

REACTION OF 1,2-DIAMINO-3-SUBSTITUTEDCYCLOPROPENIUM  
IONS WITH ARYLMAGNESIUM BROMIDES

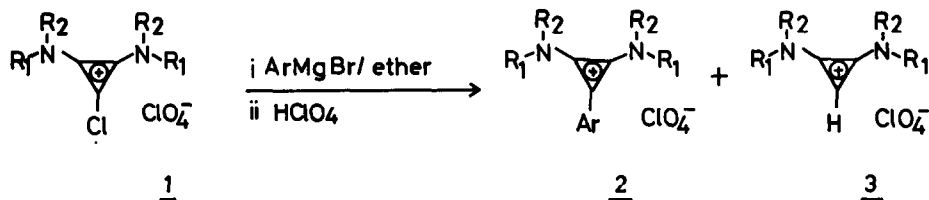
Zen-ichi Yoshida,\* Hisatoshi Konishi,<sup>1)</sup> Yoshikiyo Miura,  
and Hisanobu Ogoshi

Department of Synthetic Chemistry, Kyoto University,  
Kyoto 606, Japan

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Syntheses and structure of the electron rich cyclopropenium ion substituted with amino groups have been investigated in our laboratory.<sup>2)</sup> It is noted that treatment of 1,2-bisdialkylamino-3-chlorocyclopropenium ion (1) with alkali gave diaminocyclopropenone *via* nucleophilic attack of hydroxy anion towards the carbon atom of the 3-position. Thus deep insight into reactivity of the pivotal carbon(C-3) should enable us to prepare novel cyclopropenium derivatives. We wish to report the reaction of 1 with arylmagnesium bromide.

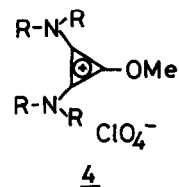
A mixture of 1,2-bisdialkylamino-3-chlorocyclopropenium perchlorate 1 and excess molar amount of arylmagnesium bromide in absolute ether was refluxed for 10 hr. The reaction mixture was poured into dil. perchloric acid and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated to dryness. Recrystallization of the residue gave the arylsubstituted compound (2)<sup>3)</sup> and a small amount of diaminocyclopropenium perchlorate (3).<sup>4)</sup> (2a); mp 215-216°; 61% yield;  $\nu_{\max}$ (KBr) 1915, 1630, 1560, 1095, 775, 732, and 680 cm<sup>-1</sup>;  $\delta$ (DMSO-d<sub>6</sub>) 1.16(d, 12H), 1.37(d, 12H), 3.94(sep, 2H), 4.10(sep, 2H), and 7.58(m, 5H).<sup>6)</sup> (2b); mp 260°(dec.); 54%  $\nu_{\max}$ (KBr) 1920, 1574, 1090, 798, 727, and 700 cm<sup>-1</sup>;  $\delta$ (DMSO-d<sub>6</sub>) 1.32(s, 18H), 3.32(s, 6H), and 7.3-7.6(m, 5H). (2c); mp 281-282°; 73%  $\nu_{\max}$ (KBr) 1915, 1609, 1560, 1555, 1253, 1095, and 841 cm<sup>-1</sup>;  $\delta$ (DMSO-d<sub>6</sub>, 80°) 1.30(d, 24H), 3.84(s, 3H), 4.03(sep, 4H), and 7.1-7.5(AA'BB', 4H). (2d); mp 295°(dec.); 8%;  $\nu_{\max}$ (KBr) 1917, 1597, 1552, 1252, 1093, and 760 cm<sup>-1</sup>;  $\delta$ (DMSO-d<sub>6</sub>, 100°)



	$\text{R}_1$	$\text{R}_2$	$\text{Ar}$		$\text{R}_1$	$\text{R}_2$	$\text{Ar}$
<u>2a</u>	i-Pr	i-Pr	$\text{C}_6\text{H}_5\text{-}$	<u>2c</u>	i-Pr	i-Pr	$4\text{-CH}_3\text{O-C}_6\text{H}_4\text{-}$
<u>2b</u>	t-Bu	Me	$\text{C}_6\text{H}_5\text{-}$	<u>2d</u>	i-Pr	i-Pr	$2\text{-CH}_3\text{O-C}_6\text{H}_4\text{-}$

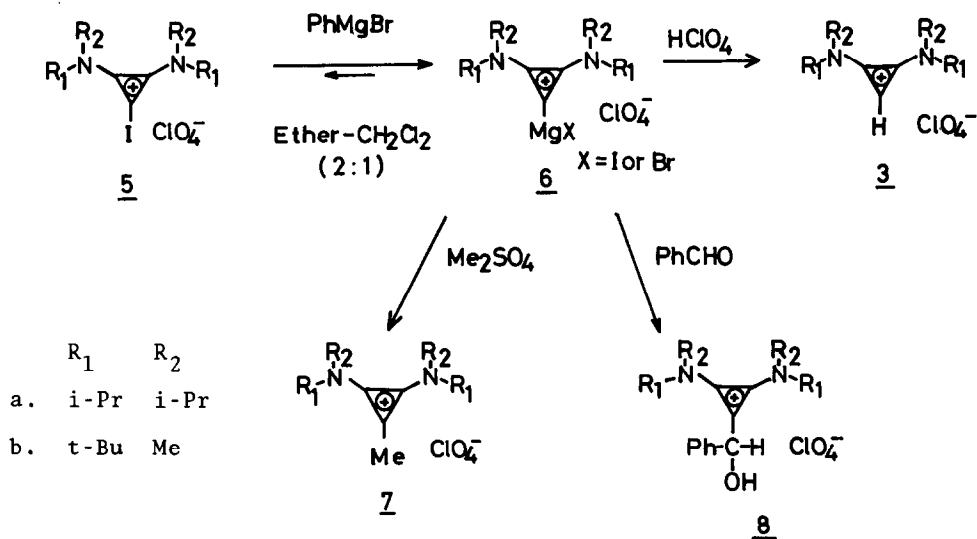
1.27(d, 24H), 3.85(s, 3H), 4.07(sep, 4H), and 7.2-7.7(m, 4H). Aryl substituted cyclopropenium salts 2 were exclusively obtained by treatment of 1,2-bisdiisopropylamino-3-methoxycyclopropenium perchlorate (4a)<sup>7</sup> with arylmagnesium bromide in ether at room temperature for 3 hr. The yields were markedly improved by changing the leaving group from Cl to OMe (2a, 74%, 2d, 58%).

The potassium iodide treatment of 1 in acetone led to the quantitative formation of 1,2-bisdiisopropylamino-3-iodocyclopropenium perchlorate (5). Addition of phenylmagnesium bromide in ether to equimolar amount of 5 in ether- $\text{CH}_2\text{Cl}_2$  (2:1) gave colorless and transparent solution within a few minutes and successive treatment of the reaction mixture with dil.  $\text{HClO}_4$  yielded only diaminocyclopropenium perchlorate 3. Formation of 3 is probably due to generation of the magnesium complex of diaminocyclopropenyliene (6). The reaction behaviour of 6 towards electrophiles have been examined (*vide infra*). The structure of the intermediate can be represented as magnesium compound of positively charged  $2\pi$  aromatic system. Thus the intermediate is regarded as Grignard reagent of the cyclopropenium ion 6. Infrared study of the equilibrium between 5 and 6 shows predominant existence of 6. The solution 6a exhibits a new band at  $1834\text{ cm}^{-1}$  assigned to the framework deformation of cyclopropenium ion bonded to magnesium in the infrared.



The reaction of the solution containing 6 with dimethylsulfate afforded 1,2-bisdialkylamino-3-methylcyclopropenium perchlorate (7). (7a); 84% yield.<sup>4)</sup> (7b); 80%; mp 179°;  $\nu_{\max}$ (KBr) 1918, 1552, 1180, and 1092  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 1.45(s, 18H), 2.27(s, 3H), and 3.25(s, 6H). The carbinol (8a)<sup>4)</sup> was obtained in quantitative yield from the reaction of 6a with benzaldehyde. The reactivity of 5 to nucleophile is markedly depressed by the substitution with strong electron-donating amino group and the carbon of cyclopropenium ion core is more electronegative than the phenyl carbon.<sup>8)</sup> Therefore, the halogen-metal exchange between the iodide 5 and phenylmagnesium bromide readily proceeds to give Grignard reagent 6. In the case of the chloride 1, slow exchange reaction of chlorine with magnesium causes formation of 2 through a nucleophilic attack of carbanion towards 1. For reaction of 7,7-dichlorocycloheptatriene, the iodide 5a was recovered in nearly quantitative yield. The Grignard reagent 6 seems to be less reactive than phenylmagnesium bromide.

The Grignard reagent 6a was also prepared by the treatment of the iodide 5a with magnesium in the presence of 1,2-dibromoethane. Generation of 6a was confirmed by successive chemical reactions such as hydrolysis, alkylation and addition to aldehyde.



References and Notes

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- 2) (a) Z. Yoshida, and Y. Tawara, J. Am. Chem. Soc., 93, 2573 (1971).  
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(d) Z. Yoshida, Top. Curr. Chem., 40, 47 (1973).  
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(f) Z. Yoshida, S. Araki, and H. Ogoshi, Tetrahedron Lett., 19 (1975).
- 3) All new compounds gave satisfactory elementary analyses.
- 4) The structure was proved by comparison of its infrared and pmr spectra with those of an authentic sample.<sup>5)</sup>
- 5) To be published elsewhere.
- 6) Recently, this compound was prepared by another method; M. T. Wu, D. Taub, and A. A. Patchett, Tetrahedron Lett., 2405 (1976).
- 7) The compound 4a was prepared by treatment of 1a with methanol in the presence of sodium bicarbonate quantitatively, mp 162°.
- 8) The <sup>13</sup>C-H coupling constant of the ring proton of 1a is 242 Hz. This value is agree with the characteristic hybridization of cyclopropenium ion core.<sup>9)</sup>
- 9) R. Breslow, and J. T. Groves, J. Am. Chem. Soc., 92, 984 (1970).