An Unusual Anionic Rearrangement in the $(CH)_{10}$ Series

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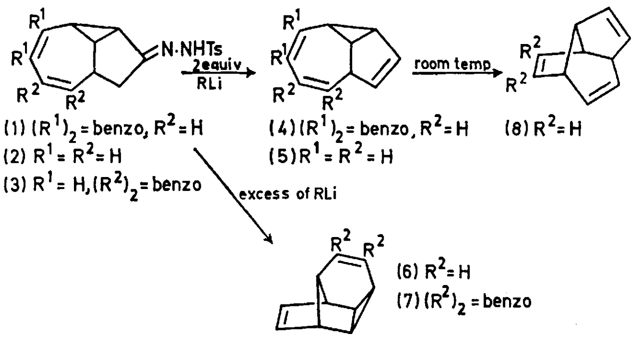
Summary Reaction of an excess of methyl-lithium with the tosylhydrazone of tricyclo[5,3,0,$0^{2,10}$]deca-3,5-dien-9-one affords tetracyclo[4,4,0,$0^{2,10}$,$0^{5,9}$]deca-3,7-diene, whereas reaction with 2 equiv. of methyl-lithium gives tricyclo[5,3,0,$0^{4,10}$]deca-2,5,8-triene.

During a study of benzo-fused $(CH)_{10}$ hydrocarbons, we found that optimum yields (60%) of the vinylcyclopropane (**4**)[1] could be obtained from (**1**) by using an excess (3—4 equiv.) of n-butyl-lithium. Surprisingly, when the same conditions were employed to generate the parent hydrocarbon (**5**), we obtained a mixture of the expected Cope rearrangement product (**8**) and a different $(CH)_{10}$ isomer identified as (**6**) by comparison with authentic material.[2] The relative yield of (**6**) increased with the amount of base. Thus, (**6**) was obtained as the sole product (20%) when 6 equiv. of methyl-lithium was used, whereas (**8**) was isolated in 15% yield along with 1—2% of (**6**) by using 2 equiv. of base. The anomalous rearrangement was also encountered in experiments with the benzo-derivative (**3**),[1] and the new hydrocarbon product (**7**) (35%) was identified by the similarity of ^1H n.m.r. spectrum† with that of (**6**).

A clue to the mechanism of this unusual rearrangement was found in the tosylhydrazone (**9**) [m.p. 158—159° (decomp)] recovered in low yield from reaction of (**2**) with an excess of methyl-lithium. Reaction of (**9**) with methyl-lithium gave (**6**) as the sole hydrocarbon product. The ^1H n.m.r. spectrum of (**9**) contained signals for cyclopropyl protons between δ 1·2 and 2·0 and for two vinyl protons as triplets (J 7 Hz) at δ 5·75 and 6·28, similar in chemical shift and appearance to the corresponding protons of (**6**).



Although this evidence allows only a tentative assignment of structure (**9**), it is clear that skeletal reorganization precedes the loss of toluenesulphinate and nitrogen.

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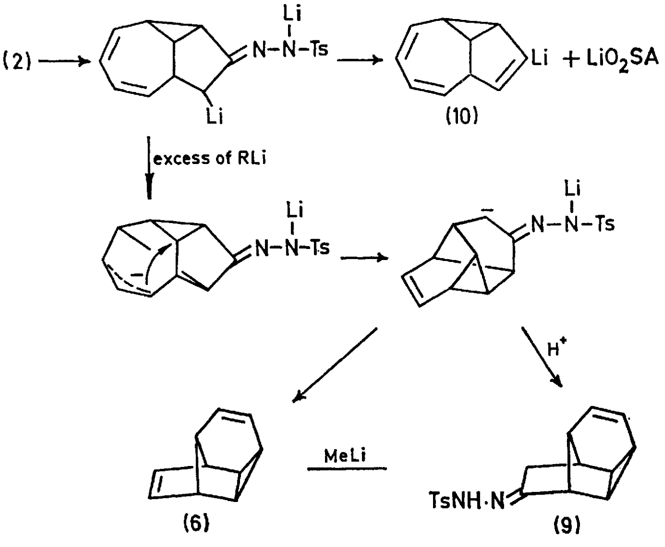
† δ ($CDCl_3$) 6·9—7·4 (4H,m), 6·62 (2H, t, J 2 Hz), 2·91 (1H, t, J 7 Hz), 2·72br (1H, s), 2·12br (2H, s), and 1·62 (2H, d, J 7 Hz).



If we assume an α-lithiated tosylhydrazone anion intermediate for the methyl-lithium-induced olefin synthesis,[3] the formation of (**6**) is presumably due to transannular addition of the carbon–lithium bond to the conjugated diene followed by nucleophilic attack at a cyclopropane carbon atom. This would result in the same anionic intermediate as expected from (**9**) and methyl-lithium, and normal fragmentation to nitrogen and lithium toluene-sulphinate would give (**6**). A similar rearrangement pathway is available to the benzo-derivative (**3**), but not to (**1**) since the transannular addition step would disrupt the aromatic ring.

To rationalize the dependence of reaction pathway on the amount of base employed, we suggest that excess of base metallates the tosyl group ('Ts' = $SO_2C_7H_6Li$?) and thereby destabilizes the corresponding sulphinate anion as a leaving group. The normal fragmentation to the vinyl anion (**10**) would thus become slower, and the transannular cyclization process could compete effectively.‡

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‡ Transannular participation in the more flexible tricyclo[5,4,0,$0^{1,11}$]undeca-3,5-dien-10-one tosylhydrazone requires no special assistance from excess of base. Even with 1·9 equiv. of butyl-lithium, the hydrocarbon product consists of rearranged tetracyclic dienes with less than 5% of the 'normal' product, tricyclo[5,4,0,$0^{2,11}$]undeca-3,5,9-triene (E. Vedejs and R. Twieg, unpublished work).

[1] E. Vedejs, R. A. Shepherd, and R. P. Steiner, *J. Amer. Chem. Soc.*, 1970, **92**, 2158.
[2] M. Jones, jun., S. D. Reich, and C. T. Scott, *J. Amer. Chem. Soc.*, 1970, **92**, 3118.
[3] R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, 1967, **89**, 5734; G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, p. 5736.