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FORMATION OF OXIRANES DURING THE PREPARATION OF AROYLACETONITRILES

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REFERENCES

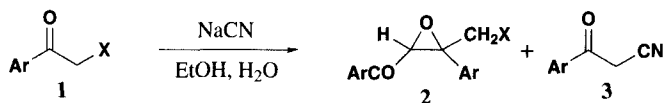
1. P. B. Dervan and B. S. Edelson, *Curr. Opin. Struct. Biol.*, **13**, 284 (2003) and reference therein.
2. E. Nishiwaki, S. Tanaka, H. Lee and M. Shibuya, *Heterocycles*, **27**, 1945 (1988).
3. J. Xiao, G. Yuan, W. Huang, A. S. C. Chan and K.-L. D. Lee, *J. Org. Chem.*, **65**, 5506 (2000).
4. N. R. Wurtz, J. M. Turner, E. E. Baird and P. B. Dervan, *Org. Lett.* **3**, 1201 (2001).
5. M. A. Marques, R. M. Doss, A. R. Urbach and P. B. Dervan, *Helv. Chim. Acta*, **85**, 4485 (2002)
6. E. Regel and K-H. Büchel, *Liebigs Ann. Chem.*, 145 (1977).

FORMATION OF OXIRANES DURING THE PREPARATION
OF AROYLACETONITRILES

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Some aroylacetonitriles have been shown to exhibit various biological activities¹⁻³ and are valuable precursors for the synthesis of a number of heterocyclic compounds.³⁻⁹ Aroylacetonitriles have been prepared *via* S_N2 displacement of halide by cyanide.^{3,8,9} The use of the literature method for the synthesis of aroylacetonitriles in our laboratory led to results somewhat different from those reported.^{3,8,9} It was found that addition of an aqueous solution of NaCN or KCN to ethanolic solutions of α -chloro- or α -bromoacetophenones at room temperature with constant stirring resulted in an exothermic reaction (temperature rises to 40-50°C) and precipitation of a solid in each case. These solids turned out to be different than the expected and known aroylacetonitriles derived from the normal displacement reaction.



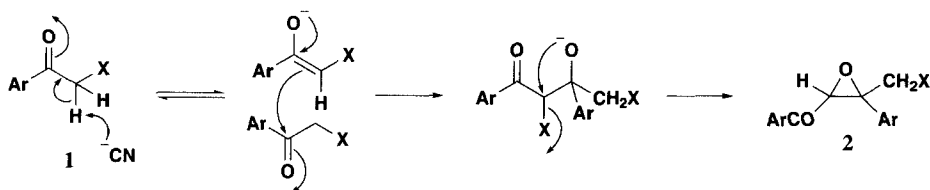
a) Ar = C₆H₅, X = Cl; b) Ar = *p*-ClC₆H₄, X = Br; c) Ar = *p*-BrC₆H₄, X = Br; d) Ar = *p*-CH₃C₆H₄, X = Br

Their IR spectra show absorptions at 1228, 920 and 813 cm⁻¹, characteristic of the oxirane system and carbon-halogen bond. The ¹H NMR in CDCl₃ showed singlet at δ 4.0 for -CH₂X and downfield methine proton at δ 4.65; the multiplets observed between δ 7.25-7.65 and δ 7.83-8.03 correspond to aromatic protons. The ¹³C NMR in CDCl₃ exhibit peaks at δ 48.27 for -CH₂X, δ 63.49 and δ 65.5 for C-1 and C-2 and at δ 191.47 for the aroyl carbonyl group. Aromatic carbons are observed between δ 127.02-136.28. Elemental analysis of the solid product showed the presence of halogen and the absence of nitrogen. On the basis of above observations, these compounds were assigned the oxirane structure **2a-d**. It was also observed that the yield of the oxiranes increases with increased temperatures (*Table 1*). Apparently, the cyanide ion acts as

Table 1. Effect of Temperature on the Yields of **2** and **3**

Temp (°C)	Yield (%)							
	2a	2b	2c	2d	3a	3b	3c	3d
0-5	7	5	5	7	58	70	73	58
20-25	30	27	30	23	52	65	67	25
40-50	50	45	40	30	30	30	32	30

a base at elevated temperature and promotes the formation of **2** while at lower temperature it behaves as a nucleophile to displace the halogen. We suggest the following mechanism for the formation of oxiranes in this reaction.



The formation of an oxirane in the reaction of aroylmethyl halides with cyanide ion does not appear to have been reported previously. The filtrates on the usual work-up did furnish the expected nitriles **3a-d** whose structures were confirmed by comparison of their mps with those in the literature.¹⁰⁻¹³ In each case, a mixture of **2** and **3** was obtained, from which the individual compounds were readily separated. The effect of temperature on the formation of either **2** or **3** is shown in *Table 1*. Development of chirality on the carbon during the formation of oxiranes and the presence of active functional groups such as ArCO and -CH₂X promise further synthetic potential of these compounds.

EXPERIMENTAL SECTION

Mps were determined on a Gallenkamp Melting point apparatus and are uncorrected. Elemental analysis were determined on a Hosli C, H Analyzer. ^1H NMR were recorded on a Varian XL-300 MHz spectrometer using TMS as an internal standard. IR spectra were obtained as Nujol mulls on a Shimadzu IR 408 spectrometer.

[3-(Chloromethyl)-3-phenyloxiran-2-yl](phenyl)methanone (2a). Typical Procedure.- To a solution α -chloroacetophenone (7.78 g, 0.05 mole) in ethanol (175 mL) at room temperature (20°C), a solution of sodium cyanide (2.45 g, 0.05 mole) in 80 mL water was added dropwise with constant stirring. After half an hour, compound **2a** precipitated and was collected, washed with water and recrystallized from ethanol. The filtrate was stirred further for half an hour at room temperature; removal of the solvent under reduced pressure gave a residue, which was stirred in cold water (700 mL) and then neutralized with acetic acid. The precipitated product was collected, washed with water and recrystallized from ethanol to give **3a**.

[3-(Chloromethyl)-3-phenyloxiran-2-yl](phenyl)methanone (2a), colorless solid, mp. 152-153°C. IR: 2924, 2329, 1687, 1595, 1177 cm^{-1} . ^1H NMR (CDCl_3): δ 4.14 (s, 2H, CH_2), 4.65 (s, 1H, C-H) 7.18-8.02 (m, 10H, Ar-H), ^{13}C NMR (CDCl_3): δ 46.26, 63.44, 65.55, 127.02, 128.18, 128.64, 128.71, 132.75, 133.76, 135.28, 191.27.

Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{ClO}_2$: C, 70.46; H, 4.80. Found: C, 70.48; H, 4.70

Benzoylacetonitrile (**3a**), mp 81-82°C, *lit.*¹⁰ 82°C.

[3-(Bromomethyl)-3-(4-chlorophenyl) oxiran-2-yl](4-chlorophenyl)methanone (2b), colorless solid, mp. 122-123°C. IR: 2920, 2330, 1690, 1578, 1166 cm^{-1} . ^1H NMR (CDCl_3): δ 4.10 (s, 2H, CH_2), 5.21 (s, 1H, C-H), 7.35-8.02 (m, 8H, Ar-H).

Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{BrCl}_2\text{O}_2$: C, 49.78; H, 2.87. Found: C, 49.67; H, 2.74

p-Chlorobenzoylacetonitrile (**3b**), mp. 127-128°C, *lit.*¹¹ 129°C

3-(Bromomethyl)-3-(4-bromophenyl) oxiran-2-yl](4-bromophenyl)methanone (2c), colorless solid, mp. 145-146°C. IR: 2927, 2335, 1680, 1580, 1180 cm^{-1} . ^1H NMR (CDCl_3): δ 4.11 (s, 2H, CH_2), 5.20 (s, 1H, C-H), 7.36-8.02 (m, 8H, Ar-H).

Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{Br}_3\text{O}_2$: C, 40.46; H, 2.33. Found: C, 40.38; H, 2.45

p-Bromobenzoylacetonitrile (**3c**), mp. 160-161°C, *lit.*¹² 162-163°C

[3-(Bromomethyl)-3-(4-methylphenyl) oxiran-2-yl](4-methylphenyl)methanone (2d), colorless solid, mp. 134-135°C. IR (Nujol): 2914, 2347, 1687, 1581, 1471, 1178 cm^{-1} . ^1H NMR (CDCl_3): δ 1.25 (s, 6H, CH_3), 3.47(s, 2H, CH_2), 3.92 (s, 1H, C-H), 7.59-7.61 (d, 4H, Ar-H), 7.63-7.82 (d, 4H, Ar-H).

Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{BrO}_2$: C, 62.64; H, 4.96. Found: C, 62.66; H, 4.98

p-Methylbenzoylacetonitrile (**3d**), mp. 103-104°C, *lit.*¹³ 104°C.

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REFERENCES

1. D. Ridge, J. Hanifin, L. Harten, B. Johnson, J. Mensehik, G. Bicolau, A. Sloboda and D. Watts. *J. Med. Chem.*, **22**, 1385 (1979).
2. S. Wong, *Annual. Rep. Med. Chem.*, **10**, 172 (1975).
3. S. Lang and E. Cohen, *J. Med. Chem.*, **18**, 441 (1975).
4. R. Toche, M. Jachak, T. Dalvi, R. Sabnis, H. Junek and T. Kappe, *Org. Prep. Proced. Int.*, **30**, 367 (1998).
5. D. Tupper and M. Bray, *Synthesis*, 337 (1996).
6. M. Aziz and H. Daboun, *J. prakt. Chem.*, **332**, 610 (1990).
7. G. Purrello and A. Vullo, *J. Heterocyclic Chem.*, **11**, 481 (1974).
8. R. Long, *J. Org. Chem.*, **69**, 990 (1947).
9. H. Gakhar, G. Gill and J. Multani, *J. Indian Chem. Soc.*, **48**, 953 (1971).
10. H. Sammour, H Fahmy and M. H. Elnagdi, *J. prakt. Chem.*, **317**, 257 (1975).
11. P. Seneci, M. Nicola, M. Inglesi, E. Vannoti and G. Resnati, *Synth. Commun.*, **29**, 311 (1999).
12. A. Daver and G. Guillanton, *Bull. Soc. Chim. Fr.*, **312**, 316 (1971).
13. P. Bravo *et al.*, *Gazz. Chim. Ital.*, **91**, 47 (1961).