INTRAMOLECULAR DIELS-ALDER REACTION WITH INVERSE ELECTRON DEMAND IN 2-(2,3-DIPHENYLCYCLO-PROPEN-1-YL)- β -TROPOLONE. CONSTRUCTION OF A BRIDGED SEMIBULLVALENE-TYPE CARBON SKELETON

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Summary: An etheno-bridged semibullvalene-type carbon skeleton has been synthesized in one pot reaction via the intramolecular Diels-Alder reaction of 2-(2,3-diphenylcyclopropen-1-yl)- β -tropolone generated in situ from the reaction of lithium β -tropolonate with diphenylcyclopropenium ion. X-ray analysis of the adduct disclosed that the (Ph)C-C(Ph) bond is longer than the other cyclopropane bonds.

Troponoid compounds undergo easily thermal cycloaddition reactions not only with electron-poor olefins but also with electron-rich olefins to give bicyclic or tricyclic compounds.¹ However, there has appeared no example of cycloaddition reaction involving β -tropolone (<u>la</u>)² and its derivatives. Moreover in troponoid chemistry, intramolecular Diels-Alder reactions which could provide one of the most useful ways to synthesize a variety of interesting polycyclic species³ have remained virtually unexplored.⁴

We report here that 2-(2,3-diphenylcyclopropen-1-yl)- β -tropolone <u>3</u>, generated in situ from the reaction of lithium β -tropolonate <u>1b</u> with diphenylcyclopropenium ion <u>2</u>, undergoes readily intramolecular Diels-Alder reaction with inverse electron demand to produce a novel polycyclic diketone <u>4</u>. This is the first examples of cycloaddition reaction concerning with β -tropolone and of intramolecular thermal cycloaddition reaction in troponoid systems. Although several examples of intramolecular cycloaddition reactions participated by a cyclopropenyl group have recently appeared, ^{3a,5} they are limited to unsubstituted, methyl-, and chloro-substituted cyclopropenes. The formation of <u>4</u> is a new entry into the intramolecular cycloaddition reactions where diphenylcyclopropene takes part in. Adduct <u>4</u> is constructed by a C₃, C₇-etheno bridged semibullvalene-type carbon skeleton⁶ including a strained cis diphenylcyclopropane moiety, and hence its photochewrical and thermal rearrangements would be of interest.

A solution of diphenylcyclopropenium fluoroborate 2^7 in acetonitrile was added dropwise into a refluxing acetonitrile solution of an equimolar amount of <u>1b</u>⁸ and further reflux was continued for 25 min. After quenching with a large excess of water, the reaction mixture was chromatographed on silica gel to give the adduct <u>4</u> as colorless prisms in 43% yield together with dicyclopropenyl compound <u>5</u> in 2.2% yield.⁹

Adduct <u>4</u> exhibits strong carbonyl bands at around 1760 cm⁻¹ which is higher by 10 cm⁻¹ than that of cyclopentanone. The ¹H NMR of <u>4</u> shows a two-proton sextet in olefinic region. The high field signals at δ 3.32, 3.84, and 4.07 were assigned to H-3, H-1,5, and H-7, respectively, since the double-triplet at δ 4.07 (H-7) was coupled to the doublet at δ 3.32 (vicinal H-3) with 4.7 Hz and to the multiplet at δ 3.84 (remote H-1,5) with 2.9 Hz. On irradiation at δ 4.07 (H-7), the olefinic proton signal and the bridgehead proton signal (H-1,5) appeared in AA'XX' pattern, which was closely parallel to the NMDR spectral behavior of



the olefinic and bridgehead protons of $\underline{7}$, revealing the presence of the similar partial structures in $\underline{4}$ and $\underline{7}$. Adduct $\underline{7}$ was obtained via $\underline{6}$ as shown in the following Scheme.¹⁰



The plane of symmetry present in <u>4</u> was clearly evidenced by the appearance of one carbonyl, one olefinic, and four aliphatic carbon signals in approximate ratio of 2:2:2:2:1:1 in addition to the four phenyl carbon signals in the ¹³C NMR spectrum.¹¹ The ¹³C chemical shift of C-3 (∂ 23.4 ppm) is almost identical with that of C-1 of quadricyclane (∂ 23.2 ppm).¹² The two phenyl groups would exist in face to face orientation, since the ¹H NMR featured a high field shift of the ortho phenyl proton signals.

A straightforward mechanistic pathway leading to $\underline{4}$ can be unequivocally visualized through the intramolecular Diels-Alder reaction of $\underline{3a}$ which is initially formed from the reaction of $\underline{1b}$ with 2. The compound 5 is regarded to be originated from $\underline{3b}$ through subsequent cyclopropenylation at the oxygen atom, since β -tropolone alkyl ether did not react with $\underline{2}$. Neither 3 nor 4 was isolable and 5 was predominantly formed in 40.8% yield at lower reaction temperature (below 60 °C), so that cyclopropenylation of $\underline{3b}$ to give 5 could occur faster than that of $\underline{1b}$ to give 3. Although the intramolecular cycloaddition of $\underline{3a}$ to $\underline{4}$ necessiates heating at refluxing temperature of acetonitrile, this reaction is much more easy than usual intermolecular cycloadditions with ordinary electron demand, since β -tropolone shows no tendency to undergo cycloadditions with maleic anhydride and tetracyanoethylene even when heated up to 100 °C for a long reaction period. Formation of $\underline{4}$ with ease is apparently attributable to i) the high HOMO level of the dienophile (diphenylcyclopropene) due to enhanced ring strain, ii) the low LUMO level of the diene due to the conjugation with carbonyl groups, and iii) the geometry of $\underline{3a}$ which is favorable to effective HOMO-LUMO overlapping and would not require any large entropy change on going to the transition state for the cycloaddition.

Recently, remarkably long (Ph)C-C(Ph) bonds in caged cis 1,2-diarylcyclobutane derivatives have been attributed to the extension of Mislow's bond-elongation mechanism and







Fig. 1. An ORTEP view of 4 with bond lengths (Å).

Fig. 2. Averaged bond angles of 4 (°).

it has been revealed that the elongation is enhanced by the effective through-bond orbital interaction between π orbitals of the phenyl groups through the strained σ bond.¹³ In order to investigate whether such kind of bond elongation is occurred or not in caged diarylcyclo-propane derivatives, an X-ray crystallographic analysis of <u>4</u> was performed.

Crystals of 4 belong to orthorhombic system with eight molecules in a unit cell of dimensions <u>a</u> = 11.693(4), <u>b</u> = 27.216(6), <u>c</u> = 9.788(2) Å. The space group is Pbca. The structure was solved by MULTAN 78 and refined by block diagonal least squares method using 2439 reflections to give the final R value of 7.0%.¹⁴ Selected bond lengths are shown in the ORTEP view of 4 (Fig. 1), where the face to face orientation of the vicinal phenyl groups is clearly seen. Averaged bond angles of 4 are shown in Fig. 2. The phenyl rings are almost perpendicular to the $C_2 - C_4$ bond having the torsion angles of -99.2° and 78.7° for $C_{12}-C_{11}-C_2-C_4$ and $C_{16}-C_{11}-C_2-C_4$, and -119.7° and 63.5° for $C_{18}-C_{17}-C_4-C_2$ and $C_{22}-C_{17}-C_4-C_2$, thus the π orbitals of the phenyl groups are in nearly parallel with the σ or σ^{\star} orbital of strained C_2-C_4 bond. Indeed the C_2-C_4 bond (1.530 Å) of <u>4</u> is somewhat longer than the other cyclopropane bonds (1.516 and 1.516 Å). Although MNDO analysis would at least be indispensable before drawing any conclusion, it is quite plausible that the through-bond interaction would also be operative in the cis-diphenylcyclopropane system comprised in 4. The mass spectrum of 4 exhibits strong peaks at m/e 284 (41%) and m/e 243 (100%) ascribed to 8 and 9, respectively. This characteristic fragmentation would be initiated by the rapid cleavage of the long and weak $C_2 - C_4$ bond followed by the decarbonylation to give 8.



A further distortion in 4 is seen in the angle between the plane of the cyclopropane ring and C_3-C_7 bond, 110.3°, which is narrower by 12.1° than the corresponding angle in alkylcyclopropane and is almost comparable to that of nortricyclane.¹⁵

Studies on thermal and photochemical rearrangements of 4 are currently in progress.

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Table 1. Physical and Spectroscopic Data of Compounds 4, 5, 6, and 7.

- 4: Colorless prisms, mp. 237-238 °C, 43% yield, MS m/e 314 (M⁺+2, 7%), 313 (M⁺+1, 17%), 312 (M⁺, 59%), 284 (M⁺-CO, 41%), 243 (100%); IR (KBr) 3060, 3040, 2960, 1760, 1730, 1720, 1600, 1500, 1440 cm⁻¹; ¹H NMR (200 MHz, in CDCl₂) & 3.32 (1H, d, <u>J</u>=4.7 Hz, H-3), 3.78-3.90 (2H, AA' part of AA'XX' signals, H-1,5), 4.07 (1H, dt, <u>J</u>=4.7 and 2.7 Hz, H-7), 6.52-6.68 (2H, XX' part of AA'XX' signals, H-9,10), 6.90-7.00 (4H, m, ortho-position of Ph), 7.04-7.18 (6H, m, meta-, para-positions of Ph); ¹³C NMR (50.3 MHz, in CDC1₃) & 23.41 (C-3), 41.92 (C-2,4), 51.59 (C-1,5), 70.37 (C-7), 131.67 (C-9,10), 200.12 (C-6,8), 126.82, 128.11, 128.11 (Ph), 137.13 (Ph-ipso); Electronic spectrum λ max (MeCN) nm (log ε) 220 sh (4.20), 305 (3.00).
- 5: Colorless crystals, mp. 162-164 °C, MS m/e 502 (M⁺, 9.6%), 424 (14%), 311 (100%), 279 (16%), 205 (68%); IR (KBr) 3060, 3040, 1630, 1605, 1530, 1495, 1445 cm⁻¹: ¹H NMR (200 MHz in CDC1₂) & 2.25 (1H, s, H-8), 3.95 (1H, s, H-11), 6.46 (1H, dd, J=11.0 and 1.5 Hz, H-4), 6.59 (1H, ddd, <u>J</u>=11.0, 8.0, and 1.2 Hz, H-5), 6.85 (1H, ddd, <u>J</u>=8.0, 12.5, and 1.5 Hz, H-6), 7.07 (1H, dd, J=12.5 and 1.2 Hz, H-7), 7.10-7.65 (18H, m, Ph), 7.82 (2H, m, Ph).
- 6: Yellow orange oil, 87% yield, MS m/e 339 (M⁺, 17%), 296 (M⁺-OAc, 100%), 227 (68%); IR (CHCl₂) 3020, 1780, 1720, 1500, 1410, 1190, 1130 cm⁻¹; ¹H NMR (60 MHz, in CDCl₂) & 2.25 (3H, OAc), 5.2-6.1 (3H, m, H-1,5,3), 6.3-7.3 (2H, m, H-6,7), 7.40 (5H, s, Ph).
- <u>7</u>: Colorless crystals, mp. 243-247 °C (dec.), 60% yield, MS m/e 297 (M⁺, 23%), 227 (100%), 119 (50%), 80 (61%); IR (KBr) 3100, 3000, 2900, 1710, 1500, 1420, 1300, 1230, 1150 cm^{-1} ; ¹H NMR (90 MHz, in CDC1₃) 8 3.80 (1H, dt, <u>J</u>=16.2 and 1.1 Hz, Ha-3), 4.44 (1H, d, <u>J</u>=16.2 Hz, Hb-3), 5.48-5.64 (2H, m, AA' part of AA'XX', H-1,5), 6.56-6.68 (2H, m, XX' part of AA'XX', H-6,7), 7.52 (5H, s, Ph).

References and Notes

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