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CONVERSION OF KETONES TO TRISUBSTITUTED OLEFINS UNDER NEUTRAL CONDITIONS

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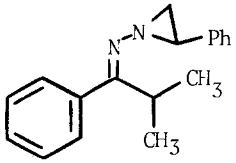
Summary: Phenylaziridine hydrazones react at 140°-160°C to provide sterically congested trisubstituted olefins in good yield.

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 <u>trisubstituted</u> olefins are rare, typically proceeding in low yield under strongly basic conditions.[1],[2] Although we were able to obtain the requisite hydrazone derivatives of 1 ($X=NNHSO_2Ar$), numerous attempts to effect the conversion to alkene 2 failed completely (<0.5% yield). Surprisingly, even the protic and aprotic Bamford-Stevens elimination[1] provided none of the desired alkene.[3]

1 2 (1)

In 1972, Eschenmoser reported that phenylaziridine hydrazones of α,β-epoxyketones afforded fragmentation products upon heating.[4] Subsequently, Evans reported that LDA-mediated Shapiro-like olefinations of similar β-ketoester hydrazones could be achieved.[5] We report herein that related thermolyses of phenylaziridine hydrazones provide congested trisubstituted olefins under essentially neutral conditions.

Phenylaziridine hydrazone 1 ($X=N\overline{NCH_2C}HPh$, $R=CH_3$), upon heating in decalin for 2 hr at 160°C is converted to olefin 2 ($R=CH_3$) 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.[1],[7]



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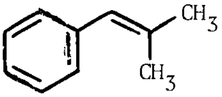
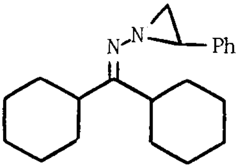


7 (86%)



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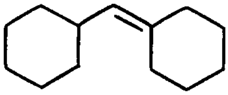
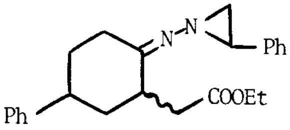


8 (83%)



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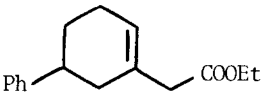
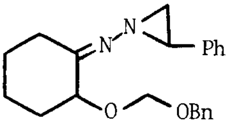


9 (75%)



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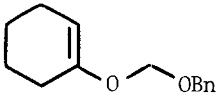

10 (80%)

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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_3I); 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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