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DUAL REACTIVITY OF CYCLOHEPTATRIENE AND NORCARADIENE VALENCE ISOMERIZATION SYSTEM: COPE REARRANGEMENT AND INTRAMOLECULAR [2+4] CYCLOADDITION REACTION OF 1-CHLORO-1-(CYCLOHEPTATRIEN-7-YL)-3,3-DIPHENYLALLENE[#]

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Titled compound (1) was prepared from benzophenone and 2-(cycloheptatrien-7-yl)ethynylmagnesium bromide. 1 gave the two isomers, i. e., a bicyclo[3.2.2]nonatriene derivative (2) and a formal [2+4] intramolecular cycloaddition product (3). Structural determination of the isomers and plausible mechanisms of the isomerization are discussed.

Valence tautomerization between cycloheptatriene and norcaradiene is an intriguing phenomenon[1)] and has been explored in active investigations.[1-5)] We have been interested in the valence tautomerization and reactivities of cycloheptatrienes and their analogous compounds.[5)] As a part of our studies, we present, in this paper, synthesis of 1-chloro-1-(cycloheptatrien-7-yl)-3,3-diphenylallene (1) and its isomerization to a bicyclo[3.2.2]nonatriene compound (2) by Cope rearrangement from its norcaradiene form and to a barbaralane derivative (3) resulting from its cycloheptatriene form by intramolecular [2+4] cycloaddition.

Reaction of benzophenone with 2-(cycloheptatrien-7-yl)ethynylmagnesium bromide[6)] gave the corresponding alcohol (4, 3-(cycloheptatrien-7-yl)-1,1-diphenylprop-2-yn-1-ol) as an oil which afforded a crystalline adduct (mp 202 °c, 84%) on treatment with N-methyltriazoline-2,5-dione. The chloroallene was obtained in 70% yield by the reaction of the alcohol 4 with thionyl chloride in the presence of an excess triethylamine. The chloroallene 1 is an oil which possesses an absorption at 1950 cm^{-1} in its IR spectrum. On standing, 1 isomerized to a mixture of two different isomers (2 and 3, ca. 1:1, mp 132-134 °C) in 60-70% yield. Heating or treatment with silica gel accelerates the above isomerization. Separation and purification of each component were difficult, but finally achieved by combination of fractional recrystallization and liquid chromatography. The physical properties of them are shown in the following:

2: mp 130-131.5 °C; mass, m/e (%), 318 (M^++2, 19.0), 316 (M^+, 56.5), 281 (M^+-Cl, 100), and 203 (281-C_6H_6, 75.4); ^{1}H NMR ($CDCl_3$) ppm, 3.47 (1H, dtt, J=8.5, 7.5,

& 1.5 Hz, H_1), 4.25 (1H, tt, J=7.5 & 1.5 Hz, H_5) 6.11 (2H, ddd, J=7.5, 6.0 & 1.5 Hz, $H_{7,8}$), 6.23 (1H, d, J=8.5 Hz, H_2), 6.53 (2H, ddd, J=7.5, 6.0 & 1.5 Hz, $H_{6,9}$), and 7.21 (10H, m, phenyl's H).

3: mp 165-166 °C; mass, m/e (%), 318 (M^++2, 20.2), 316 (M^+, 60.4), 281 (M^+-Cl, 100), and 203 (281-C_6H_6, 71.7); ^{1}H NMR ($CDCl_3$) ppm, 3.18 (1H, t, J=7.0 Hz, H_1), 3.68 (2H, dd, J=7.0 & 6.5 Hz, $H_{2,8}$), 4.80 (2H, d, J=7.5 Hz, $H_{4,6}$), 5.63 (2H, dd, J=7.5 & 6.5 Hz, $H_{3,7}$), and 7.16 (10H, m, phenyl's H); UV_{max} (cyclohexane), nm (ε), 209 (20100), 235 (13100), and 269 (shoulder, 9300).

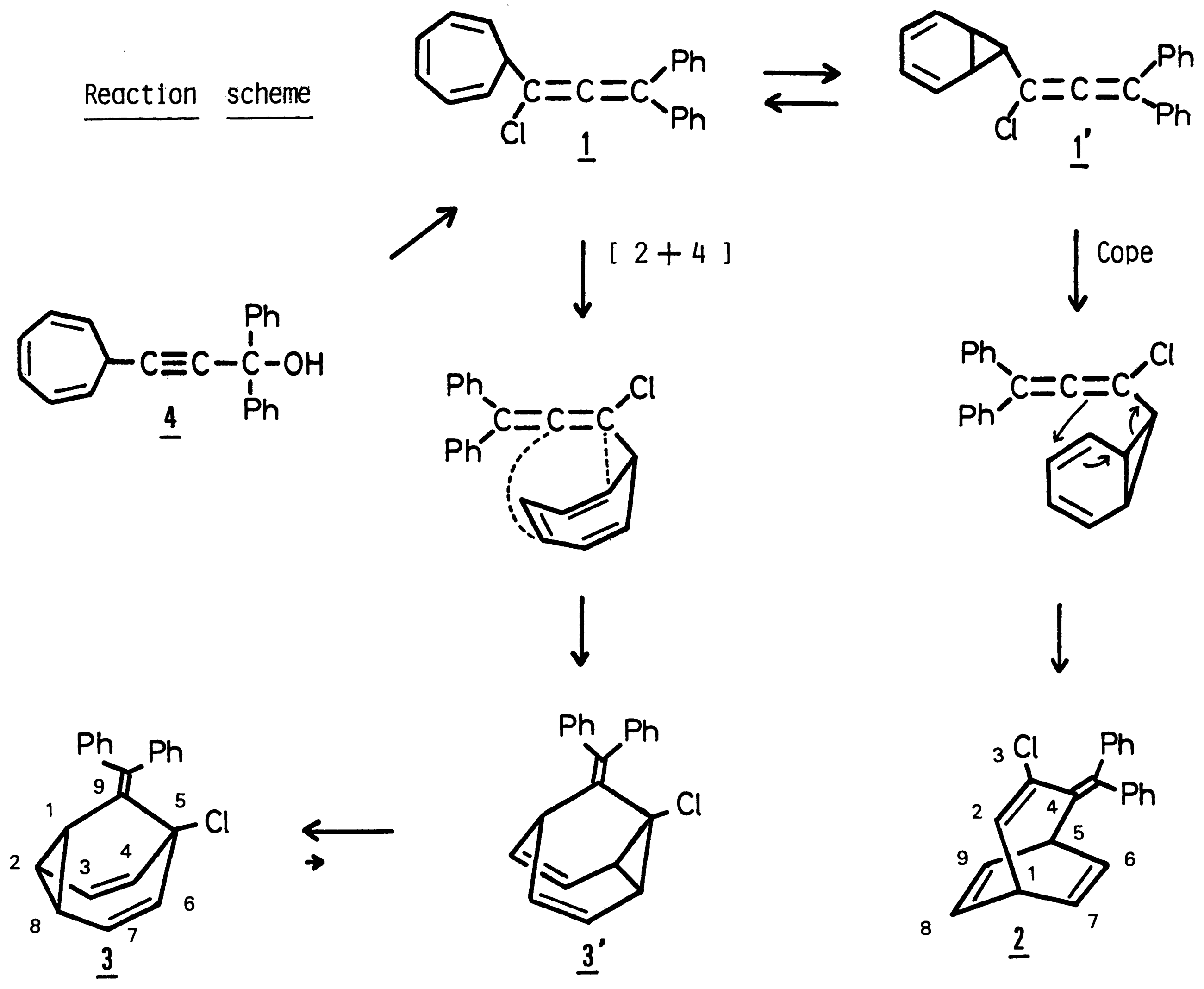
The structure of 2 was assigned as 3-chloro-4-diphenylmethylene bicyclo[3.2.2]nona-2,6,8-triene by analogous coupling pattern of 2 with that of bicyclo[3.2.2]nona-2,6,8-triene system$^{7)}$ in their NMR spectra.

The electronic spectrum of 3 indicates that 3 possesses a styrene chromophore. The NMR spectra of 3 suggest presence of a cyclopropane moiety (3.18 and 3.68 ppm in ^{1}H NMR; 31.47 and 61.39 ppm in ^{13}C NMR). The peak at 61.39 ppm of ^{13}C spectrum shows a saturated C-Cl bond. Analogous pattern between the ^{1}H NMR spectrum of 3 and that of barbaralone (5)$^{8)}$ and the above analyses of the NMR spectrum of 3 lead to the conclusion that the structure of 3 is elucidated as 5-chloro-9-diphenylmethylenebarbaralane. For confirmation of the structure of 3, 9-diphenylmethylenebarbaralane (6) was synthesized from 5 by modified method of Barton's olefin synthesis.$^{9)}$ Reaction of 5 with diphenylmercaptoacetic acid afforded the oxathiolan-5-one derivative (7, mp 61-63 °C, IR (CCl_4), 1775 cm^{-1}), and subsequent treatment of 7 with tris(diethylamino)phosphine gave 9-diphenylmethylenebarbaralane 6 (mp 151-152 °C, UV_{max} (cyclohexane), nm (ε), 210 (22100), 236 (1200), and 272 (13800); ^{1}H NMR ($CDCl_3$) ppm, 3.13 (2H, d, J=6.4 Hz, $H_{1,5}$), 4.10 (4H, ddd, J=6.4 Hz, $H_{2,4,6,8}$), 5.65 (2H, d, J=6.4 Hz, $H_{3,7}$), and 7.20 (10H, m, phenyl's H)). Although reductive removal of the chlorine atom of 3 failed, the electronic spectra of 3 and 6 are very similar each other, and ^{1}H NMR spectra are consistent with the assigned structures.$^{10)}$

As for plausible mechanisms of the above isomerization, we propose the Cope rearrangement from norcaradiene form in the case of 2 and a formal [2+4] intramolecular cycloaddition reaction from cycloheptatriene form in the case of 3 as shown in the scheme. Analogous Cope rearrangements to that of 1 have been reported for other cycloheptatrienes.$^{7)}$ The primary product of the cycloaddition must be 3' (the valence isomer of 3). However, the chlorine atom on the cyclopropane ring of 3' interferes with one of the phenyl groups according to the investigation of Dreiding model of 3'. This steric interference causes to fix to the other isomer 3 in which the steric interference between the chlorine atom and the phenyl group is not as big as in the case of 3'.

The reason why 3 was obtained by formal [2+4] intramolecular cycloaddition from the triene form 1 is not clear yet. Although there are no detectable amounts

Reaction scheme



of norcaradiene isomers are present in the system, cycloaddition reactions of cycloheptatrienes have been reported to result from their norcaradiene forms.[1] Cycloadditions from their cycloheptatriene forms are rare or occur in very poor yields (~1%)[11] except for special spiro[2.6]nonatriene's cases[12] or additions with singlet oxygen.[13] It is known that substituents at C_7 position of cycloheptatrienes cause the equilibrium between cycloheptatrienes and norcaradienes to norcaradiene side.[1,3,4] However, formation of 3 from 1 shows opposite tendency to the experimental facts and theoretical predictions.

Cycloadditions of allenes proceed by radical processes.[14] Therefore, the reaction of 1 to 3 is also possible to proceed by a radical mechanism, but no ESR or CIDNP signals were observed during the reaction. An ionic multi-step mechanism is other possible one for the formation of 3. Actually, ionic mechanisms for cycloadditions of allenes have been suggested from experimental facts[15] and theoretical calculation.[14] Thus, further investigation is necessary for confirmation of the mechanism of the formation of 3, and studies under this program are in progress.

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