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Studies on 1,3-Dipolar Cycloaddition Reactions of Some Cycloimmonium Ylides

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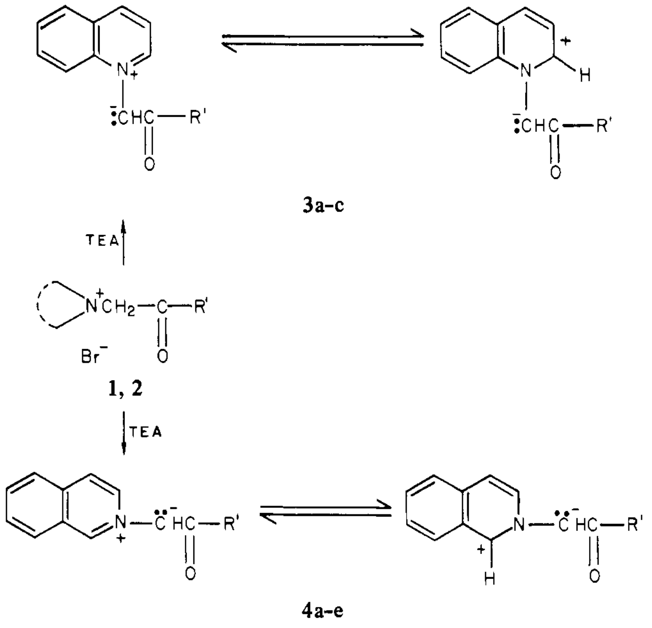
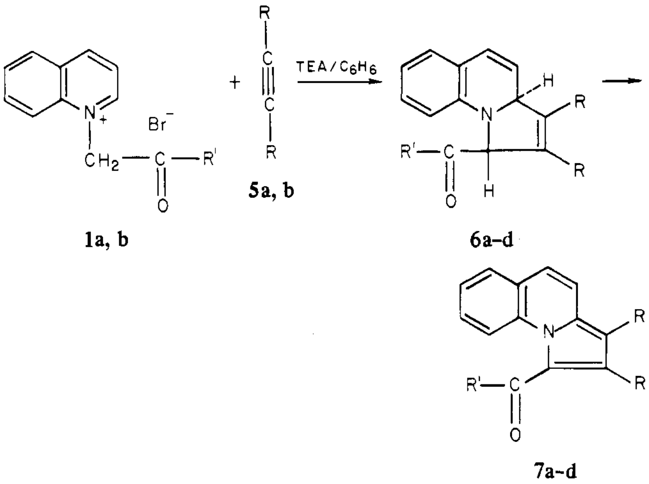
A wide variety of some new benzoindolizine derivatives have been synthesized by the interaction of quinolinium and isoquinolinium ylides generated in situ from their precursors with acetylenic dipolarophiles. Triethylamine in benzene media was used as the dehydrohalogenating agent for generation of ylides. The structures of resulting products have been confirmed on the basis of elemental analyses as well as spectroscopic evidence.

An enormous amount of literature (*1-4*) reveals that cycloimmonium ylides have gained an important position among other 1,3-dipolar reactive intermediates as evidence by their selective reactivity toward dipolarophiles offering the most accessible route for the synthesis of fused-ring heterocyclic compounds, though the syntheses of such heterocyclics with low yields have already been reported in the literature (*5*). We have, therefore, carried out some reactions of quinolinium and isoquinolinium ylides with acetylenic dipolarophiles (*6*) so as to extend the utilization of 1,3-dipolar cycloaddition reactions, leading to the formation of some new benzoindolizine derivatives (see Table I) which are quite inaccessible via other synthetic routes. The reaction presumably proceeds via intermediacy of a nonaromatic primary addition product dihydrobenzoindolizine derivative formed by the addition of the above-mentioned ylides generated in situ (Scheme I) on to acetylenic dipolarophiles. The same on dehydrogenation gave rise to the formation of aromatized benzoindolizine derivatives (Schemes II and III).

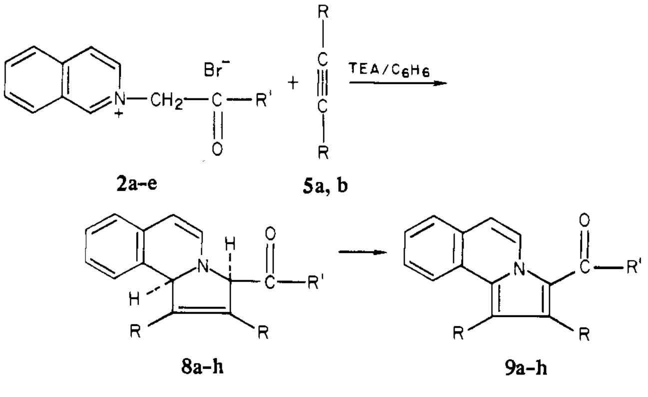
Scheme I



Scheme II



Scheme III



Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer spectrophotometer in Nujol/KBr. NMR spectra ($CDCl_3$) were run by using Varian A-60 and A-90 spectrometers with Me_4Si as an internal standard and chemical shifts are expressed in δ values (Table II). Analytical samples were purified by column chromatography over neutral silica gel 60-120 mesh and purity was checked by thin-layer chromatography.

***Preparation of Benzoindolizines* (7a-d *via Quinolinium Ylides*.** To a stirred suspension of phenacylquinolinium bromide (**1a**,**b** = 5 mmol) and acetylenic dipolarophile (**5a**,**b**, 5 mmol) in anhydrous benzene (100 mL) was added dropwise a solution of 0.7 mL of triethylamine in 10 mL of benzene. After the solution was stirred for 1 h, the whole mass was refluxed on a water bath for 4-6 h. After completion of reaction the resulting mixture was concentrated to 1/10 of its original volume and kept overnight at room temperature. Next day, triethylamine hydrobromide was filtered off from the residue and the filtrate was concentrated to give the crude product. The crude product on column chromatography over silica gel with benzene as the eluent gave a fraction which on recrystallization with appropriate solvent (Table I) yielded benzoindolizine derivatives (**7a-d**) in approximately 50-60% yields.

***Preparation of Benzoindolizines* (9a-h) *via Isoquinolinium Ylides*.** The reaction between phenacylisoquinolinium bromide (**2a-e**, 5 mmol), acetylenic dipolarophiles, (**5a**,**b**, 5 mmol), and triethylamine was conducted under similar conditions and the

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Table I. Structure and Physical Properties of Benzoindolizine Derivatives (7 and 9)[a]

compound no.	formula	R'	R	mp, °C	yield, %	crystn soln
7a	$C_{23}H_{16}NO_5$	4-ClC$_6$H$_4$	CO$_2$Me	169-171	56	MeOH-H$_2$O
7b	$C_{25}H_{20}NO_5Cl$	4-ClC$_6$H$_4$	CO$_2$Et	144-146	50	EtOH
7c	$C_{27}H_{19}NO_5$	2-C$_{10}$H$_7$	CO$_2$Me	240-242	60	CHCl$_3$-MeOH
7d	$C_{29}H_{23}NO_5$	2-C$_{10}$H$_7$	CO$_2$Et	139-141	57	CHCl$_3$-MeOH
9a	$C_{25}H_{20}NO_5Cl$	4-ClC$_6$H$_4$	CO$_2$Et	135-137	54	CHCl$_3$-MeOH
9b	$C_{26}H_{23}NO_5$	4-CH$_3$C$_6$H$_4$	CO$_2$Et	140-142	60	CHCl$_3$-MeOH
9c	$C_{23}H_{16}N_2O_7$	4-NO$_2$C$_6$H$_4$	CO$_2$Me	195-196	58	CHCl$_3$-MeOH
9d	$C_{25}H_{20}N_2O_7$	4-NO$_2$C$_6$H$_4$	CO$_2$Et	143-145	50	CHCl$_3$-MeOH
9e	$C_{27}H_{19}NO_5$	1-C$_{10}$H$_7$	CO$_2$Me	164-166	52	C$_6$H$_6$-PE
9f	$C_{29}H_{23}NO_5$	1-C$_{10}$H$_7$	CO$_2$Et	134-135	55	CHCl$_3$-MeOH
9g	$C_{27}H_{19}NO_5$	2-C$_{10}$H$_7$	CO$_2$Me	208-210	50	CHCl$_3$-MeOH
9h	$C_{29}H_{23}NO_5$	2-C$_{10}$H$_7$	CO$_2$Et	128-129	56	MeOH-H$_2$O

[a] Satisfactory elemental analyses were obtained for all compounds.

Table II. Spectral Properties of Benzoindolizine Derivatives

	spectral analysis			
compd	^{1}H NMR (CDCl$_3$), δ	IR,[a] cm^{-1}	no. of protons	assignment
7a		1720		C=O (ester)
		1600		C=O
		1460		C=C
		1410		C–N
		3000		C–H
7b	8.26 (d, J = 7.5 Hz)		1	C$_5$–H
	7.23 (d, J = 7.5 Hz)		1	C$_6$–H
	7.40-8.97 (m)		8	Ar–H
	1.09 (t, J = 7.5 Hz)		3	methyl
	1.35 (t, J = 7.5 Hz)		3	methyl
	3.92 (q, J = 7.5 Hz)		2	methylene
	4.35 (q, J = 7.5 Hz)		2	methylene
		1700		C=O (ester)
		1600		C=O
		1480		C=C
		1400		C–N
		2980		C–H
7c	8.8 (d, J = 7.5 Hz)		1	C$_5$–H
	7.03 (d, J = 7.5 Hz)		1	C$_6$H$_6$–H
	7.23-8.07 (m)		11	Ar–H
	3.67 (s)		3	methoxy
	3.83 (s)		3	methoxy
7d		1730		C=O (ester)
		1600		C=O
		1540		C=C
		1360		C–N
		2840		C–H
9a	8.77 (d, J = 8 Hz)		1	C$_5$–H
	7.06 (d, J = 8 Hz)		1	C$_6$–H
	7.53-7.8 (m)		8	Ar–H
	0.95 (t, J = 8 Hz)		3	methyl
	1.32 (t, J = 8 Hz)		3	methyl
	3.69 (q, J = 8 Hz)		2	methylene
	4.35 (q, J = 8 Hz)		2	methylene
		1710		C=O (ester)
		1620		C=O
		1490		C=C
		1350		C–N
		3120		C–H
9b		1730[b]		C=O (ester)
		1630[b]		C=O
		1500[b]		C=C
		1360[b]		C–N
		3000[b]		C–H
9c	9.19 (d, J = 7.5 Hz)		1	C$_5$–H
	7.29 (d, J = 7.5 Hz)		1	C$_6$–H
	7.67-8.47 (m)		8	Ar–H
	3.37 (s)		3	methoxy
	4.00 (s)		3	methoxy
		1720		C=O (ester)
		1600		C=O
		1520		C=C
		1340		C–N
		2960		C–H
9d	8.94 (d, J = 8 Hz)		1	C$_5$–H
	7.14 (d, J = 8 Hz)		1	C$_6$–H
	7.43-8.05 (m)		8	Ar–H
	0.95 (t, J = 8 Hz)		3	methyl
	1.29 (t, J = 8 Hz)		3	methyl
	3.62 (q, J = 8 Hz)		2	methylene
	4.35 (q, J = 8 Hz)		2	methylene
		1700		C=O (ester)
		1630		C=O
		1510		C=C
		1390		C–N
		3120		C–H
9e	9.39 (d, J = 7.5 Hz)		1	C$_5$–H
	7.23 (d, J = 7.5 Hz)		1	C$_6$–H
	7.37-9.00 (m)		11	Ar–H
	2.70 (s)		3	methoxy
	3.80 (s)		3	methoxy
9f	9.34 (d, J = 8 Hz)		1	C$_5$–H
	7.20 (d, J = 8 Hz)		1	C$_6$–H
	7.33-9.13 (m)		11	Ar–H
	0.45 (t, J = 8 Hz)		3	methyl
	1.22 (t, J = 8 Hz)		3	methyl
	3.05 (q, J = 8 Hz)		2	methylene
	4.29 (q, J = 8 Hz)		2	methylene
		1710		C=O (ester)
		1620		C=O
		1500		C=C
		1390		C–N
		3120		C–H
9g	8.87 (d, J = 7.5 Hz)		1	C$_5$–H
	7.13 (d, J = 7.5 Hz)		1	C$_6$–H
	7.47-8.20 (m)		11	Ar–H
	2.97 (s)		3	methoxy
	3.83 (s)		3	methoxy
		1720		C=O
		1610		C=O
		1500		C=C
		1360		C–N
		2940		C–H
9h		1730		C=O (ester)
		1610		C=O
		1470		C=C
		1370		C–N
		2980		C–H

[a] In Nujol unless otherwise specified. [b] KBr pellet.

crude product was isolated in the usual manner. Chromatography over silica gel with benzene as the eluent gave a fraction which on recrystallization with appropriate solvent (Table I) yielded benzoindolizine derivatives (**9a**–**h**) in 50–60% yields.

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Registry No. **1a**, 75613-96-6; **1b**, 6276-89-7; **2a**, 57269-96-2; **2b**, 75573-22-7; **2c**, 39954-59-1; **2d**, 7357-47-3; **2e**, 6276-88-6; **5a**, 762-42-5; **5b**, 762-21-0; **7a**, 84801-85-4; **7b**, 84801-86-5; **7c**, 84801-87-6; **7d**, 84801-88-7; **9a**, 84801-89-8; **9b**, 84801-90-1; **9c**, 84801-91-2; **9d**, 84801-92-3; **9e**, 84801-93-4; **9f**, 84801-94-5; **9g**, 84801-95-6; **9h**, 84801-96-7.

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Synthesis of Novel Energetic Compounds. 6

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Reported here are the syntheses and physical properties of five novel energetic aliphatic azido compounds. These include azido nitramines, esters, and amines. The compounds have been characterized in terms of freezing point, refractive index, and impact sensitivity. The properties of these azides indicate that these compounds have a wide liquid range and are relatively insensitive to impact.

The synthesis of novel energetic azido compounds has been reported in previous papers of this series (*1*). This chemistry has been extended in the current work to include azido nitramines, esters, and amines.

The nitramino azides that were prepared included *n*-butyl(2-azidoethyl)nitramine (I), bis[(2-azidoethoxy)methyl]nitramine (II), and 1,12-diazido-3,10-dioxa-5,8-dinitrazadodecane (III). The following are the synthetic routes that were utilized:

$$C_4H_9N(NO_2)CH_2CH_2ONO_2 \xrightarrow{NaN_3} \underset{\text{I}}{C_4H_9N(NO_2)CH_2CH_2N_3}$$

$$N(NO_2)\text{–}[CH_2Cl]_2 + 2HOCH_2CH_2Cl \rightarrow$$

$$N(NO_2)\text{–}[CH_2OCH_2CH_2Cl]_2 \xrightarrow{2NaN_3} \underset{\text{II}}{N(NO_2)\text{–}[CH_2OCH_2CH_2N_3]_2}$$

$$[CH_2N(NO_2)CH_2Cl]_2 + 2HOCH_2CH_2Cl \rightarrow$$

$$[CH_2N(NO_2)CH_2OCH_2CH_2Cl]_2 \xrightarrow{2NaN_3} \underset{\text{III}}{[CH_2N(NO_2)CH_2OCH_2CH_2N_3]_2}$$

An azido ester, 6-azidohexyl 6-azidohexanoate (IV), and an azido amine, tris(2-azidoethyl)amine (V), were also synthesized:

$$Br(CH_2)_5COCl + HO(CH_2)_6Cl \rightarrow$$

$$Br(CH_2)_5CO_2(CH_2)_6Cl \xrightarrow{NaN_3} \underset{\text{IV}}{N_3(CH_2)_5CO_2(CH_2)_6N_3}$$

$$N[CH_2CH_2Cl]_3 \xrightarrow{NaN_3} \underset{\text{V}}{N[CH_2CH_2N_3]_3}$$

Table I. Properties of Novel Energetic Azides[a]

compd	$n^{24}{}_D$	fp, °C	impact sensitivity,[b] in.-lb
$C_4H_9N(NO_2)CH_2CH_2N_3$	1.4870	<–78	>150
$N(NO_2)\text{–}[CH_2OCH_2CH_2N_3]_2$	1.5022	<–78	>150
$[CH_2N(NO_2)CH_2OCH_2CH_2N_3]_2$	1.5218	–15	>150
$N_3(CH_2)_5CO_2(CH_2)_6N_3$	1.4723	<–78	>150
$N[CH_2CH_2N_3]_3$	1.5090	–19	60-65

[a] Purity by GC analyses was 99+%. Elemental analyses, in every case, were consistent with the proposed structure. [b] By comparison, trimethylethane trinitrate = 40 in.-lb.

The indentity of these new compounds was confirmed by infrared spectroscopy and elemental analyses. The compounds have been characterized in terms of freezing point, refractive index, and impact sensitivity. The properties of these azides, as summarized in Table I, indicate that these compounds have a wide liquid range and are relatively insensitive to impact.

Experimental Section

***General Procedures*. Caution!** Most of the products and starting materials described are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, and other means and should be handled with care.

Isolation and purification were accomplished by liquid chromatography, using silica gel as the adsorbent, for safety reasons. Infrared analyses were carried out with a Perkin-Elmer 137 infrared spectrophotometer. Gas-chromatographic analyses were carried out on an F&M 700 instrument using a 10 ft × 3/16 in. stainless-steel column packed with 3% QF-1 on 40/80 mesh Chromosorb T. Elemental analyses were by Galbraith Laboratories.

***n-Butyl(2-azidoethyl)nitramine* (*I*).** A mixture of 19.4 g (0.094 mol) of *n*-butyl[2-(nitrooxy)ethyl]nitramine (*2*), 9.4 g (0.145 mol) of sodium azide, and 20 mL of dimethylformamide was heated at 90 °C for 24 h. After the mixture was cooled, the solvent was removed in vacuo. Methylene chloride was added and the insoluble solid was removed by filtration. Re-

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