

REACTION OF DIMETHYLVINYLDENECARBENE WITH AZOBENZENE.

A NOVEL FORMATION OF BENZIMIDAZOLE DERIVATIVE¹

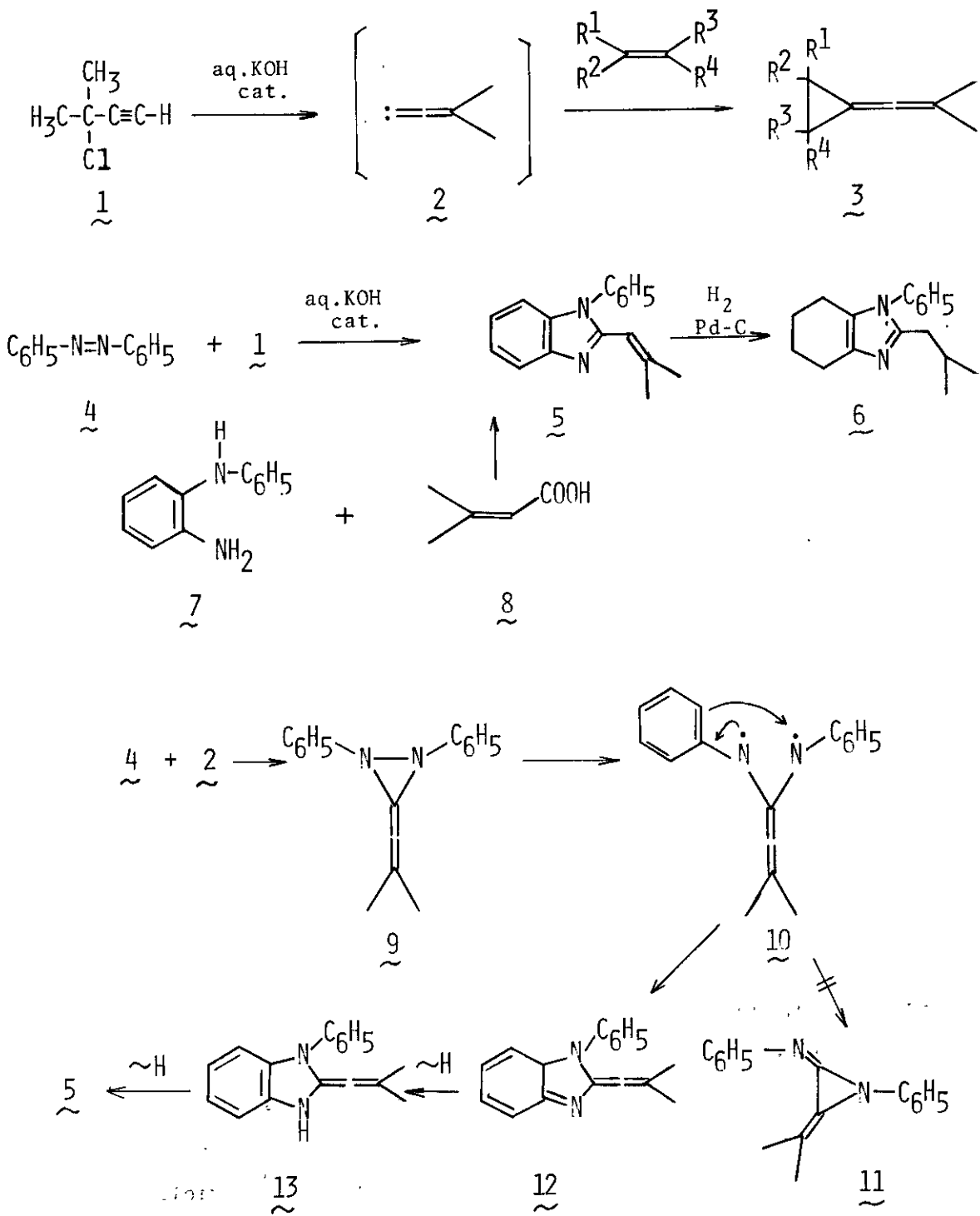
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Dimethylvinylidenecarbene (2) generated from 3-chloro-3-methyl-1-butyne (1) and alkali by the phase-transfer method reacted with azobenzene (4) to afford 1-phenyl-2-isobutenylbenzimidazole (5).

Recently Julia et al.² and we reported that dimethylvinylidenecyclopropanes (3) are synthesized effectively by using the phase-transfer technique⁴ from 3-chloro-3-methyl-1-butyne (1) and olefins in the presence of alkali. Now we wish to report the reaction of azobenzene (4) with dimethylvinylidenecarbene (2) generated by the phase-transfer method. To a vigorously stirred mixture of 51% aqueous potassium hydroxide (50 ml), benzene (20 ml), benzyltriethylammonium chloride (0.15 g) and 4 (15 mmol) was added 1 (10 mmol) slowly (in ca. 2.5 hr), and the mixture was stirred for further 14 hr at ambient temperature.

The diluted mixture with water was extracted with ether to afford crude product which was purified on an alumina column (benzene as an eluent) to give a 1:1 adduct (5) (10% yield,



Scheme

nonoptimized), mp 65.5-66.5°;† m/e 248 (M⁺); δ (CDCl₃) 7.3-7.9 (9H, m), 6.17 (1H, broad s), 1.95 (3H, s), and 1.80 (3H, s).

The spectral characteristics suggested 5 to be 1-phenyl-2-isobutenylbenzimidazole, a rearranged product of an initial adduct 9 but not to be 11 as expected from the rearrangement of carbocyclic dimethylvinylidenecyclopropanes.⁵ The structure of 5 was further confirmed by the chemical conversion on catalytic hydrogenation (10% Pd-C) to hexahydro derivative 6 (72% after recrystallization from *n*-hexane), mp 53-54°; m/e 254 (M⁺); δ (CDCl₃) 7.29 (5H, m), 2.4-2.7 (6H, m), 1.6-1.9 (5H, m), and 0.77 (6H, d, J=6.9Hz), and by the same glc retention time with a sample prepared by the condensation⁶ of N-phenyl-*o*-phenylenediamine (7) with β -methylcrotonic acid (8).

The formation of 5 in the above reaction could be rationalized by an initial trap of 2 by 4 to give the corresponding adduct 9 which should be thermally labile compared with the carbocyclic analogue because of much smaller bond dissociation energy of N-N than C-C,⁷ and hence, rearranged to 5 probably via 10, 12 and 13 as explained in the scheme.

It should be mentioned also that above reaction of 2 with the N=N bond of azobenzene is quite different from that of dichlorocarbene from PhHgCCl₂Br which gives only fragmentation product, phenylcarbonimidoyl dichloride.⁸

† All melting points are uncorrected. Satisfactory analyses were obtained on the new compounds reported in this communication.

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