

A NOVEL INDOLE SYNTHESIS

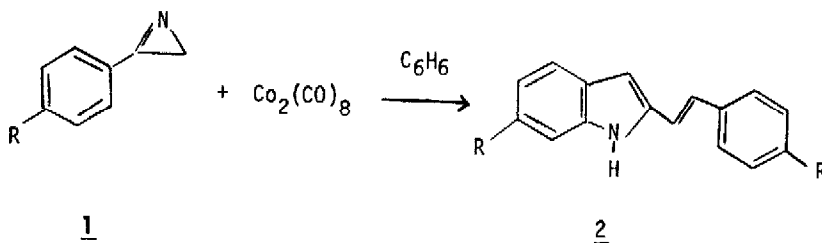
Howard Alper* and John E. Prickett

Department of Chemistry, University of Ottawa,
Ottawa, Ontario, Canada K1N 6N5

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The organometallic chemistry of azirines was unexplored until quite recently. Group VI metal carbonyls $[M(CO)_6]$, $M = Cr, Mo, W$ are useful reagents for converting 2-aryl azirines to pyrazines and dihydropyrazines in good combined yields.¹ Pyrroles were obtained in modest yields using diiron enneacarbonyl as the reagent.² Mechanistic studies indicate that the latter reaction proceeds via carbon-nitrogen bond cleavage of the azirine ring, while the heterocycle undergoes carbon-carbon bond cleavage with $M(CO)_6$.³ This communication describes a third, and very useful, reaction of azirines with metal carbonyls.

Treatment of azirines [1, $R = H, CH_3, OCH_3, Br$] with dicobalt octacarbonyl $[Co_2(CO)_8]$ in benzene at room temperature for 24 hr. affords 2-styrylindoles (2) in good-excellent yields [2, $R = H$, 77%⁴; $R = CH_3$, 95%, m.p. 213-214°; $R = OCH_3$, 90%, m.p. 233 - 235°; $R = Br$, 52%, m.p. 242 - 244°].⁵ 2-Arylethylene derivatives of indole are useful intermediates in alkaloid



synthesis,⁶ and therefore this reaction represents a simple, convenient, and novel approach to such heterocycles. In addition, 2-substituted indoles are not as readily accessible as

3-substituted indoles.⁷

The following general procedure was used; a mixture of the azirine and $\text{Co}_2(\text{CO})_8$ in benzene (30-70 ml.) was stirred, under nitrogen, at room temperature for 24 hr. The solution was filtered, and the filtrate was concentrated to a small volume and then purified by chromatography on Florisil or silica gel.

An investigation of the mechanism of this reaction is in progress.

ACKNOWLEDGMENT

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REFERENCES AND NOTES

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2. H. Alper and J.E. Prickett, J. Chem. Soc., Chem. Commun., 191 (1976).
3. H. Alper and J.E. Prickett, unpublished results.
4. J.A. Eenkhoorn, S.O. de Silva, and V. Snieckus, Can. J. Chem., 51, 792 (1973).
5. The structures of the products were elucidated on the basis of analytical (C, H, N) as well as infrared, nuclear magnetic resonance, ultraviolet, and mass spectral results. Indole 2, R = H, is a known compound.⁴
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7. R.J. Sundberg, "The Chemistry of Indoles", Academic Press, New York, N.Y., 1970.