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FORMATION OF STABLE [3 + 2] CYCLOADDUCTS IN REACTIONS OF BENZOTHIAZOLIUM N-PHENACYLIDE WITH METHYLENECYCLOPROPENES

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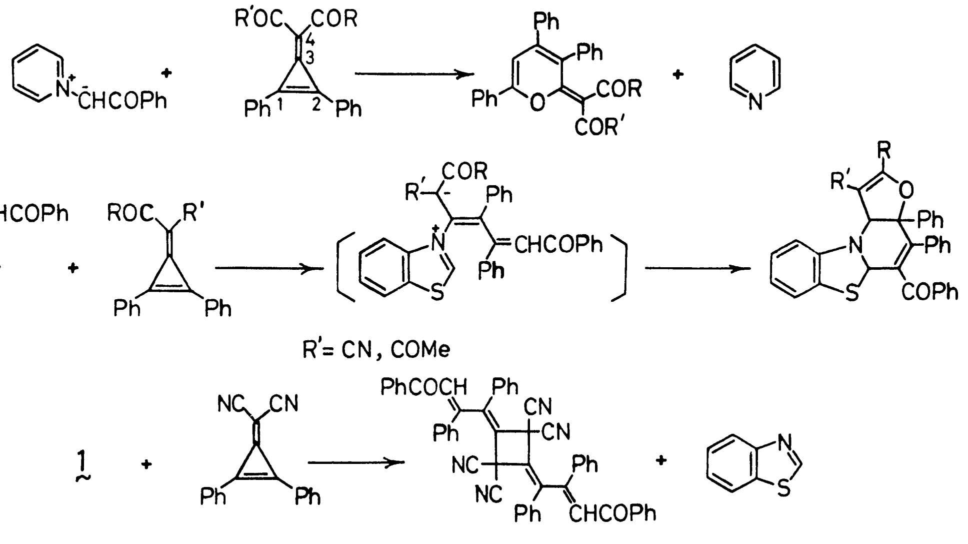
Benzothiazolium N-phenacylide adds to the cyclic double bond of methylenecyclopropenes having no acyl group on the 4-position to give stable [3 + 2] cycloadducts. This is the first example for the formation of stable [3 + 2] cycloadducts in the reaction of 1,3-dipoles with methylenecyclopropenes.

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 on the 4-position of methylenecyclopropenes. It has been reported that the reaction of pyridinium N-phenacylide with methylenecyclopropenes having two acyl groups afforded pyran derivatives with the elimination of pyridine.[1] In contrast to the above observation, however, we have recently found that benzothiazolium N-phenacylide **1** reacted with methylenecyclopropenes bearing an acyl group to give 3a,11a-dihydro-5aH-furo[3',2':2,3]pyrido[6,1-b]benzothiazole derivatives via intermediary 3-butadienylbenzothiazolium betaines, whereas the reaction of **1** with a methylenecyclopropene having two cyano groups gave a cyclobutane together with benzothiazole[2] (Scheme 1).



Scheme 1

During the course of an investigation of the effect of the nature of substituents of methylenecyclopropenes on the reaction with **1**, we have found that certain methylenecyclopropenes added to **1** to give stable [3 + 2] cycloadducts. It has been demonstrated that diazoalkanes,[3,4] mesoionic oxazolones,[5] and a nitrile ylide[6] added to the cyclic double bond of methylenecyclopropenes to yield initial [3 + 2] cycloadducts, which were transformed into stable compounds. However, evidence for the formation of intermediary [3 + 2] cycloadducts has so far been obtained in only one case; benzonitrilium-p-nitrobenzylide reacted with a methyelnecyclopropene to yield a [3 + 2] cycloadduct, which was easily transformed into a pyridine derivative.[6)]

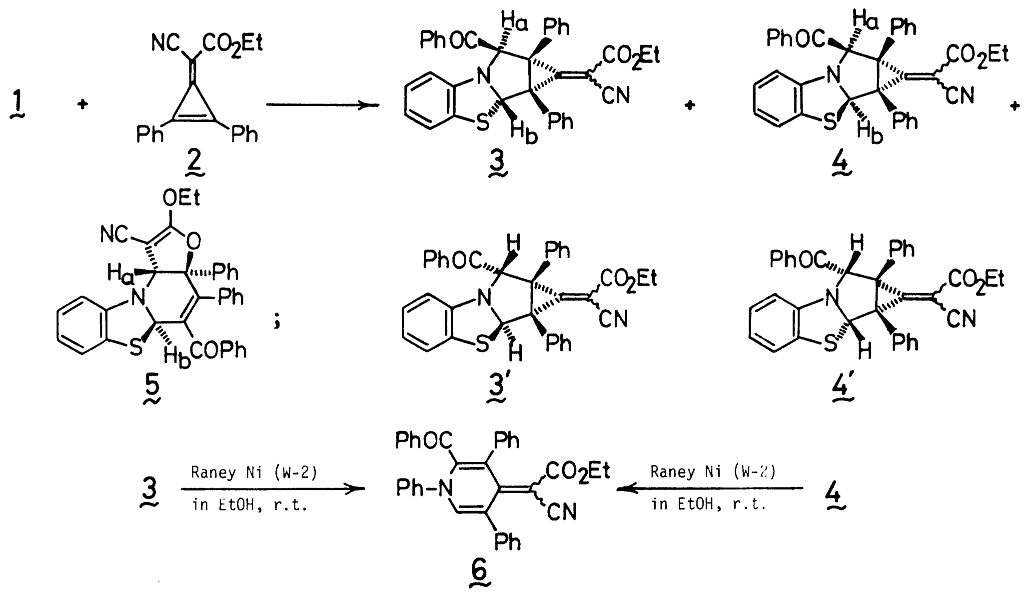
In this paper we wish to report the reaction of benzothiazolium N-phenacylide **1**, generated in situ from 3-phenacylbenzothiazolium bromide[8)] and triethylamine, with certain methylenecyclopropenes leading to the formation of stable [3 + 2] cycloadducts. This is the first example for the isolation of [3 + 2] cycloadducts from the reaction of 1,3-dipoles with methylenecyclopropenes.

Typical procedure for the reaction is as follows; 3-phenacylbenzothiazolium bromide (1.0 mmol) was added to a solution of triethylamine and a methylenecyclopropene (each 1.0 mmol) in dry THF (50 ml) at 0°C. Under nitrogen, the reaction mixture was stirred at 0°C for 3 h, and then at room temperature for 1 h. The precipitated triethylammonium bromide (quantitative) was removed by filtration, and then the filtrate was concentrated in vacuo to leave a residue, which was purified by chromatography on silica gel.

In order to compare with 2-cyano-2-(2,3-diphenyl-2-cyclopropenylidene)acetophenone giving two isomeric dihydrofurans,[2)] the reaction of **1** with ethyl 2-cyano-2-(2,3-diphenyl-2-cyclopropenylidene)-acetate **2**[9)] was first performed. In this reaction three 1:1 adducts **3** [mp 158-160°C (dec)], **4** [mp 168-170°C (dec)], and **5** [mp 188-189°C (dec)] were obtained in 58, 9, and 7% yields, respectively.[10)]

On the basis of chemical conversions and spectral data[11)], especially ^{13}C NMR spectra indicating the presence of two quaternary carbon atoms, the products **3** and **4** were assumed to be stereoisomeric [3 + 2] cycloadducts.

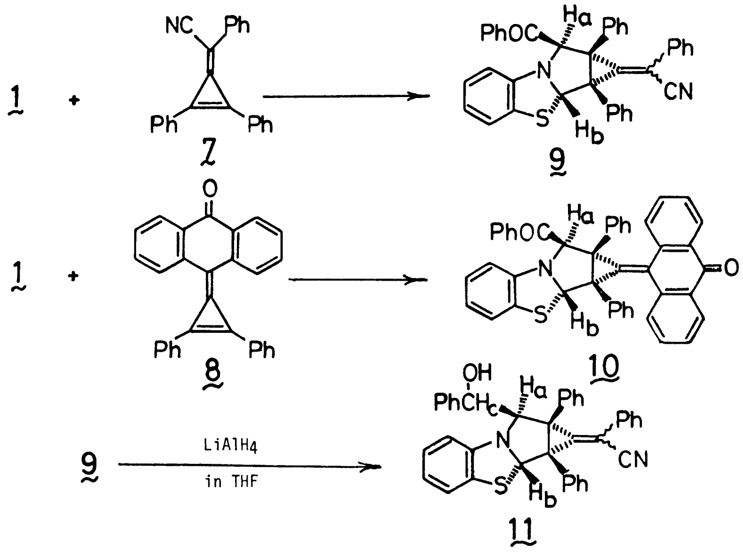
On treatment with Raney Ni (W-2) both **3** and **4** afforded the same desulfurized dihydropyridine **6**.[12)] If the geometry of exo-methylene moiety is neglected, four stereoisomers **3**, **3'**, **4**, and **4'** are possible for the [3 + 2] cycloadducts. An inspection of Dreiding models indicates that the order of favorable configurations is as follows: **3** >> **3'**, **4** >> **4'**. In the ^{1}H NMR spectra the long-range coupling between H_a and H_b was observed in the minor adduct, but not in the major one. This implies that H_a and H_b are situated syn in the minor adduct, whereas those anti in the major one. It thus seems reasonable to assume that the major adduct is **3**, and the minor one is **4**.



Scheme 2

On the other hand, another 1:1 adduct **5** was assigned as the dihydrofuran derivative on the basis of spectral data.[13)] Its stereochemisty was assumed by comparison with spectral data of analogous dihydrofurans reported previously.[2)]

Similarly, 1 reacted with 2-phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile 7[14] and 9-(2,3-diphenyl-2-cyclopropenylidene)anthrone 8[9] to give the corresponding [3 + 2] cycloadducts 9 and 10 as the sole products in 82 and 81% yields, respectively (Scheme 3). Structural elucidation of 9 and 10 was accomplished on the basis of spectral data.[15]



Scheme 3

Reduction of 9 with LiAlH$_4$ in THF at room temperature for 1 h afforded the corresponding alcohol 11 in 66% yield.[16]

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10) All new compounds in this paper gave satisfactory elemental analyses.
11) 3: IR (KBr) 2230, 1740, 1710, 1685 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.13 (3H, t), 4.08 (2H, q), 6.29 (1H, s, H$_b$), 6.56 (1H, s, H$_a$), 6.71-8.29 (19H, m); ^{13}C NMR (CDCl$_3$) δ 13.9 (q, CH$_3$), 48.6, 49.8 (each s, quat. C), 62.1 (t, CH$_2$), 71.7, 85.3 (each d, CH), 103.0 (=C(CN)(CO$_2$Et)), 147.0 (C=C(CN)(CO$_2$Et)), 159.7 (CO$_2$Et), 193.9 (COPh); MS m/e 554 (M$^+$).
4: IR (KBr) 2210, 1730, 1710, 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.10 (3H, t), 4.09 (2H, q), 5.69 (1H, d, H$_b$, J=0.5 Hz), 6.74 (1H, d, H$_a$, J=0.5 Hz), 6.75-7.70 (19H, m); ^{13}C NMR (CDCl$_3$) δ 13.7 (q, CH$_3$), 46.1, 48.8 (each s, quat. C), 62.6 (t, CH$_2$), 80.0, 85.0 (each d, CH), 103.6 (=C(CN)(CO$_2$Et)), 147.8 (C=C(CN)(CO$_2$Et)), 159.7 (CO$_2$Et), 195.2 (COPh); MS m/e 554 (M$^+$).
On the basis of ^{1}H NMR data of alcohol 11 described later,[16] it was deduced that H$_a$ appeared at lower field than H$_b$ in all [3 + 2] cycloadducts.

12) 6: yield 47% (from 3), 64% (from 4); red needles; mp 127-129°C; IR (KBr) 2160, 1670 (broad), 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (3H, t), 3.60 (2H, q), 6.95-7.67 (21H, m); ^{13}C NMR ($CDCl_3$) δ 14.1 (q, $\underline{C}H_3$), 59.6 (t, $\underline{C}H_2$), 166.2 ($\underline{C}O_2Et$), 188.9 ($\underline{C}OPh$); MS m/e 522 (M^+).

13) 5: IR (KBr) 2200, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (3H, t), 3.95 (2H, q), 5.74 (1H, s, H_a), 5.96-8.20 (20H, m, H_b + Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 14.4 (q, $\underline{C}H_3$), 64.0 (t, $\underline{C}H_2$), 67.7, 70.3 (each d, $\underline{C}H$), 88.3 (s, quat. $\underline{C}$), 107.0 (=$\underline{C}$(CN)), 172.3 (=$\underline{C}$(OEt)), 195.5 ($\underline{C}OPh$); MS m/e 554 (M^+).

14) H.-U. Wagner, R. Seidl, and H. Faß, Tetrahedron Lett., 1972, 3883.

15) 9: mp 187-189°C (dec); IR (KBr) 2230, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.39 (1H, s, H_b), 6.52-8.05 (25H, m, H_a + Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 46.5, 49.5 (each s, quat. $\underline{C}$), 72.0, 79.9 (each d, $\underline{C}H$), 196.1 ($\underline{C}$=O); MS m/e 558 (M^+).

10: mp 214-217°C (dec); IR (KBr) 1690, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.39 (1H, s, H_b), 6.46-8.37 (27H, m, H_a + Ar$\underline{H}$), 8.90 (1H, m, Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 46.8, 48.4 (each s, quat. $\underline{C}$), 70.2, 75.7 (each d, $\underline{C}H$), 183.7, 195.4 (each $\underline{C}$=O); MS m/e 635 (M^+). One aromatic proton at the 1-position of anthrone moiety appeared at a very low field due to the anisotropic effect with sulfur atom. This fact supports the assigned stereochemistry of 10.

16) 11: mp 190-191°C; IR (KBr) 3470, 2220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (1H, broad, O$\underline{H}$, exchanged with D_2O), 4.97 (1H, broad d, H_c, J=4.5 Hz), 5.11 (1H, d, H_a, J=4.5 Hz), 5.90 (1H, s, H_b), 6.43-7.73 (24H, m); ^{13}C NMR ($CDCl_3$) δ 45.2, 49.2 (each s, quat. $\underline{C}$), 73.9, 77.7, 78.9 (each d, $\underline{C}H$); MS m/e 560 (M^+).

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