reverse phase, liquid chromatography from aqueous solution on a Bondapak C-18 column (4 ft × ³⁄₈ in., Waters Associates). (c) 2-Azahypoxanthine[1a] was *not* found in the various reaction mixtures. (d) The products were assigned from their elemental analyses and/or exact masses, NMR (D₂O) and IR spectra, and melting points and by comparison with literature values.
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(6) (a) N. Kornblum, *Org. React.*, **2**, 262 (1944). (b) Aryldiazonium salts are generally assumed to react with alcohols to form ethers by S_N1 and S_N2 mechanisms, whereas oxidation–reduction to arenes and carbonyl compounds proceeds by free-radical chain processes. Recent study[6c–e] has indicated however the mechanistic complexities of these reactions. Such complications may well be involved in the present systems. (c) D. F. DeTar and T. Kosuge, *J. Am. Chem. Soc.*, **80**, 6072 (1958). (d) T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970). (e) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Am. Chem. Soc.*, **91**, 419 (1969), and E. S. Lewis and D. J. Chalmers, *ibid.*, **93**, 3267 (1971).
(7) Photolyses of **1** (1.0 g, respectively) in solvents (550 mL) under nitrogen were effected in Pyrex with a 450-W medium-pressure Hanovia lamp.
(8) (a) The C–H insertions appear subject to statistical steric factors; the conversions to **6** also correlate with the proton donor abilities of the alcohols. (b) 4(5)-[2-(2-Hydroxypropyl)]imidazole-5(4)-carboxamide was not detected.
(9) 1,5-Sigmatropic rearrangements of **13** are allowed.
(10) (a) W. Kirmse, *Justus Liebigs Ann. Chem.*, **9**, 666 (1963); (b) D. Bethell, A. R. Newall, and D. Whittaker, *J. Chem. Soc. B*, 23 (1971), and references therein; (c) W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1971, pp 423–425; (d) D. Bethel, *Adv. Phys. Org. Chem.*, **7**, 153 (1969).
(11) Benzylidene[3] and phenyl(ethylphosphonyl)carbene[3] are presumed to insert into the C–H bonds of alcohols in matrix at −110 to −196 °C by triplet abstraction–recombination mechanisms upon repression of the singlet ylidic reactions of the carbenes at the O–H groups. We should like to add that the C–H insertions of alcohols may become prominent because at these temperatures the proton-donor activities of the carbinols are greatly depressed and conversions of the carbenes to their carbonium ions are significantly retarded.
(12) (a) Protonation of **12a–12b** at its carbenic center will also yield a highly energetic cation. (b) **12a–12b** is expected to be very electrophilic because of the 6π-electron character of its imidazole ring, the inductive effect of its ring nitrogens, and the electron withdrawal of its carboxamido group.
(13) B. Radziszewski, *Chem. Ber.*, **10**, 70 (1877).

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Metal–Metal Bonded Clusters in Transition Metal Groups 3 and 4. Synthesis and Structure of Three M_6X_{12}-Type Clusters for Scandium and Zirconium

Sir:

Knowledge of halogen-containing clusters of the types $M_6X_{12}^{n+}$ and $M'_6X_8^{m+}$ (X = Cl, Br, I) has been substantially limited to the well-known examples from group 5 for M = Nb and Ta and n = 2, 3, and 4, and to group 6, M' = Mo and W and m = 4 principally, together with a few smaller clusters for such elements as rhenium.[1,2] There have been no previous reports of either examples containing fewer than the 14 to 16 bonding electrons per M_6 group or discrete clusters of any sort containing elements earlier in the transition block than group 5. Results reported here for scandium and zirconium suggest that the scarcity of these examples may be attributed to kinetic[3] rather than thermodynamic limitations since metal–metal bonding and extensive halogen bridging appear to contribute appreciably to the stability of the products. In the case of scandium the lower number of valence electrons available for delocalized bonding is remedied through the formation of *anionic* M_6X_{12} clusters.

Cluster synthesis reactions in these metal–halogen binary systems are carried out under very reducing conditions near 800–1000 °C for several weeks using welded tantalum tubing as a container material; even so they are characteristically very slow, and the yields, low. All products are evidently formed by vapor phase transport. Thus, of the order of 10–20 mg of well-crystallized ZrI_2 is transported in the presence of excess