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REARRANGEMENT OF CYCLOPROPYL, SUBSTITUTED VINYL AND ALKYL GROUPS TO DIVALENT CARBON

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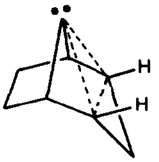
Abstract. The relative carbenic migratory abilities of cyclopropyl, β,β-dimethylvinyl, methyl, ethyl and isopropyl groups have been determined.

Although homoconjugative participation of cyclopropyl groups with beta cationic centers in conformationally rigid and mobile systems has been intensely investigated,[1a] information is limited with respect to carbenic analogs. Endo-tricyclo[3.1.0.$0^{2,4}$]octan-8-ylidene (1) is presumed to be stabilized as illustrated and give bicyclo[3.3.0]octa-1,6- and 1,7-dienes upon formation of 2.[1b] 7,7-Dimethoxy-exo-tricyclo[3.2.1.$0^{2,4}$]octan-6-ylidene(3) however does not reveal involvement of its cyclopropyl group and isomerizes by methoxyl migration to 6,7-dimethoxy-exo-tricyclo[3.2.1.$0^{2,4}$]oct-2-ene(4).[1c] A study is now reported of the rearrangement and insertion reactions of 2-cyclopropyl-2-methylpropylidene(5). Comparison has also been made with 2-methyl-2-phenylpropylidene(6),[1d] 2,2,4-trimethyl-3-penten-1-ylidene(7), 2,2-dimethyl-1-butylidene(8) and 2,2,3-trimethyl-1-butylidene(9). The results allow definition of significant π and σ electronic effects and steric factors in intramolecular reactions of primary carbenes.



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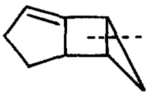

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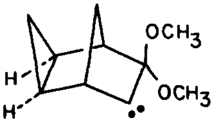

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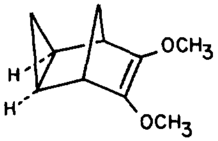

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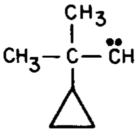

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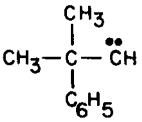

$CH_3-C(CH_3)(C_6H_5)-\ddot{C}H$

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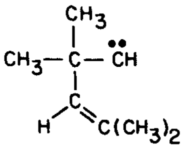

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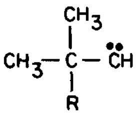
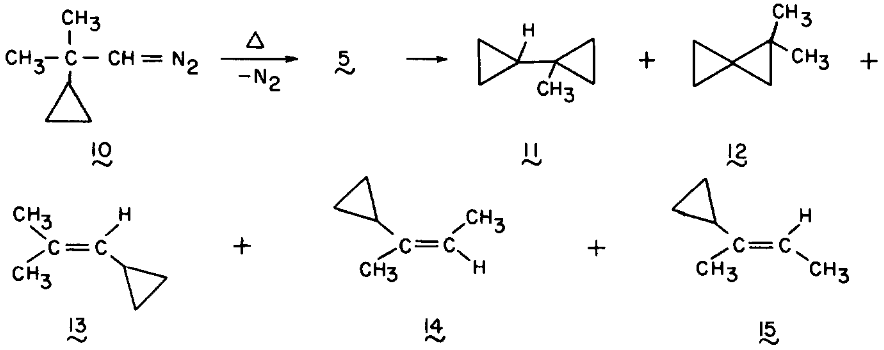


$CH_3-C(CH_3)(R)-\ddot{C}H$

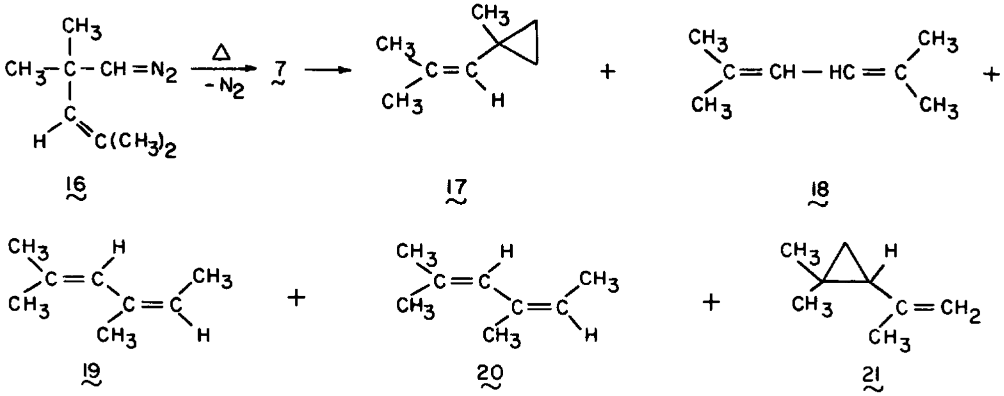
8, R = CH_2CH_3
9, R = $CH(CH_3)_2$

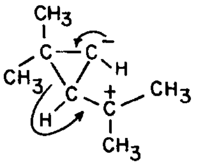
Generation of 5 was effected from 2-cyclopropyl-1-diazo-2-methylpropane (10) as formed from 2-cyclopropyl-2-methylpropanal p-tosylhydrazone and sodium hydride (1.1-1.2 equiv) in diglyme at 160-200°C. Products (Eq 1) of carbon-hydrogen insertion are 1-cyclopropyl-1-methylcyclopropane (11, 64.0-68.5%) and 2,2-dimethylspiropentane (12, 2.6-2.4%). 1-Cyclopropyl-2-methyl-1-propene (13, 15.0-13.4%) arises from rearrangement of the cyclopropyl group, methyl migration gives E-(14, 7.6-6.4%) and Z-(15, 5.6-4.8%)-2-cyclopropyl-2-butenes. Decomposition of 10 thus



reveals that (1) the principal reactions of 5 involve carbon-hydrogen insertion rather than rearrangement, (2) insertion into methyl hydrogen to give 11 occurs much more readily than into other carbon-hydrogen bonds, (3) insertion into cyclopropyl hydrogen is a recognizable reaction and (4) the migration aptitude of cyclopropyl relative to methyl is 2 9-2 7.1 at 160-200°C The greater carbenic migratory ability of cyclopropyl versus methyl in 5 is understandable on the basis of dominant delocalization of the σ bonds of the cyclopropane ring upon interaction with the electrophilic carbenic center The specific interactions and the stereochemistry of the cyclopropyl group in rearrangement of 5, be it corner, edge or multi ring-bond participation, are not yet clear however Of further note is that the cyclopropyl methyl migration aptitude in 5 is much smaller than that for phenyl relative to methyl (~9 1)[1d] in 6 at 160-200°C.

Decomposition of 1-diazo-2,2,4-trimethyl-3-pentene (16, Eq 2), generated from sodium 2,2,4-trimethyl-3-pentenal p-tosylhydrazonate in diglyme at 160°C, yields 1-(1-methylcyclopropyl)-2-methyl-1-propene (17, 19 0%) by C-H insertion into a methyl group at C-2 in 7, 2,5-dimethyl-2,4-hexadiene (18, 75 3%) by migration of the β,β-dimethylvinyl moiety and Z-(19, 1.2%)- and E-(20, 0.6%)-2,4-dimethyl-2,4-hexadienes by methyl rearrangement 2-(2,2-Dimethylcyclopropyl)-2-propene (21, 1.1%) is also formed By far the most prominent product is 18 (the β,β-dimethylvinyl·methyl migration ratio statistically corrected is ~85 1). Further, the migratory ability of the dimethylvinyl group is much greater than that of phenyl in thermolysis of 1-diazo-2-methyl-2-phenylpropane.[1d] Formation of 17, 19 and 20 likely results from carbenic processes involving 7 It is not yet clear however whether (1) migration of the dimethylvinyl group results upon participation of the double bond in 7 and rearrangement as in 22, (2) 7 yields 2,2,4,4-tetramethyl[1.1 0]bicyclobutane(23) which then isomerizes to 18 or (3) cycloaddition of 16 gives intermediates such as 24 which lose nitrogen and convert to 18 Indeed, allyldiazomethane and many of its analogs form [1 1 0]bicyclobutanes thermally and 23 converts quantitatively to 18 under the above conditions for pyrolysis of 16 [2] Isomerization of 7 and/or collapse of 24 involving a dipolar process[3] as for 25 will account for 21

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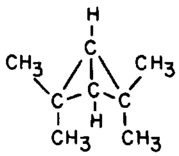
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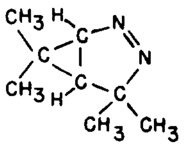
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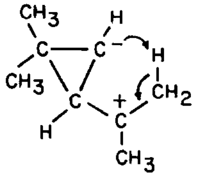
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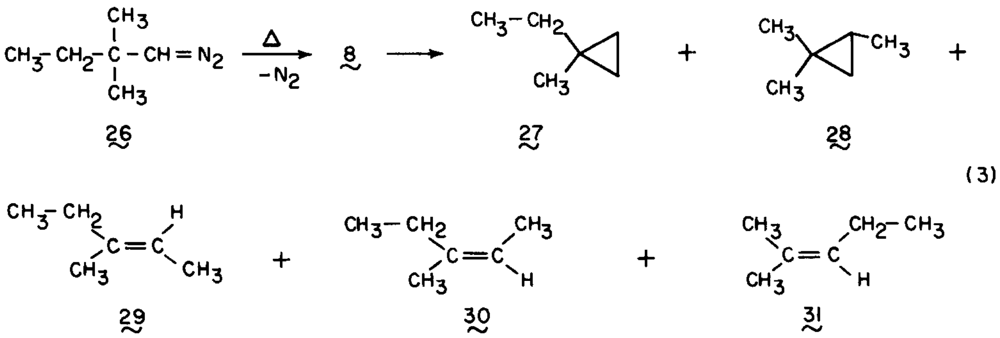
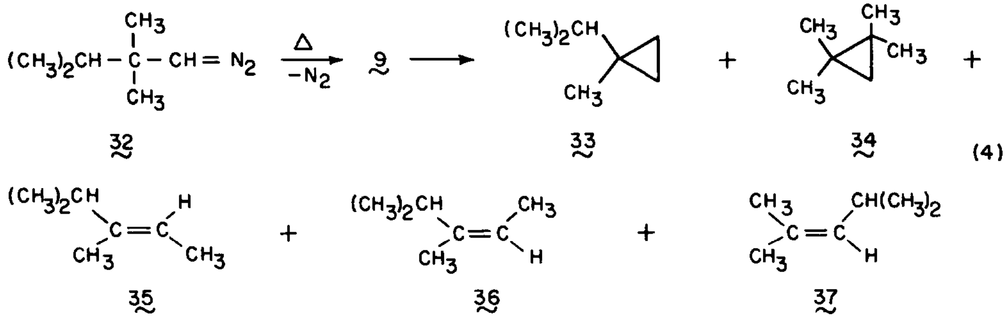
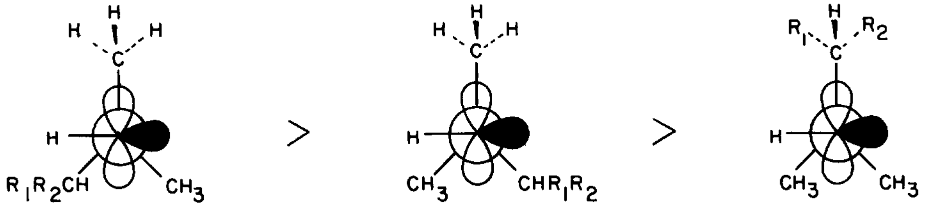
To determine the migratory abilities and the insertabilities of the alkyl groups in 8 and 9, thermolyses of 1-diazo-2,2-dimethylbutane(26) and 1-diazo-2,2,3-trimethylbutane(32) in diglyme were investigated At 160°C 8 yields 1-ethyl-1-methylcyclopropane (27, 73 5%) and 1,1,2-trimethylcyclopropane(28, 17 1%) by C-H insertion, E-(29, 4 2%) and Z-(30, 3.2%)-3-methyl-2-pentenes by methyl migration and 2-methyl-2-pentene(31, 2 0%) by rearrangement of its ethyl group Similarly (160°C), 32 forms 1-methyl-1-(2-propyl)cyclopropane(33, 87 9%) and 1,1,2,2-tetramethylcyclopropane(34, 5 0%) by insertion into C-H bonds, E-(35, 3 9%) and Z-(36, 2 5%)-3,4-dimethyl-2-pentenes upon methyl movement and 2,4-dimethyl-2-pentene(37, 0 7%) by isopropyl migration The ratios of ethyl methyl and isopropyl methyl migration in 8 and 9 statistically corrected are 0 54 1 and 0 22 1, respectively Further, the statistically corrected ratios of insertion into secondary primary γ-hydrogen in 8 and into tertiary primary γ-hydrogen in 9 are 0 70 1 and 0 34 1 Of note are (1) the migratory abilities of alkyl groups are methyl > ethyl > isopropyl, the opposite of that predicted on the basis of inductive electron release, (2) the insertabilities into C-H bonds are 1° > 2° > 3°, the opposite of that for intermolecular insertions of electrophilic carbenes[4] and (3) in the carbon-skeleton rearrangements in which there are steric preferences, the lesser strained olefins are the dominant products It thus appears that the transition states leading to rearrangement, insertion and E and Z-isomerism in the products from 8 and 9 are controlled by steric factors in which there is preferred attack on the smaller alkyl group in the conformational order as illustrated for 38-40 Thus, transition states involving migration and C-H insertion are less strained from 38 than 39 than 40 Finally, the migratory ability order of the alkyl groups in 8 and 9 provides support for the premise that the aptitudes of cyclopropyl, β,β-dimethylvinyl and phenyl groups to migrate carbenically are related to their participative π-electron capacities







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$R_1 = H$, $R_2 = CH_3$

R_1 and $R_2 = CH_3$

39

$R_1 = H$, $R_2 = CH_3$

R_1 and $R_2 = CH_3$

40

$R_1 = H$, $R_2 = CH_3$

R_1 and $R_2 = CH_3$

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3. Isomerization via diradical processes analogous to **25** will also rationalize formation of 21.

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