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FORMATION OF PRIMARY ADDUCTS IN 1,3-DIPOLAR CYCLOADDITION OF DISUBSTITUTED CYCLOIMMONIUM YLIDES WITH 1,2,3-TRIPHENYLCYCLOPROPENE

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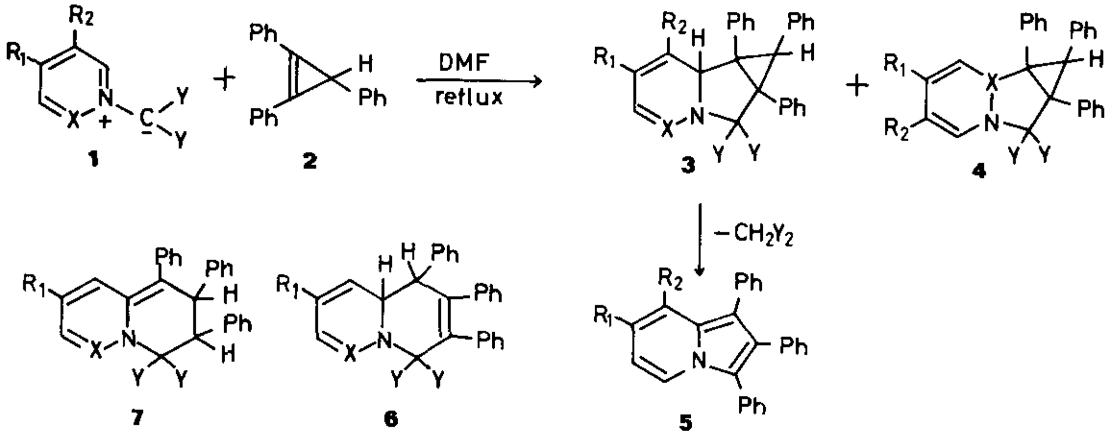
Abstract — Pyridazinium, phthalazinium, 3-cyanopyridinium and 4-cyanopyridinium dicyanomethylides and isoquinolinium bis-(methoxycarbonyl)methylide underwent cycloaddition with triphenylcyclopropene to give the corresponding primary adducts (3 or 4). In the latter two cases, the indolizines (5a and 5e) were also isolated.

It is well documented that cycloadditions of cyclopropenes to dienes and 1,3-dipoles are useful for construction of the five-, six-, or seven-membered carbo- or heterocyclic systems.[1,2] However, little is known on the isolation of the primary adducts in 1,3-dipolar cycloaddition of cycloimmonium ylides with cyclopropenes, the indolizines[3] and quinolizines[4] being obtained with opening of the three-membered rings of the primary adducts. Recently, Igeta et al.[2] reported the formation of the primary adducts in the reactions of pyridinium N-ylides with perhalocycloalkenes and it seems, therefore, to be desirable to describe briefly our results.

Reaction of 4-cyanopyridinium dicyanomethylide (1a) with triphenylcyclopropene (2) in refluxing dimethylformamide for 4 hr produced the 1:1 adduct (3a),[5] together with the indolizine (5a).[5] The structures such as (6) and (7) may be ruled out on the basis of the coupling pattern in the ^{1}H-nmr spectrum of (3a); δ (CDCl$_3$) 3.40 (1H, s, C$_2$-H), 5.21 (1H, d, *J* 2.5 Hz, C$_{10}$-H), 5.80 (1H, d, *J* 2.5 Hz, C$_9$-H), 6.40, 6.65 (2H, ABq, *J* 8 Hz, C$_6$- and C$_7$-H), 6.8-7.5 (14H, m). Furthermore, the ^{13}C-^{1}H coupling constant (*J* 157 Hz) of C-2 shows that the three-membered ring is retained in the adduct.

3-Cyanopyridinium dicyanomethylide (1b) reacted with (2) under the same condition to afford the isomeric adducts (3b)[5] and (4b)[5] in 22 and 35 % yields, respectively,



	1				Reaction Time	**3** (**4**)		**5**
	X	Y	R_1	R_2	(hr)	Yield(%)	m.p.(°C)	Yield(%)
a	CH	CN	CN	H	4	36	235-238	25
b	CH	CN	H	CN	5	22	117-118	0
						(35	215-216)	
c	N	CN	H	H	4	91	233-235	0
d	N	CN	CH=CH-CH=CH		8	89	250-253	0
e	CH	CO_2Me	CH=CH-CH=CH		4	21	187-188	62

where no indolizine was formed even upon prolonged heating of the reaction mixture. Support for these isomeric assignments was provided by ^{1}H-nmr spectra; the signal due to the 7-proton of (**3b**) appeared at δ ($CDCl_3$) 5.42 as double doublet, while those of the 8- and 9-protons of (**4b**) at δ 5.20 and 6.05 as AB quartet.

In the analogous manner, pyridazinium dicyanomethylide (**1c**)[6] and phthalazinium dicyanomethylide (**1d**) underwent cycloaddition with (**2**) to give the primary adducts (**3c**)[5] and (**3d**),[5] respectively. No indolizine was obtained upon prolonged heating of these reaction mixtures. Examination of ^{1}H-nmr spectrum of (**3c**) suggests that the adduct consists of two configurational isomers, which could not be separated by thin layer chromatography. However, no differences between the chemical shifts of these possible isomers were observed in the ^{13}C-nmr spectrum.

Finally, isoquinolinium bis(methoxycarbonyl)methylide (**1e**)[7] reacted with (**2**) to produce the 1:1 adduct (**3e**),[5] in addition to the indolizine (**5e**).[5] In this case, thermolysis of (**3e**) in refluxing xylene or dimethylformamide gave the indolizine (**5e**) in good yield.

Table 1. ^{1}H-Nmr spectral data of the 1:1 adducts (**3a**-**e** and **4b**)[*1]

	C_2-H (1H, s)	C_{10}-H (1H, s)	Olefinic and Aromatic-H
3a	3.40	5.21[*2]	5.80 (1H, d, *J* 2.5 Hz, C_9-H) 6.40, 6.65 (2H, ABq, *J* 8 Hz, C_6- and C_7-H) 6.8-7.5 (14H, m)
3b	3.52	5.18	5.42 (1H, dd, *J* 6.0, 6.5 Hz, C_7-H) 6.3-7.6 (17H, m)
4b	3.23	5.31	5.20, 6.05 (2H, ABq, *J* 10 Hz, C_8- and C_9-H) 6.3-7.5 (16H, m)
3c	3.73, 4.66[*3]	5.99, 6.02[*3]	6.37 (1H, d, *J* 8 Hz, C_6-H) 6.8-7.5 (17H, m)
3d	3.75	5.17	6.4-7.2 (19H, m) 7.32 (1H, s, C_7-H)
3e	3.58	5.58	5.71 (1H, d, *J* 7.5 Hz, C_{10}-H) 6.4-7.7 (20H, m) 3.47, 3.73 (each 3H, s, methoxy-H × 2)

[*1] Spectrum were obtained in $CDCl_3$, chemical shifts are in δ relative to tetramethylsilane as an internal standard. [*2] Doublet, *J* 2.5 Hz. [*3] Two singlets.

References and Notes

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Table 2. ^{13}C-Nmr spectral data of the 1:1 adducts (**3a**-**e** and **4b**)[*1]

	C-2 (d)	C-1, 3 (s)	C-4 (s)	C-10 (d)	Others
3a	30.76 (157)[*2]	45.86 46.83	63.71	68.18 (148)	100.64 (d, *J* 179 Hz, C-7) 111.11, 111.68, 112.98, 115.33 (each s, $\underline{\text{C}}$N × 3 and C-8) 126.13-132.95 (complex)
3b	30.52 (—[*3])	46.51 46.91	64.20	67.93 (—[*3])	87.41 (s, C-9) 110.54, 111.19, 117.60 (each s, $\underline{\text{C}}$N) 114.77, 122.72 (each d, —[*3], C-7 and 8) 126.21-133.02 (complex) 139.19 (d, —[*3], C-6)
4b	32.37 (157)	45.08 47.02	63.76	66.56 (151)	95.71 (s, C-7) 103.51 (d, *J* 177 Hz, C-8) 111.43, 112.00, 116.26 (each s, $\underline{\text{C}}$N) 127.19-134.33 (complex) 140.99 (d, *J* 195 Hz, C-6)
3c	30.68 (160)	43.91 46.67	64.85	63.55 (140)	118.84 (s, $\underline{\text{C}}$N) 120.93 (d, *J* 162 Hz, C-9) 126.57-133.11 (complex) 141.63 (d, *J* 188 Hz, C-7)
3d	31.65 (159)	42.57 46.83	65.05	65.38 (139)	112.12, 112.33 (each s, $\underline{\text{C}}$N) 123.28-133.19 (complex) 145.04 (d, *J* 187 Hz, C-7)
3e	34.98 (163)	43.26 48.13	79.70	71.75 (139)	52.43 (q, *J* 147 Hz, O$\underline{\text{C}}$H$_3$ × 2) 104.21 (d, *J* 168 Hz, C-10) 123.02-135.85 (complex) 167.28, 170.03 (each s, COO × 2)

[*1] Spectra were obtained in CDCl$_3$, chemical shifts are in δ relative to tetramethylsilane as an internal standard. [*2] The ^{13}C-^{1}H coupling constants (Hz) are shown in parenthesis. [*3] The sample is not enough in quantity to measure the ^{13}C-^{1}H coupling constants.

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