

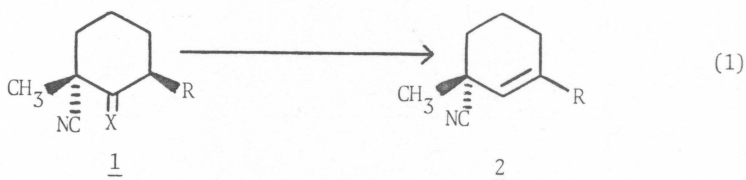
CONVERSION OF KETONES TO TRISUBSTITUTED OLEFINS UNDER NEUTRAL CONDITIONS

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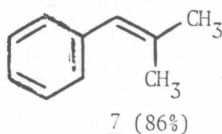
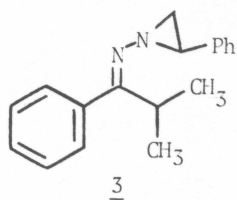
Summary: Phenylaziridine hydrazones react at 140°-160°C to provide sterically congested trisubstituted olefins in good yield.

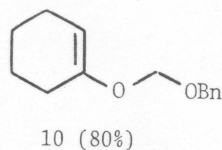
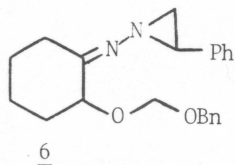
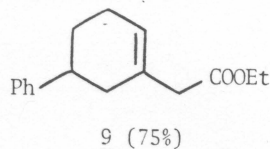
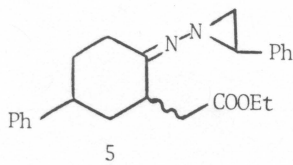
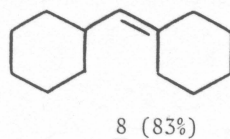
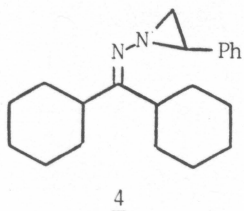
In total synthesis efforts ongoing in our laboratory we were backed into a corner by a very demanding olefination similar to that illustrated in equation 1. Analogous Shapiro eliminations of arylsulfonyl hydrazones leading to trisubstituted olefins are rare, typically proceeding in low yield under strongly basic conditions.<sup>1,2</sup> Although we were able to obtain the requisite hydrazone derivatives of 1 (X=NNHSO<sub>2</sub>Ar), numerous attempts to effect the conversion to alkene 2 failed completely (<0.5% yield). Surprisingly, even the protic and aprotic Bamford-Stevens elimination<sup>1</sup> provided none of the desired alkene.<sup>3</sup>



In 1972, Eschenmoser reported that phenylaziridine hydrazones of  $\alpha,\beta$ -epoxyketones afforded fragmentation products upon heating.<sup>4</sup> Subsequently, Evans reported that LDA-mediated Shapiro-like olefinations of similar  $\beta$ -ketoester hydrazones could be achieved.<sup>5</sup> We report here-in that related thermolyses of phenylaziridine hydrazones provide congested trisubstituted olefins under essentially neutral conditions.

Phenylaziridine hydrazone 1 (X=NNCH<sub>2</sub>CHPh, R=CH<sub>3</sub>), upon heating in decalin for 2 hr at 160°C is converted to olefin 2 (R=CH<sub>3</sub>) in 92% yield after flash chromatography. Similarly, hydrazones 3-6 are converted to olefins 7-10, respectively (yields in parentheses). Eliminations of 5 and 6 exhibit regioselectivities analogous to the Bamford-Stevens elimination.<sup>1,7</sup>





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#### References and Footnotes

1. Reviews: Shapiro, R. H.; *Org. React.* (1976), 23, 405; Adlington, R. M.; Barrett, A. G. M. *Acct. Chem. Res.* (1983), 16, 55.
2. See Kolonko, K. J.; Shapiro, R. H. *J. Org. Chem.* (1978), 43, 1404.
3. A 1,4-elimination of LiCN from the monoanion may initiate the eventual destruction.
4. Felix, von D.; Muller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* (1972), 55, 1276.
5. Evans, D. A.; Nelson, J. V. *J. Amer. Chem. Soc.* (1980), 102, 774.
6. Hydrazone 1 is prepared from 2-cyano-6-methylcyclohexanone hydrazone by a modification of an alkylation procedure described elsewhere (LDA/THF-CH<sub>3</sub>I); Collum, D. B.; Kahne, D.; Gut, S. A.; DePue, R. S.; Mohamadi, F. submitted for publication. Hydrazones 3-6 are prepared in 60-80% yields by the method described (ref. 4). We note that it is imperative to keep the reaction vessel at 0°C for the duration of the hydrazone formation.
7. Although the alternative regioisomeric disubstituted olefin derived from 5 has not been found, elimination of 6 provides an 8% yield of 1-(benzyloxymethoxy)-2-cyclohexene in addition to 10.

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