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A CYCLOPROPANONE - TOSYLHYDRAZIDE ADDUCT: DEHYDRATION TO A TOSYLHYDRAZONE AND DECOMPOSITION; OXIDATIVE RING-EXPANSION TO A BETA-LACTAM[1]

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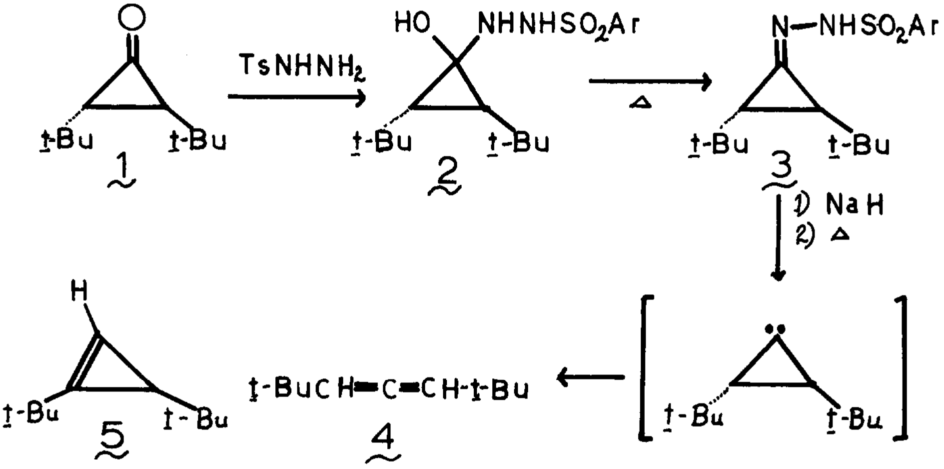
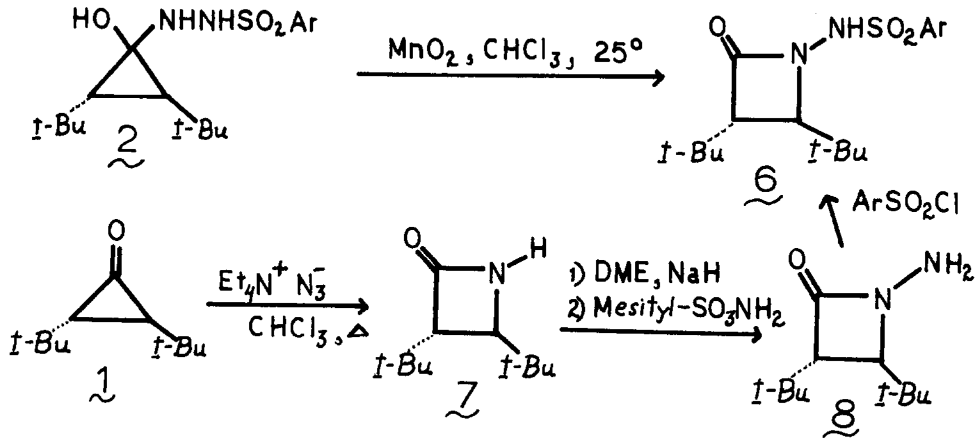
Decomposition of toluenesulfonylhydrazones (Bamford Stevens Reaction) has received much attention over a range of structural variations.[2] We report here the formation and decomposition of the toluenesulfonylhydrazone of trans-2,3-di-tert-butylcyclopropanone. Also reported is an oxidative ring expansion by manganese dioxide of the cyclopropanone-tosylhydrazide adduct to a beta-lactam, a reaction of possible applicability to other cyclopropanone derivatives.

Reaction of cyclopropanone **1**[3a] with tosylhydrazide affords a 1:1 adduct **2**. Heating (80°, 10 hr, 0.1 mm) effects dehydration to the corresponding tosylhydrazone, **3**, mp 113-114.5°. Conversion to the sodium salt by sodium hydride and heating (120-190°, 2hr, 0.4 mm), affords 1,3-di-tert-butylallene **4**[3b] (47% yield) and 1,3-di-tert-butylcyclopropene **5** in 10% yield, ir 1750 cm^{-1},[4] nmr (CCl_4) 6.45 (S, 1H),[4] 1.47 (S, 1H), 1.17 (S, 9H), 0.71 (S, 9H), mass spectrum at 70 eV m/e (rel intensity) 152 (molecular ion, 4.5), 137(49.5), 123.5(1), 122(8.0), 109(25.9), 95 (loss of t-butyl, 100), 81(28), 67(49.5), 65.6(0.5), 57(59.5), 55(46), 41(51.7).

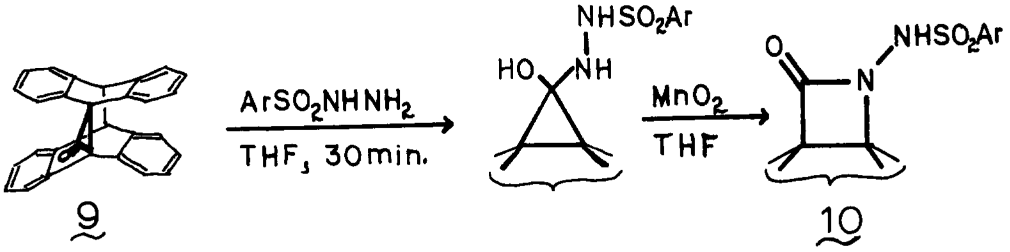


Base-induced decompositions of tosylhydrazones in aprotic media have been shown to give diazo compounds which may decompose to carbenes and nitrogen.[2] Base-induced decomposition of optically active N-(trans-2,3-diphenylcyclopropyl)-N-nitrosourea affords optically active 1,3-diphenylallene.[5] Carbenoid intermediates from reaction of mono-, di-, and trialkyl-substituted gem-dibromocyclopropanes with methyllithium give only allenes.[6] The tetraalkyl derivative, 1,1-dibromo-2,2,3,3-tetramethylcyclopropane, reacts with methyllithium to give 1,2,2-trimethylbicyclobutane (98%) and tetramethylallene (2%).[6] With the cyclopropylidene from 3, bicyclobutane formation is not possible. Instead one sees the ring-opening to the allene and rearrangement to the cyclopropene, presumably by 1,2-hydrogen migration, a well-known path with carbenes[2] although not observed in the reactions of the cyclopropylidenes described above.[7]

A second reaction of interest with the tosylhydrazide-cyclopropanone adduct 2 is oxidative ring expansion by activated manganese dioxide to a beta-lactam derivative 6,* in 25% yield, mp 184-186°, ir 1770 cm^{-1}, nmr ($CDCl_3$), 0.95 (S, 9H), 1.0 (S, 9H), 2.27 (broad S, 4H), 3.62 (d, 1H, J = 3Hz), 7.2-8 (m, 4H). Assignment of structure 6, rather than an alternative 2-imino-oxetane structure,[8] is based on synthesis. Reaction of cyclopropanone 1 with azide ion in refluxing chloroform effected ring expansion to beta-lactam 7,[9]* mp 169-170°, ir ($CHCl_3$) 1745 cm^{-1}, nmr ($CDCl_3$), 0.95 (S, 9H), 1.05 (S, 9H), 2.66 (m, 1H), 3.14 (d, 1H, J = 2Hz), 6.3 (broad, 1H). Amination with O-mesitylenesulfonyl hydroxylamine[10] afforded the N-amino beta-lactam 8, mp 89-91°, ir ($CHCl_3$) 1740 cm^{-1}, which was converted to 6,* identical in all respects with the material from oxidation of 2.



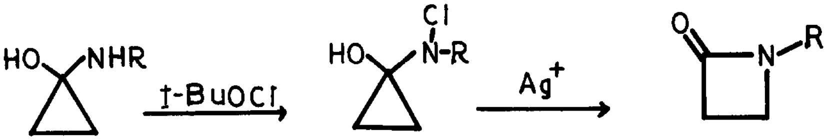
The oxidative ring-expansion by manganese dioxide also occurs with the adducts of cyclopropanone **9**[11] and arylsulfonylhydrazides.



10a* Ar = p-CH_3-C_6H_4 dec. pt. 211-212°
ir (KBr) 1780 cm^{-1}; yield 65%

10b* Ar = p-NO_2-C_6H_4 dec. pt. 210-211°
ir (KBr) 1778 cm^{-1}; yield 45%

This oxidative ring expansion is similar in over-all result to that reported by Wasserman, Adickes, and deOchoa[12] in the conversion of a 1-aminocyclopropanol to a beta-lactam by the action of *tert*-butyl hypochlorite followed by silver ion.



* Satisfactory elemental analyses were obtained.

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7) Reaction conditions and cyclopropylidene precursors of this work and references 5 and 6 differ considerably.

8) Not distinguished by ir; for an example of a 2-imino-oxetane and the corresponding beta-lactam see L.A. Singer and G.A. Davis, *J. Amer. Chem. Soc.*, **89**, 941 (1967).

9) For another example of this reaction, see H.H. Wasserman and M.S. Baird, *Tetrahedron Lett.*, 3721 (1971).

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11) For preparation and physical data of **9**, see E. Wasserman, V.J. Kuck, W.A. Yager, R.S. Hutton, F.D. Greene, V.P. Abegg, and N.M. Weinshenker, *J. Amer. Chem. Soc.*, **93**, 6335 (1971).

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