

THE REDUCTIVE METHYLATION OF LINEAR CONJUGATED DIENONES

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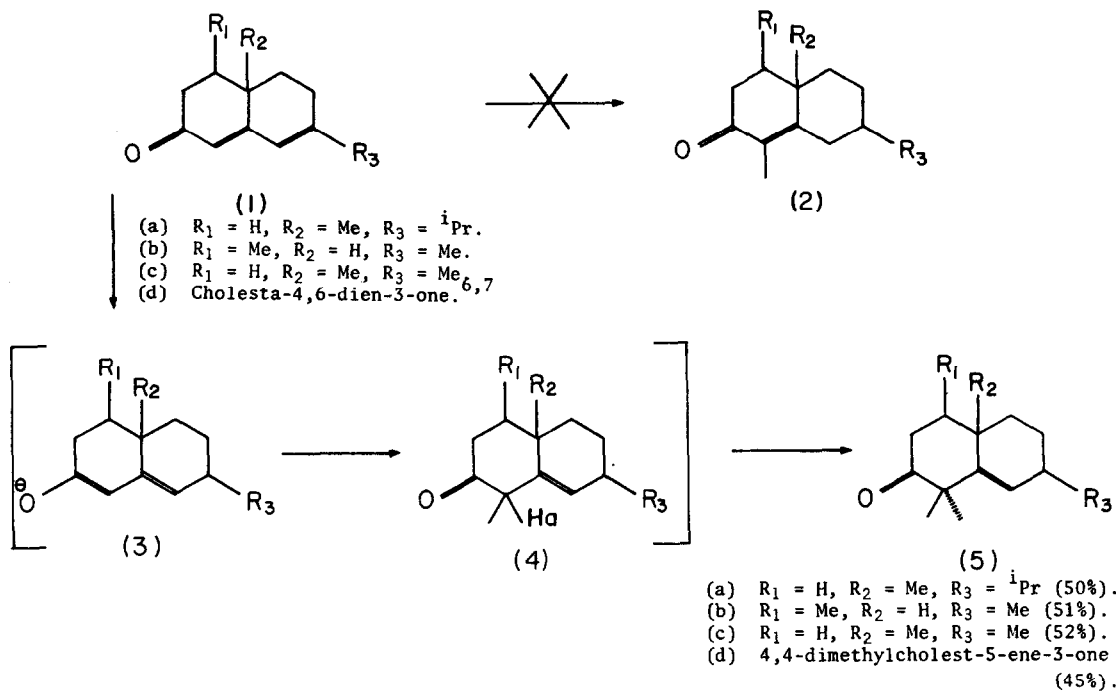
(Received in UK 3 September 1973; accepted for publication 21 September 1973)

The reductive methylation of α,β -unsaturated carbonyl compounds with lithium in ammonia has been studied in some detail by Stork¹. By analogy with this work, linear conjugated dienones (1) would be expected to give rise to the corresponding monomethylenones (2). It is of interest, therefore, that these dienones, upon reductive methylation, yield predominantly the gem-dimethyl ketones (5) (Scheme 1) with very minor proportions of (2). In contrast to Stork's results where at least 17% reduction occurs without alkylation¹, no compounds arising from such direct reduction could be detected in the products of the present sequence.

Gem-dimethyl ketones of the type (5) represent important synthetic intermediates in the steroid and terpene fields^{2,3,4}. They have been previously prepared by base catalysed alkylation of α,β -unsaturated ketones^{2,3,4}. This report offers an alternative route to these compounds by a simple reaction from linear dienones. A representative procedure is as follows: the dienone (1c)⁵ (1.3 g in 30 ml dry THF) was added to liquid ammonia (500 ml) followed by sodium (380 mg, slightly in excess of 2 equivalents). After 0.5 hr of stirring, methyl iodide (3 ml) was rapidly added. Evaporation of the ammonia, aqueous work-up and chromatography afforded the pure ketone (5c) (790 mg, 52%).

The mechanism of this process initially involves a one electron addition by sodium, protonation at the β -carbon by ammonia and a further one electron addition¹. Quenching of the resulting enolate anion (3) with excess methyl iodide gives the monomethylenone (4). However, due to the acidity of H_a in (4) this is accompanied by rapid base catalysed alkylation (sodium amide present in the system) giving rise to the observed products.

Scheme 1*



The author is indebted to Dr. W.M.P. Johnson for experimental assistance leading to the successful reductive alkylation of (1d) which had initially failed due to solubility problems.

References and Notes:

1. G. Stork, P. Rosen, N. Goldman, R.V. Coombs and J. Tsuji, *J.Amer.Chem.Soc.*, **87**, 275 (1965).
2. R.B. Woodward, A.A. Patchett, D.H.R. Barton, D.A.J. Ives and R.B. Kelly, *J.Chem.Soc.*, Part 1, 1131 (1957).
3. W.G. Dauben and A.C. Ashcraft, *J.Amer.Chem.Soc.*, **85**, 3673 (1963).
4. R.E. Ireland and P.W. Schiess, *J.Org.Chem.*, **28**, 6 (1963).
5. A.J. Birch and K.P. Dastur, to be published.
6. A.L. Wilds and C. Djerassi, *J.Amer.Chem.Soc.*, **68**, 1713 (1946).
7. 300 ml of ammonia, 200 ml of THF and a reaction time of 3 hr were used to successfully alkylate 0.5 g of (1d).

* All compounds have satisfactory spectral data.