

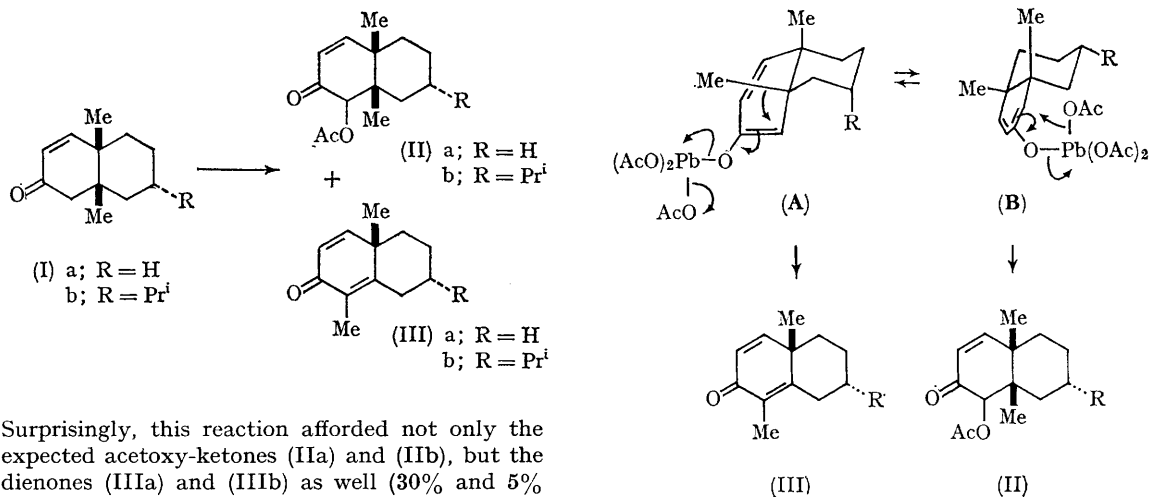
Methyl Migration in Lead Tetra-acetate Oxidations of Cyclohexenones

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THE conversion of ketones into their α -acetoxy-derivatives can often be effected quite smoothly with lead tetra-acetate in acetic acid.¹ In the

course of studies aimed at the synthesis of valeranone and related compounds,² we applied this method to the unsaturated ketones (Ia)³ and (Ib)².



Surprisingly, this reaction afforded not only the expected acetoxy-ketones (IIa) and (IIb), but the dienones (IIIa) and (IIIb) as well (30% and 5% yield respectively). These compounds were isolated by preparative gas chromatography and identified through their characteristic infrared, ultraviolet, and n.m.r. spectra.⁴ Additional structural confirmation was obtained by comparison with authentic samples prepared *via* dehydrogenation⁴ of the related 10-methyl-1(9)-octal-2-ones.^{3a,5} Gas-chromatographic analysis of aliquots taken from the reaction mixture after various time intervals showed that (IIa) and (IIIa) arise independently from (Ia) (*i.e.*, IIa \nrightarrow IIIa).

Although a rigorous mechanism for reactions of lead tetra-acetate with ketones has not been established, our findings are nicely accommodated by the enol-lead triacetate intermediate proposed by Corey and Schaefer⁶ for acetoxylation reactions.

Accordingly, in the present case steric effects retard the usually favoured attack by acetate on the enol double bond (**B** \rightarrow II) thereby enabling methyl migration to occur (**A** \rightarrow III). The observed disparity in the yields of dienones (IIIa) and (IIIb) can be understood in terms of the stereoelectronic requirements expected for such a methyl migration. Thus for enone (Ib) the favourable transition state arrangement (**A**) leading to methyl migration suffers from a serious 1,3-diaxial interaction. This can be alleviated *via* rotation to conformer (**B**), a form possessing an unfavourable geometry for methyl migration.

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¹ C. Fenselau in C. Djerassi, ed. "Steroid Reactions," Holden-Day, San Francisco, 1963, p. 537.

² J. A. Marshall and G. L. Bundy, *Tetrahedron Letters*, 1966, in the press.

³ Prepared *via* bromination and dehydrobromination of the corresponding decalone. Cf. (a) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, 1966, **31**, 1016; (b) J. A. Marshall and N. H. Andersen, *ibid.*, p. 667.

⁴ Cf. D. Caine and J. B. Dawson, *J. Org. Chem.*, 1964, **29**, 3108; P. J. Kropp, *ibid.*, p. 3110 and references cited therein.

⁵ F. J. McQuillin, *J. Chem. Soc.*, 1955, 528.

⁶ E. J. Corey and J. P. Schaefer, *J. Amer. Chem. Soc.*, 1960, **82**, 918. See also, H. B. Henbest, D. N. Jones, and G. P. Slater, *J. Chem. Soc.*, 1961, 4472.