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FORMATION OF NOVEL CAGE COMPOUNDS VIA ENDO-[3 + 2] CYCLOADDUCTS BETWEEN THIAZOLIUM N-METHYLIDES AND METHYLENECYCLOPROPENES

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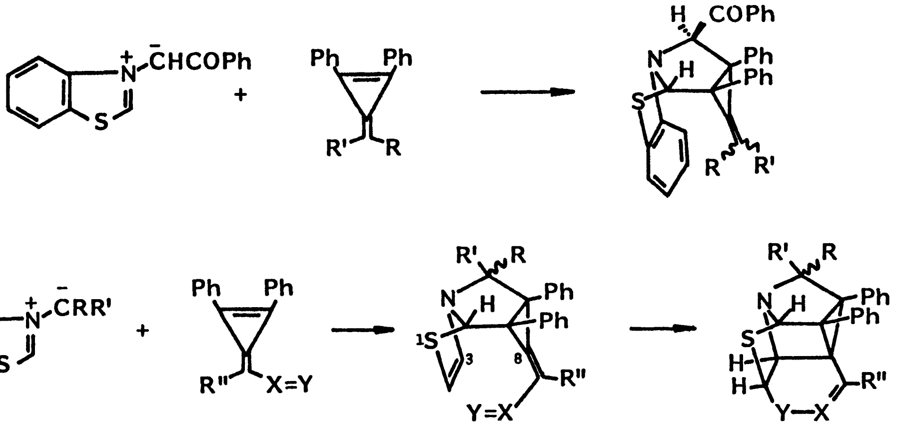
Thiazolium N-phenacylide and N-dicyanomethylide react with a methylenecyclopropene bearing an aryl group on the 4-position to give novel cage compounds, 6,8-thiazapentacyclo[6.3.1.$0^{1,10}$.$0^{5,12}$.$0^{7,11}$]dodecenes. The reaction proceeds via an intramolecular Diels-Alder reaction of the initially formed endo-[3 + 2] cycloadducts, followed by a hydrogen shift.

Methylenecyclopropenes undergo cycloaddition reactions with a variety of 1,3-dipoles.[1-7] The modes of these reactions depend not only on the nature of 1,3-dipoles, but also on the substituents at the 4-position of methylenecyclopropenes.[8] We have recently found that benzothiazolium N-phenacylide adds to the cyclic double bond of certain methylenecyclopropenes to give endo-[3 + 2] cycloadducts in good yields[9]: This is the first example for the formation of stable [3 + 2] cycloadducts in the reactions of 1,3-dipoles with methylenecyclopropenes. If a similar endo-[3 + 2] cycloadduct is formed in the reaction of a thiazolium N-methylide with a methylenecyclopropene bearing an appropriate functional group at the 4-position, a cage compound might be expected to be formed via an intramolecular cyclization reaction of the endo-[3 + 2] cycloadduct, whose Dreiding model indicates that the carbons at the 3- and 8-positions are located closely enough to be linked[10] (Scheme 1).

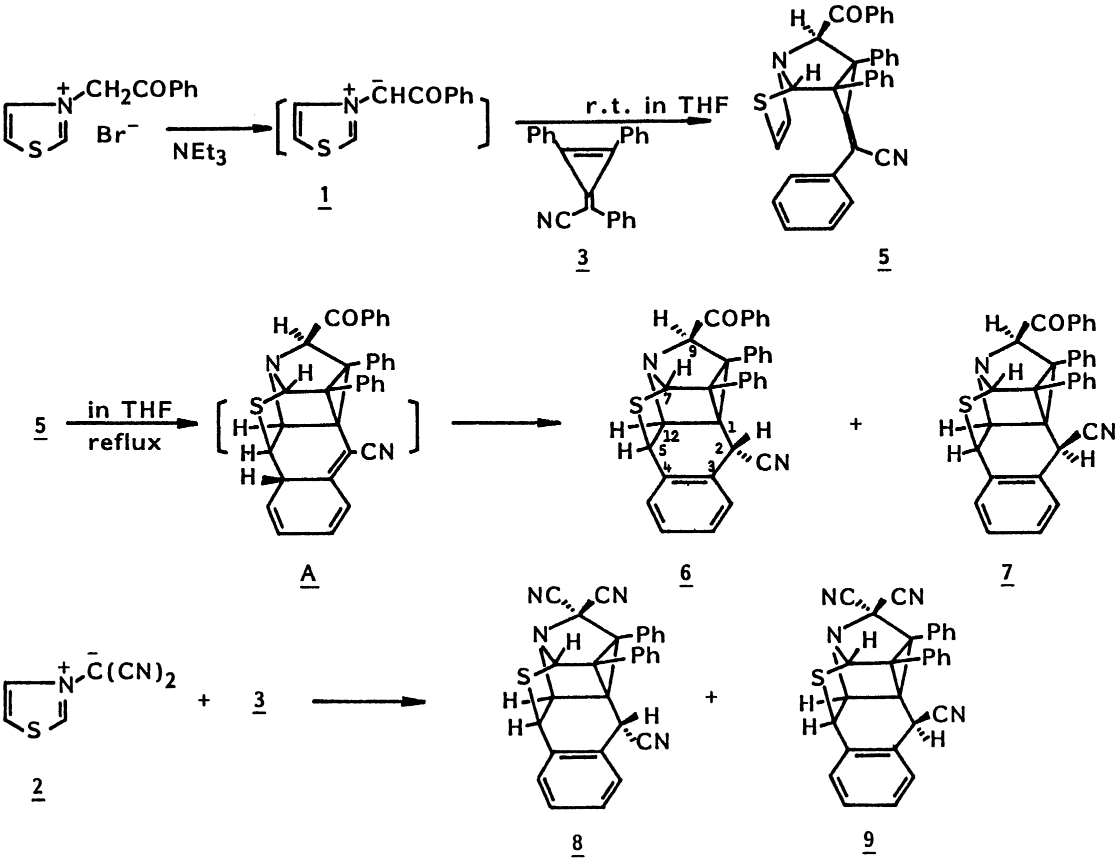


Scheme 1

This expectation is now realized: We wish to report here the formation of novel cage compounds from the reaction of thiazolium N-phenacylide 1 and N-dicyanomethylide 2 with 2-phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile 3 and 9-(2,3-diphenyl-2-cyclopropenylidene)anthrone 4, which reacted with benzothiazolium N-phenacylide to afford the corresponding endo-[3 + 2] cycloadducts as the sole products.[9]

First, we have investigated the reaction of 1 with 3. To a solution of 3-phenacylthiazolium bromide (622 mg, 2.2 mmol) and 3[11] (610 mg, 2.0 mmol) in dry THF (100 mL) was added NEt_3 (221 mg, 2.2

mmol) at 0°C, with stirring, under nitrogen. After the reaction mixture was stirred at 0°C for 2 h, and then at room temperature for 3 h, the precipitated triethylammonium bromide (quantitative) was removed by filtration. The filtrate was concentrated in vacuo to leave a residue, which was purified by chromatography on silica gel using benzene as an eluent to give 807 mg (79%) of the 1:1 adduct 5, mp 150-152°C (dec), as pale yellow prisms. On the basis of spectral data[12] as well as of the chemical conversion described below, 5 was assigned as the expected endo-[3 + 2] cycloadduct. Upon heating in THF under reflux for 3 h, 5 was transformed into two isomeric cage compounds 6, mp 177-178°C (dec), and 7, mp 170-172°C (dec), in 51 and 31% yields, respectively.

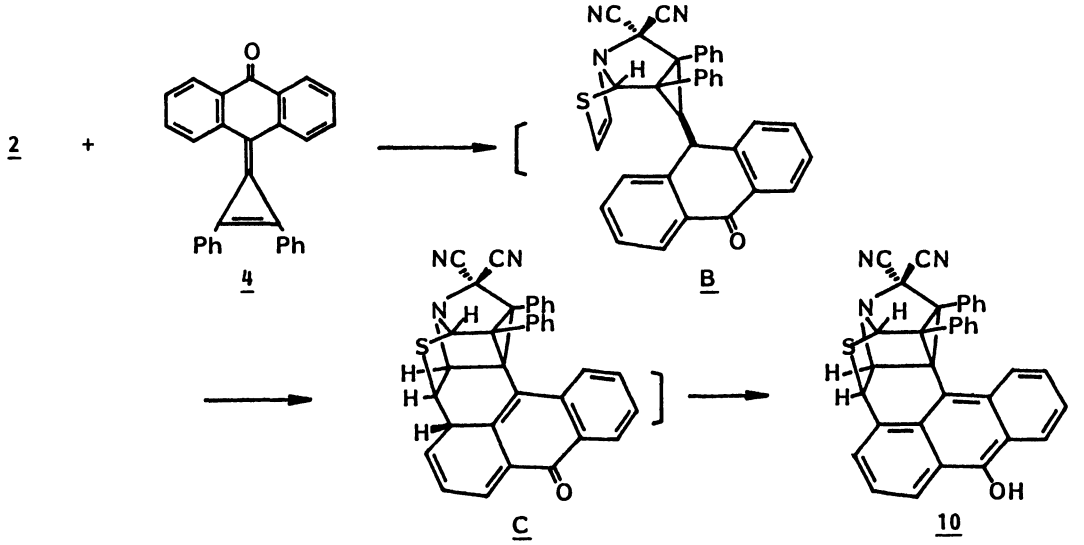


Scheme 2

On the other hand, the methylide 2[13] reacted with 3 to give directly analogous two cage compounds. A solution of 2 (298 mg, 2.0 mmol) and 3 (610 mg, 2.0 mmol) in dry THF (30 mL) was stirred at room temperature for 4 days until 3 was completely consumed. The reaction mixture was concentrated in vacuo to leave a residue, which was chromatographed on silica gel using benzene as an eluent to give 460 mg (51%) and 329 mg (36%) of the 1:1 adducts 8, mp 274-276°C (dec), and 9, mp 259-260°C (dec), respectively.

On the basis of spectral data,[14] each of isomers 6, 7 or 8, 9 was assigned as a stereoisomerc cage compound arising from an intermediary Diels-Alder adduct like A, followed by a hydrogen shift. A few Diels-Alder reactions involving aromatic nucleus as a part of diene component have been reported in intermolecular reactions.[15] In the ^{1}H NMR spectra the 12-hydrogen in each higher melting cage compound appeared at lower field than that in each lower melting one. An inspection of the Dreiding models indicates that the 12-hydrogen in 6 or 8 is located in the deshielding cone of the cyano group on the 2-position. Thus it can be concluded that the higher melting cage compound is 6 or 8 and the lower melting one is 7 or 9, respectively.

The reaction of 2 with the methylenecyclopropene 4[16] in refluxing THF for 2 h gave a 76% yield of the cage compound 10, mp 192-194°C (dec), whose structure was again confirmed on the basis of spectral data.[17] It is evident that the reaction proceeds via an initial formation of the endo-[3 + 2] cycloadduct B, followed by an intramolecular Diels-Alder reaction to yield C, which is converted to 10 by a hydrogen shift (Scheme 3).



Scheme 3

References

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2. Th. Eicher and E. v. Angerer, Chem. Ber., 103, 339 (1970).
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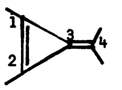
8. The numbering of methylenecyclopropene system is as follows (Th. Eicher and J. L. Weber, Topics in Current Chem., 57, 1 (1975)).



9. O. Tsuge, H. Shimoharada, and M. Noguchi, Chem. Lett., 1981, 1493.
10. The distance between the C_3 and C_8 was estimated at ca. 2.4 Å by an inspection of the Dreiding model.
11. H.-U. Wagner, R. Seidl, and H. Faβ, Tetrahedron Lett., 1972, 3883.
12. All new compounds in this paper gave satisfactory elemental analyses.

5: IR (KBr) 2210, 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.02, 5.97 (each 1H, d, =CH, J=5.0 Hz), 6.13 (1H, s, $\geq$CH), 6.77-8.15 (21H, m, $\geq$CH + ArH); ^{13}C NMR (CDCl$_3$) δ 46.7, 50.3 (each s, quat. C), 72.5, 81.0 (each d, tert. C), 195.6 (C=O); MS m/e 508 (M^{+}).

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14. 6: colorless prisms; IR (KBr) 2240, 1675 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.21 (1H, s, 2-H), 4.41 (1H, d, 12-H, J=5.0 Hz), 4.64 (1H, s, 9-H), 5.06 (1H, d, 5-H, J=5.0 Hz), 5.49 (1H, s, 7-H), 6.63-8.32 (19H, m); ^{13}C NMR (CDCl$_3$) δ 28.0 (d, tert. C), 33.4, 37.1, 43.3 (each s, quat. C), 45.7, 71.5, 80.4 (each d, tert. C), 195.5 (C=O); MS m/e 508 (M^{+}).

7: colorless prisms; IR (KBr) 2230, 1670 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.07 (1H, d, 12-H, J=5.0 Hz), 4.68, 4.71 (each 1H, s, 2-H, 9-H), 4.97 (1H, d, 5-H, J=5.0 Hz), 5.18 (1H, s, 7-H), 7.07-8.23 (19H, m); ^{13}C NMR (CDCl$_3$) δ 29.7 (d, tert. C), 29.9, 36.7, 42.4 (each s, quat. C), 45.4, 74.1, 74.6, 81.7 (each d, tert. C), 195.8 (C=O); MS m/e 508 (M^{+}).

8: colorless prisms; IR (KBr) 2230 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.29 (1H, s, 2-H), 4.83 (1H, d, 12-H, J=5.0 Hz), 5.17 (1H, s, 7-H), 5.19 (1H, d, 5-H, J=5.0 Hz), 6.65-7.60 (14H, m); ^{13}C NMR (CDCl$_3$) δ 27.9 (d, tert. C), 32.9, 41.7, 44.5 (each s, quat. C), 45.4 (d, tert. C), 63.3 (s, quat. C), 70.1, 79.7 (each d, tert. C); MS m/e 454 (M^{+}).

9: colorless prisms; IR (KBr) 2230 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.47 (1H, d, 12-H, J=5.0 Hz), 5.03 (2H, s, 2-H, 7-H), 5.14 (1H, d, 5-H, J=5.0 Hz), 7.05-7.77 (14H, m); ^{13}C NMR (DMSO-d$_6$) δ 27.8, 28.6, 39.5, 42.9, 44.8, 64.6, 71.7, 81.5; MS m/e 454 (M^{+}).

15. For example, L. S. Povarov and B. M. Mikhailov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1963, 955.

16. Th. Eicher, T. Pfister, and N. Krüger, Org. Prep. Proced. Int., 6, 63 (1974).

17. 10: pale green prisms; IR (KBr) 3500, 2230 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 4.96 (1H, d, 12-H, J=5.0 Hz), 5.53 (1H, s, 7-H), 5.54 (1H, d, 5-H, J=5.0 Hz), 6.26-8.63 (18H, m, ArH + OH); ^{13}C NMR (DMSO-d$_6$) δ 25.0, 38.0, 41.4, 46.2, 62.7, 66.9, 79.0; MS m/e 531 (M^{+}).

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