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NOVEL REACTIONS OF BENZOTHIAZOLIUM N-PHENACYLIDE WITH METHYLENECYCLOPROPENES

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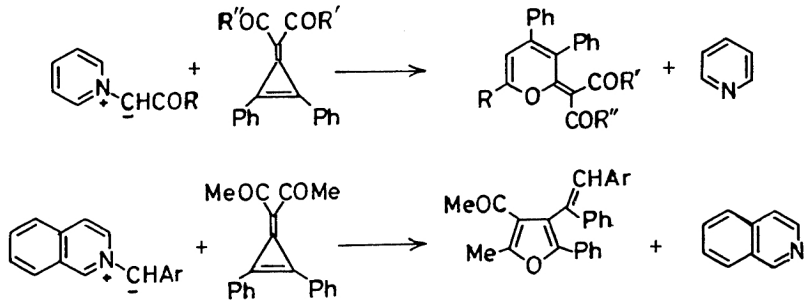
Benzothiazolium N-phenacylide reacted with methylenecyclopropenes having an acyl group on the 4-position to give 3a,11a-dihydro-5aH-furo[3',2':2,3]pyrido[6,1-b]-benzothiazole derivative via an intermediary 3-butadienylbenzothiazolium betaine. The reaction of the ylide with a methylenecyclopropene bearing two cyano groups on the 4-position in THF gave a cyclobutane together with benzothiazole, whereas a 3-butadienyl-2-ethoxybenzothiazoline derivative was obtained in the reaction in EtOH.

Methylenecyclopropenes undergo cycloaddition reactions with a variety of 1,3-dipoles.[1-6] 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.[7] Two examples have been reported on the reaction of hetero-aromatic N-ylides with methylenecyclopropenes: pyridinium[1] and isoquinolinium ylides[2] reacted with methylenecyclopropenes having two acyl groups to give pyran and furan derivatives with the elimination of pyridine and isoquinoline respectively (Scheme 1).



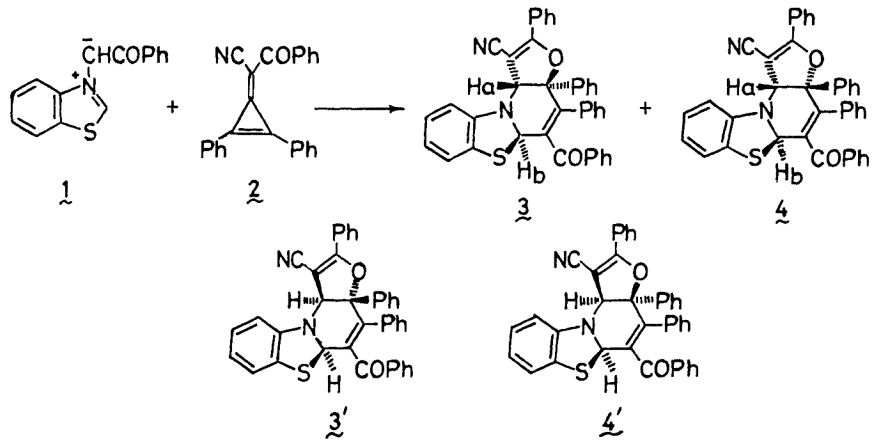
Scheme 1

In the present paper we wish to report novel reactions of benzothiazolium N-ylide 1, generated in situ from 3-phenacylbenzothiazolium bromide[8] and triethylamine, with methylenecyclopropenes having an acyl group on the 4-position leading to the formation of 3a,11a-dihydro-5aH-furo[3',2':2,3]pyrido-[6,1-b]benzothiazole derivatives. In connection with the above reaction, the reaction of 1 with a (cyclopropenylidene)malononitrile is also described.

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 the reaction of 1 with 2-cyano-2-(2,3-diphenyl-2-cyclopropenylidene)acetophenone 2[9], two isomeric 1:1 adducts were obtained in 53 and 42% yields respectively. On the basis of spectral data[10] as well as the mode of formation described later, these 1:1 adducts were assumed to be stereoisomeric dihydrofuran derivatives. Now, four stereoisomers 3, 4, 3', and 4' are possible for the dihydrofurans.

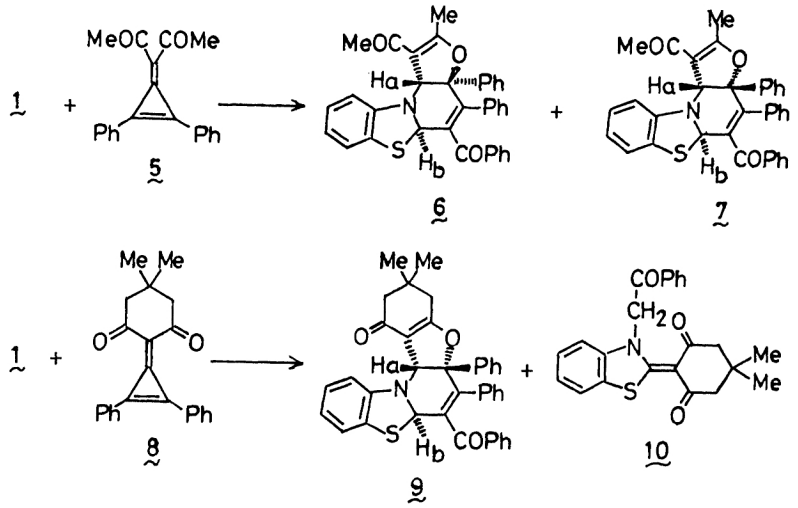
However, an inspection of Dreiding models indicates that there are significant steric interactions between the cyano group and benzo ring in both 3' and 4', but not in 3 and 4. It thus seems reasonable to assume that the 1:1 adducts obtained from the reaction are 3 and 4. The distinction between 3 and



Scheme 2

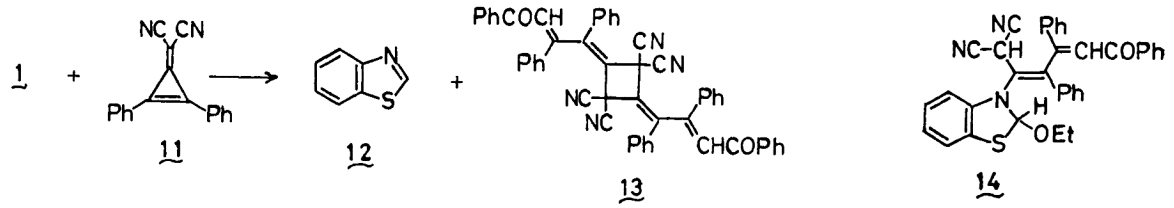
4 is readily accomplished by an examination of ^{1}H NMR data. The proton H_a in the adduct, mp 180-182°C (dec), appears at δ 5.91, whereas H_a appears at δ 5.52 in the adduct, mp 202-204°C (dec). An inspection of models reveals that H_a in 4 is orientated in the shielding cone of the benzo ring. Thus it can be concluded that the lower melting adduct is 3 and higher melting one is 4.

Similarly, 1 reacted with 3-(2,3-diphenyl-2-cyclopropenylidene)-2,4-pentanedione 5[11] to give two stereoisomeric dihydrofuran derivatives 6 and 7 in 55 and 31% yields respectively. On the other hand, the reaction of 1 with 2-(2,3-diphenyl-2-cyclopropenylidene)-5,5-dimethyl-1,3-cyclohaxanedione 8[9] afforded a single dihydrofuran derivative 9 (48%) together with 2-methylenebenzothiazoline 10 (15%).[12] Structural elucidation of compounds 6, 7, 9, and 10 was accomplished on the basis of spectral data.[13]

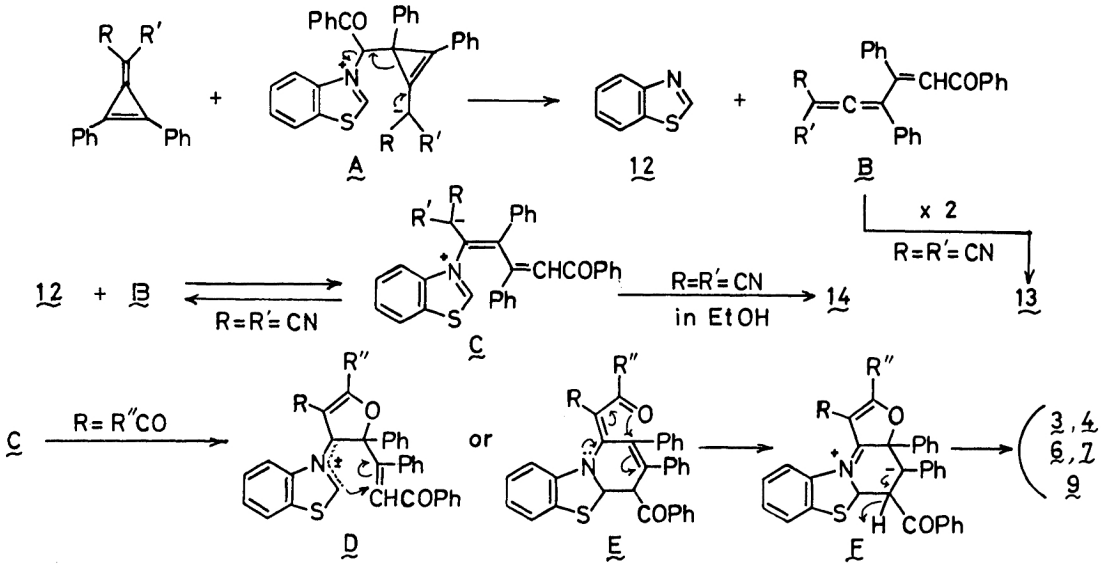


Scheme 3

On the other hand, it has been found that the reaction of 1 with 2-(2,3-diphenyl-2-cyclopropenylidene)malononitrile 11[9] in THF afforded a cyclobutane 13 (32%) with the elimination of benzothiazole 12 (31%). The structure of 13 was confirmed by an examination of spectral data.[14] In the same reaction in EtOH, however, 3-butadienyl-2-ethoxybenzothiazoline 14, whose structure was elucidated on the basis of spectral data[15], was isolated in 46% yield.



The pathways for these novel reactions can be explained as depicted in Scheme 4. The reaction proceeds via initial formation of betaine A, followed by dissociation to benzthiazole 12 and allene intermediate B. Subsequent recombination between 12 and B forms new betaine C. The intervention of C in the reaction process is supported by the isolation of 14. Although the formation of cyclobutane 13 can be interpreted by the dimerization of B, 12 and B may be also formed via dissociation of C. When



Scheme 4

R' is an acyl group (R"CO), C undergoes intramolecular cyclization to yield either D or E, which gives final adduct (3, 4, 6, 7 or 9) via F. Since a similar type compound to E was not formed in the reaction of 1 with 11, it seems reasonable to assume that dihydrofurans are formed via D rather than E.

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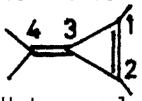
4. Th. Eicher and E. v. Angerer, Chem. Ber., 103, 339 (1970).
5. Th. Eicher and V. Schäfer, Tetrahedron, 30, 4025 (1974).
6. L. Toupet and R. Carrié, J. Chem. Soc. Chem. Commun., 1975, 384.
7. The numbering of methylenecyclopropene system is as follows (Th. Eicher and J. L. Weber, Topics in Current Chem., 57, 1 (1975)).

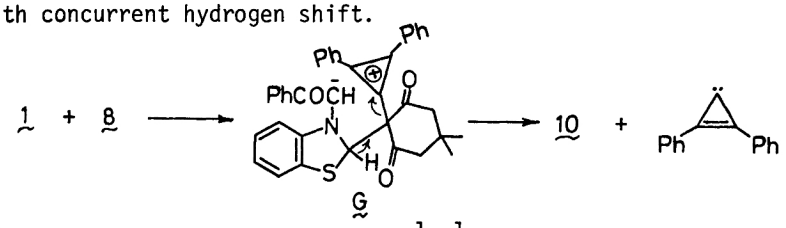


8. O. Tsuge, H. Shimoharada, and M. Noguchi, Heterocycles, 15, 807 (1981).
9. Th. Eicher, T. Pfister, and N. Krüger, Org. Prep. Proced. Int., 6, 63 (1974).
10. All new compounds in this paper gave satisfactory elemental analyses.
3: IR (KBr) 2200, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (1H, s, H_a), 6.66 (1H, s, H_b), 6.67-7.95 (24H, m); ^{13}C NMR ($CDCl_3$) δ 62.6 (d, $\geq \underline{C}H_a$), 77.2 (d, $\geq \underline{C}H_b$), 85.5, 90.9 (each s, quat. C, $=\underline{C}(CN)$), 170.6

(s, =C(Ph)O), 193.8 (s, C=O); UVλ_{max}($CHCl_3$) nm (log ε) 248 (4.44), 345 (4.18); MS m/e 586 (M^+).
4: IR (KBr) 2200, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.52 (1H, s, H_a), 6.63-8.00 (25H, m, H_b + ArH); ^{13}C NMR ($CDCl_3$) δ 72.8 (d, $\geqslant CH_a$), 76.2 (d, $\geqslant CH_b$), 86.7, 88.7 (each s, quat. C, =C(CN)), 169.6 (s, =C(Ph)O), 195.9 (s, C=O); UVλ_{max}($CHCl_3$) nm (log ε) 247 (4.37), 350 (4.11); MS m/e 586 (M^+).

11. Th. Eicher and A. Löshner, Z. Naturforsch., 21B, 899 (1966).

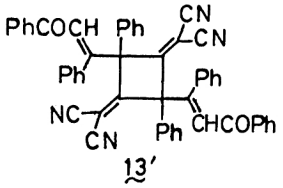
12. A possible pathway for the formation of 10 is as follows. A nucleophilic attack of the exo-double bond of 8 toward 2-carbon atom of 1 forms betaine G, which gives 10 via elimination of cyclopropylidene with concurrent hydrogen shift.



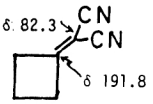
1 + 8 → G → 10 + diphenylcyclopropylidene

13. 6: mp 173-175°C (dec); IR (KBr) 1960, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22, 2.14 (each 3H, s, CH_3), 5.84 (1H, s, H_a), 6.60-7.87 (20H, m, H_b + ArH); ^{13}C NMR ($CDCl_3$) δ 15.0, 29.1 (each q, CH_3), 61.4 (d, $\geqslant CH_a$), 78.2 (d, $\geqslant CH_b$), 91.6 (s, quat. C), 171.2 (s, =C(Me)), 194.2, 194.9 (each s, C=O); UVλ_{max}($CHCl_3$) nm (log ε) 243 (4.28), 252 (4.28), 285 (4.09); MS m/e 541 (M^+).
7: mp 169-170°C (dec); IR (KBr) 1680 cm^{-1} (broad); ^1H NMR ($CDCl_3$) δ 1.47, 2.09 (each 3H, s, CH_3), 5.18 (1H, s, H_a), 6.33 (1H, s, H_b), 6.50-7.82 (19H, m); ^{13}C NMR ($CDCl_3$) δ 14.7, 29.4 (each q, CH_3), 71.0 (d, $\geqslant CH_a$), 74.6 (d, $\geqslant CH_b$), 88.4 (s, quat. C), 168.5 (s, =C(Me)), 195.7, 198.7 (each s, C=O); UVλ_{max}($CHCl_3$) nm (log ε) 246 (4.37), 252 (4.35), 290 (4.13); MS m/e 541 (M^+).
9: mp 174-176°C (dec); IR (KBr) 1690-1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89, 0.97 (each 3H, s, CH_3), 2.06, 2.29 (each 2H, s, CH_2), 5.28 (1H, s, H_a), 6.55-7.56 (20H, m, H_b + ArH); ^{13}C NMR ($CDCl_3$) δ 28.0, 28.5 (each q, CH_3), 33.6 (s, quat. C), 38.7, 52.1 (each t, CH_2), 73.7 (d, $\geqslant CH_a$), 75.2 (d, $\geqslant CH_b$), 90.4 (s, quat. C), 179.4 (s, =C-O-), 190.1, 197.0 (each s, C=O); UVλ_{max}($CHCl_3$) nm (log ε) 247 (4.33), 254 (4.32), 285 (4.12); MS m/e 581 (M^+).
10: mp 215-217°C; IR (KBr) 1695, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (6H, s, CH_3), 2.42 (4H, s, CH_2), 5.78 (2H, s, NCH_2), 7.20-8.10 (9H, m); ^{13}C NMR ($CDCl_3$) δ 28.3 (CH_3), 30.6 (quat. C), 51.7 (CH_2), 58.1 (NCH_2), 106.7 ($\overset{N}{S}\!>\!C$), 169.9 ($\overset{N}{S}\!>\!C=$), 190.8, 192.7 (C=O); UVλ_{max}($CHCl_3$) nm (log ε) 250 (3.78), 368 (3.78); MS m/e 391 (M^+).

14. 13: mp 273-274°C (dec); IR (KBr) 2230, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.30 (2H, s, =CH), 6.81-7.97 (30H, m); ^{13}C NMR ($CDCl_3$) δ 34.1 (s, quat. C), 92.2, 95.3 (each s, =C(Ph)-C(Ph)=), 102.0 (d, =CH), 155.9 (s, =C<), 191.1 (C=O); UVλ_{max}($CHCl_3$) nm (log ε) 242 (4.50), 266 (4.47), 333 (4.21); MS m/e 744 (M^+).
Another structure 13' could be excluded by comparing ^{13}C NMR data with those of 2-cyclobutylidenemalononitrile.[16]



13'



15. 14: mp 150-153°C (dec); IR (KBr) 2240, 1620, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (3H, t, CH_3), 3.21, 3.60 (each 1H, q, CH_2), 4.42, 4.83 (each 1H, s, $\geqslant CH$), 6.35 (1H, m, ArH), 6.48 (1H, s, =CH), 6.61-7.63 (18H, m); ^{13}C NMR ($CDCl_3$) δ 15.2 (q, CH_3), 66.0 (d, $\geqslant CH$), 67.2 (t, CH_2), 70.4 (d, $\geqslant CH$), 82.0 (d, =CH), 88.4, 91.1 (each s, =C(Ph)-C(Ph)=), 185.2 (s, C=O); UVλ_{max}($CHCl_3$) nm (log ε) 240 (4.10), 286 (3.65), 388 (2.83); MS m/e 553 (M^+).

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