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

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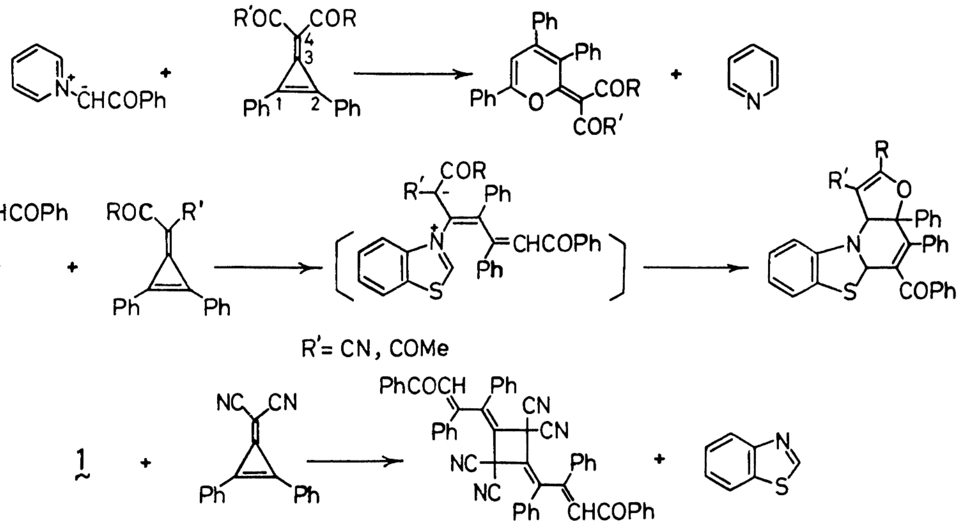
Benzothiazolium N-phenacylide adds to the cyclic double bond of methylenecyclopropenes having no acyl group on the 4-position to give stable [3 + 2] cycloadducts. This is the first example for the formation of stable [3 + 2] cycloadducts in the reaction of 1,3-dipoles with methylenecyclopropenes.

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 benzothiazole2) (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 ylide6) 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)

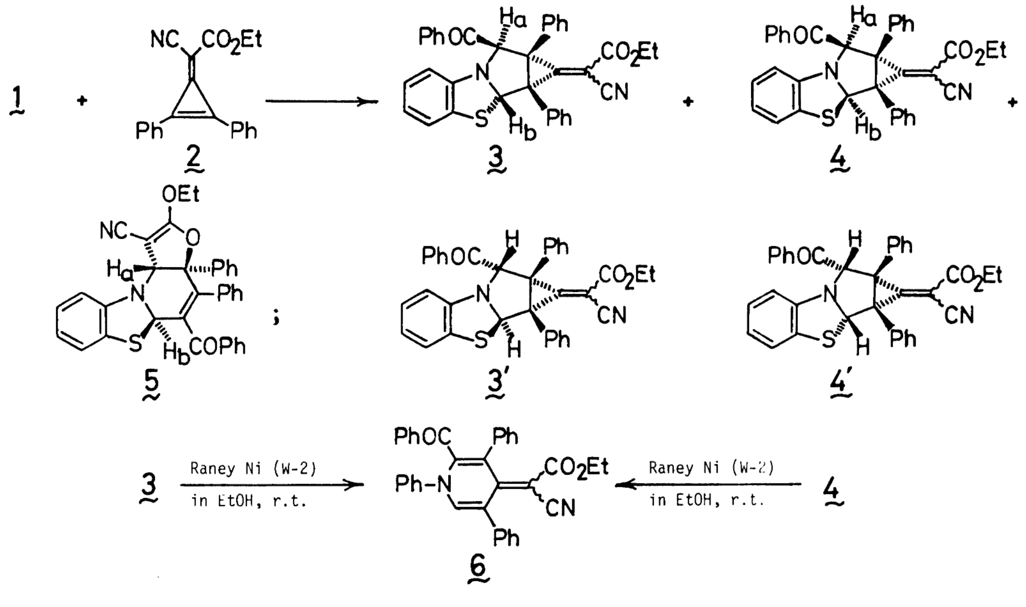
In this paper we wish to report the reaction of benzothiazolium N-phenacylide 1, generated in situ from 3-phenacylbenzothiazolium bromide8) and triethylamine, with certain methylenecyclopropenes leading to the formation of stable [3 + 2] cycloadducts. This is the first example for the isolation of [3 + 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 29) 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 data11), 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.

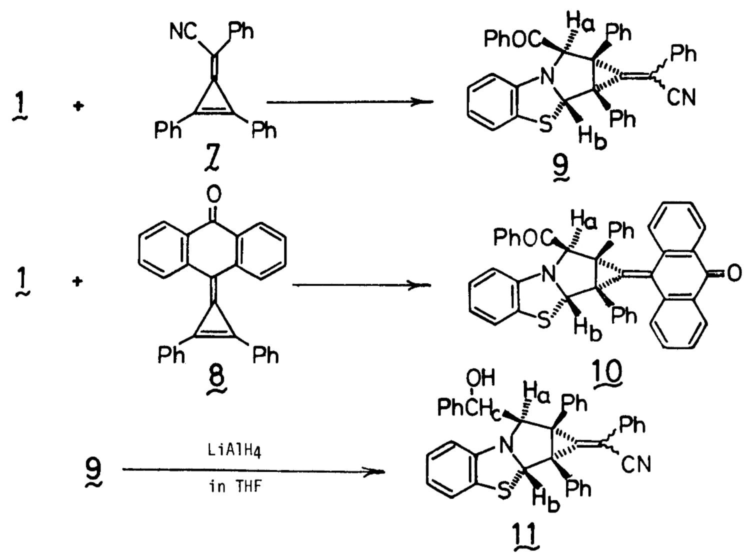
On treatment with Raney Ni (W-2) both 3 and 4 afforded the same desulfurized dihydropyridine 6.12) If the geometry of exo-methylene moiety is neglected, four stereoisomers 3, 3', 4, and 4' are possible for the [3 + 2] cycloadducts. An inspection of Dreiding models indicates that the order of favorable 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}; ^1H 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, $\underline{C}H_3$), 48.6, 49.8 (each s, quat. $\underline{C}$), 62.1 (t, $\underline{C}H_2$), 71.7, 85.3 (each d, $\underline{C}H$), 103.0 ($=\underline{C}(CN)(CO_2Et)$), 147.0 ($\underline{C}=C(CN)(CO_2Et)$), 159.7 ($\underline{C}O_2Et$), 193.9 ($\underline{C}OPh$); MS m/e 554 ($M^+$).

4: IR (KBr) 2210, 1730, 1710, 1680 cm^{-1}; ^1H 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, $\underline{C}H_3$), 46.1, 48.8 (each s, quat. $\underline{C}$), 62.6 (t, $\underline{C}H_2$), 80.0, 85.0 (each d, $\underline{C}H$), 103.6 ($=\underline{C}(CN)(CO_2Et)$), 147.8 ($\underline{C}=C(CN)(CO_2Et)$), 159.7 ($\underline{C}O_2Et$), 195.2 ($\underline{C}OPh$); MS m/e 554 ($M^+$).

On the basis of ^1H 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 ^{o}C; IR (KBr) 2160, 1670 (broad), 1610 cm^{-1}; ^{1}H 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}; ^{1}H 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 ^{o}C (dec); IR (KBr) 2230, 1680 cm^{-1}; ^{1}H 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 ^{o}C (dec); IR (KBr) 1690, 1650 cm^{-1}; ^{1}H 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 ^{o}C; IR (KBr) 3470, 2220 cm^{-1}; ^{1}H 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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