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REACTIONS OF AZIRINES WITH N-BROMOSUCCINIMIDE

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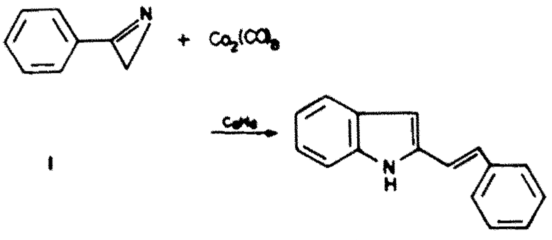
Abstract—Reaction of 2-aryl azirines with N-bromosuccinimide in dioxane or carbon tetrachloride at −23°, affords α,α′-dibromoketones, dibromoazines, bromopyrazines, 2,5-diarylpyrazines and 3,6-diarylpyrazines.

There has been considerable recent interest in the organic[1] and organometallic[2] chemistry of azirines. These 3-membered ring heterocycles can undergo interesting ring-opening and cycloaddition reactions (e.g. 1 → 2).



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2, 77%

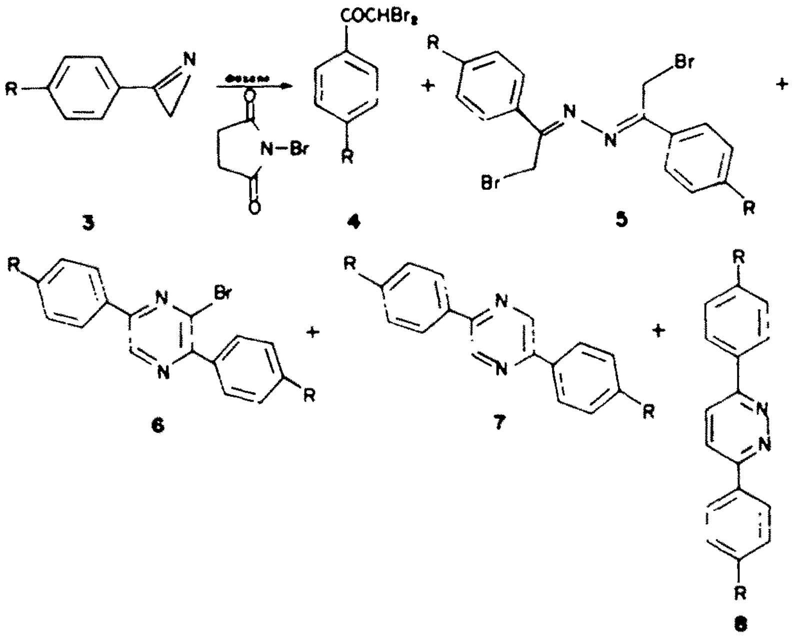
An important reagent in organic chemistry is N-bromosuccinimide (NBS), which can effect allylic bromination,[3] oxidation,[4] and dehydrogenation[5] reactions, subject to the nature of the organic substrates. All of these reactions are conceivable with azirines. We now report on the reaction of NBS with 2-aryl azirines.

Treatment of a 2-aryl azirine [3, R = H(1), OCH_3, CH_3, Br] with two equivalents of N-bromosuccinimide in dioxane or carbon tetrachloride, at −23°, affords one or more of the following products: α,α′-dibromoketones (4), azines (5), bromopyrazines (6), 2,5-diarylpyrazines (7) and 3,6-diarylpyrazines (8). The yields, m.ps of new compounds, and pertinent spectral data are listed in Table 1. Except for 6, all of the products are known compounds, whose m.ps and spectral data were in good accord with literature data.

Table 1. Products obtained from reaction of 3 with NBS

3, R =	Products	Yield (%)	Mp, °C	NMR[c] δ, ppm	Mass spec. m/e
H	4	1		—	278
	5	3		4.56 (s, 4H, CH_2), 7.4–8.1 (m, 10H, Ph)	—
	6	23	116[a]	7.3–8.0 (m, 10H, Ph), 8.67 (s, 1H, CH)	311
	8	13		7.23–7.80 (m, 10H, Ph), 8.01 (s, 2H, CH)	232
CH_3	4	3		2.43 (s, 3H, CH_3), 6.73 (s, 1H, CH), 7.30 (d, 2H, Protons *ortho* to methyl bearing carbon, J = 8Hz), 8.00 (d, 2H protons *meta* to methyl bearing carbon)	292
	7	24		2.40 (s, 6H, CH_3), 7.22 (d, 4H, protons *ortho* to methyl bearing carbons, J = 8Hz), 7.73 (d, 4H, protons *meta* to methyl bearing carbons), 8.93 (s, 2H, heterocyclic protons)	—
OCH_3	4	2		3.85 (s, 3H, OCH_3), 6.65 (s, 1H, CH), 6.90 (d, 2H, protons *ortho* to methoxy bearing carbon, J = 9 Hz), 8.06 (d, 2H, protons *meta* to methoxy bearing carbon)	308
	6	12	192[b]	3.82 (s, 6H, OCH_3), 6.87–7.97 (m, 8H, aromatic), 8.80 (s, 1H, heterocyclic)	371
	7	1		3.90 (s, 6H, OCH_3), 7.01 (d, 4H, protons *ortho* to methoxy bearing carbons, J = 9Hz), 8.00 (d, 4H, protons *meta* to methoxy bearing carbons), 8.98 (s, 2H, heterocyclic)	—
Br	7	18		7.65 (d, 4H, aromatic, J = 9Hz), 7.95 (d, 4H, aromatic), 9.22 (s, 2H, heterocyclic)	—

[a] Analysis Calc. for $C_{16}H_{11}BrN_2$: C, 61.77; H, 3.56. Found: C, 62.03; H, 3.17%.
[b] Analysis Calc. for $C_{18}H_{15}BrN_2O_2$: C, 58.25; H, 4.07. Found: C, 57.96; H, 4.22%.
[c] $CDCl_3$ solution (TMS as internal standard).



The reaction proved difficult to control unless effected as described in the Experimental. The reaction is highly exothermic, even at −23°, and generally has an induction period of 1 hr. However, the reaction proceeded much more smoothly (no induction period) in the presence of catalytic amounts of *p*-toluenesulfonic acid.

EXPERIMENTAL

General. M.pts were obtained on a Fisher–Johns apparatus and are uncorrected. IR spectra were recorded on a Beckman IR-20A spectrometer. NMR spectra were determined using a Varian T-60 spectrometer with TMS as the internal standard. A Varian MS 902 spectrometer was used to record mass spectra.

2-Aryl azirines were prepared according to the procedures of Hortman *et al.*[6] Solvents were dried and purified by standard techniques. All reactions were effected under a dry N_2.

General procedure for reaction of 2-aryl azirines (3) *with NBS.* The azirine (10 mmol) was dissolved in dioxane (5 ml—except for 3, R = OCH_3, where CCl_4 was used as the solvent) and the soln was cooled to −23° (dry ice –CCl_4). The reagent (NBS; 20 mmol) was added in small portions, and the mixture was then stirred and allowed to warm to room temp. After approximately 1 hr, a vigorous reaction took place. CCl_4 (100 ml) was added, and the soln was filtered to remove succinimide. The filtrate was repeatedly washed with water, dried and evaporated *in vacuo.* Work-up was effected as follows in the individual cases: (a) R = H, CH_3. The products were separated by column chromatography on Florisil using a 5:1 ether–petroleum ether mixture as eluant. (b) R = OCH_3. The products were separated by chromatography on Florisil with benzene-ether (10:1). (c) R = Br. The solid was redissolved in CCl_4, filtered and the filtrate was evaporated to give the pyrazine. Recrystallization from acetone gave analytically pure pyrazine.

The exothermic reaction noted above could be avoided by use of 15–30 mg of *p*-toluenesulfonic acid.

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