A Novel Preparation of Electrophilic Cyclopropanes

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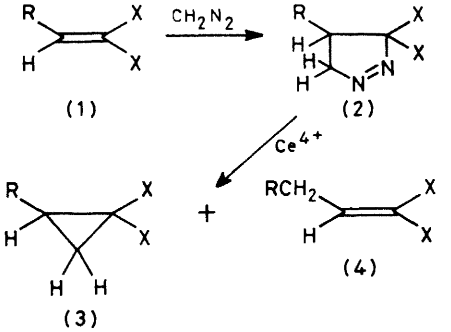
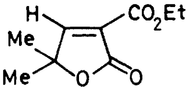
Summary Electrophilic cyclopropanes are conveniently prepared by decomposition of the corresponding Δ^1-pyrazolines in the presence of a small amount of $Ce(NH_4)_2(NO_3)_6$.

ELECTROPHILIC cyclopropanes are very useful intermediates in organic synthesis and we report a new method for their preparation[1] The corresponding pyrazolines appear to be attractive starting materials but their thermolyses lead mostly or exclusively to olefinic compounds or to five-membered heterocycles[2,3] We have found that treatment of the pyrazolines (**2**) with a small amount (3—10 mol %) of $Ce(NH_4)_2(NO_3)_6$ in acetone at 0 °C results in rapid loss of N_2 with quantitative formation (n m r control) of the cyclopropanes (**3**) alone or, for olefins (**1h**—**1j**), mixtures of (**3**) and the olefins (**4**) † This method, then, provides a convenient synthesis, under very mild conditions, of various electrophilic cyclopropanes, the olefins (**1**) are readily accessible[4] and react quantitatively with diazomethane



(1g) =

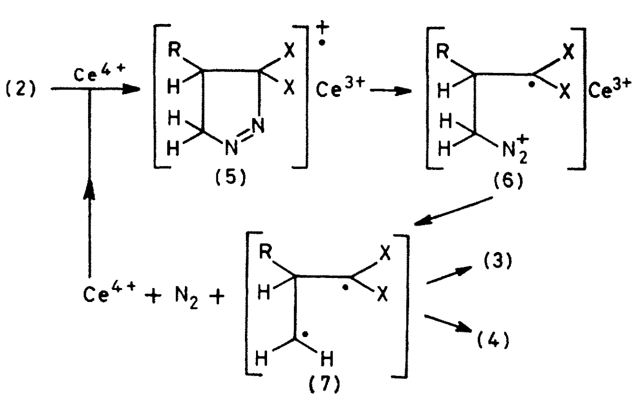


a, R = CO_2Me
b, R = COMe
c, R = Et
d, R = MeCHBr
e, R = p-$MeOC_6H_4CH_2$
f R = p $NO_2C_6H_4$
h R = Ph
i, R = p $MeOC_6H_4$
j *trans*-CHPh=CH

X = CO_2Me for **a**—**f** and **h**—**j**

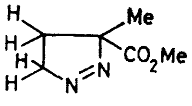
(**1a**—**g**) give (**3**) alone (**1h**—**j**) give (**3**) and (**4**) in the following ratios [(**3**) (**4**)] (**1h**), 56 44 (**1i**), 10 90 (**1j**) 50 50

We propose the mechanism in the Scheme for this reaction Oxidation of (**2**) by Ce^{4+} gives a radical cation (**5**) which undergoes bond cleavage to give the diazonium radical (**6**) In the presence of Ce^{3+}, this diazonium ion rearranges to give Ce^{4+} back together with the biradical (**7**) Depending upon the nature of R, (**7**) then rearranges either to the cyclopropane (**3**) or to the olefin (**4**) This mechanism not only accounts for the catalytic activity of Ce^{4+} but is also in agreement with the migratory aptitudes of the groups studied in 1,2 radical rearrangements, aryl and vinyl substituents are known to migrate more readily than the other groups[5] Furthermore, the large effect of substituents on the aromatic ring (R = p-$MeOC_6H_4$ and p-$NO_2C_6H_4$) may be due to the high zwitterionic character of type (**7**) biradicals[6] The presence of two electron-withdrawing substituents seems to be necessary for this reaction (**8**) was found to be non-reactive toward Ce^{4+}, even at +60 °C



X = CO_2Me

SCHEME



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† All these compounds gave spectral data (^1H n m r , i r) in agreement with the structures shown Satisfactory analytical data were obtained for the new compounds

[1] S Danishefsky, *Acc Chem Res* , 1979, **12**, 66

[2] J Hamelin and R Carrie, *Bull Soc Chim Fr* , 1968 2513 3000 R Danion-Bougot and R Carrie, *ibid* , 1969, **313**, and references therein

[3] It has been shown in a few cases that thermolysis of pyrazolines, in the presence of copper salts, increases the yields of cyclopropanes, K Tortschanoff, H Kisch, and O E Polansky, *Justus Liebigs Ann Chem* , 1975, 449

[4] Olefins (**1a**) and (**1b**) M S Ouali, M Vaultier, and R Carrie, *Synthesis*, 1977, 626 (**1c**), (**1f**), (**1h**), (**1i**), and (**1j**) 'Organic Reactions,' Wiley, New York, 1967, vol 15, p 204, and references therein (**1d**) J Kristensen and S O Lawesson, *Bull Soc Chim Belg* , 1978, **87**, 609 (**1g**) J Kristensen, I Thomsen, and S O Lawesson, *ibid* , p 721

[5] J March, 'Advanced Organic Chemistry, McGraw-Hill, 2nd Edn, 1977, p 974

[6] L Salem and C Rowland, *Angew Chem* , *Int Ed Engl* , 1972, **11**, 92