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METHYLCYCLOPROPANE-SOFT ACID REACTION II. NOVEL CYCLOPROPANYLMERCURIALS FROM MERCURY (II) OXIDATION OF LONGICYCLENE AND CYCLENE[1,2]

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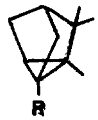
During the recent past, the fifth-row Periodic Table soft acid trio of neighbours - mercury (II), thallium (III) and lead (IV) (atomic Nos. 80, 81 and 82) - have assumed considerable importance in the technique of oxymetallation[3] of olefinic and cyclopropanic organic substrates. The rates of oxidative cleavage of cyclopropanes[4], indicative of the relative electrophilicity of the three soft acids, stand in the order[5] Tl(III) > Hg(II) > Pb(IV). The synthetic utility of the oxymetallation reaction stems from the comparative ease of solvolysis of the carbon-metal bond (Pb > Tl > Hg) which allows for easy conversion to non-metal-containing oxygenated products.

As part of our study of the action of soft acids [Hg(II), Tl(III) and Pb (IV)] on the methylcyclopropane moiety in isoprenoid bridged systems of increasing complexity as exemplified in the monoterpene tricyclene 1 (R=H) and its sesquiterpene analog longicyclene 2 (R=H) we first investigated the $Pb(OAc)_4$[2] reaction on these two substrates. The high lability of these oxyplumbation adducts (e.g. 3, M = Pb, x = 4) at once led to solvolytic deplumbation with concomitant 1,3-elimination of AcOH to the homoenolacetate 2 (R=OAc), easily convertible into the novel ketone 4 [2].



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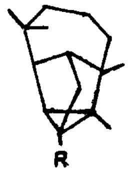

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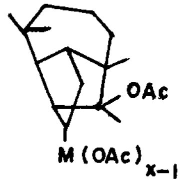

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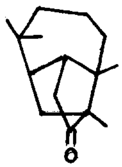

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Oxymercuration of longicyclene (AcOH, room temp./7 days) gave the crude acetoxymercurial 2 (R = HgOAc) [s, 1.90 ppm, *vide infra* 2 (R=HgCl)] as an intractable gum, however amenable to facile crystallisation on exposure to aqueous NaCl. The crystalline chloromercurial (m.p. 229-30°; yield[6]: *ca* 50%) was clearly an anomalous oxymercuration product since it was devoid of any oxygen function. Its PMR spectrum [*four* tertiary Me singlets at 1.08, 0.97, 0.88 and 0.85 ppm] dictated a unique structure 2 (R=HgCl) for the product which was vindicated chemically by its transformation to 2 (R=H) by demercuration ($LiAlH_4$).

In the case of tricyclene 1 (R=H), the $Hg(OAc)_2$/NaCl reaction was somewhat complicated by the formation of a sparingly soluble amorphous solid (*ca* 270° decomp.) which had to be separated before chromatography. The pure compound (mp. 153-54°), eluted with light petroleum, was readily assigned the chloromercurial structure 1 (R=HgCl) [yield: 44%; cf. 2 (R=HgCl); PMR: *three* tertiary Me singlets at 1.17, 0.93 and 0.87 ppm] for the reasons stated earlier [absence of oxygen function and chemical reduction to cyclene 1 (R=H)].

The displacement of the chloromercury residue by halogen ($C_5H_5N.Br_2$) generating the novel tertiary[7] bromides 2 (R=HgCl) → 2 (R=Br) [PMR: *four* tertiary Me singlets at 1.13, 0.98 and 0.90 (3H x 2) ppm and cyclopropyl 1H singlet at 0.80 ppm] and 1 (R=HgCl) → 1 (R=Br) [PMR: *three* tertiary Me singlets at 1.13, 0.88 and 0.83 ppm] constitutes a reaction of both structural and synthetic significance.

The genesis of the anomalous organomercurial [e.g. 2 (R=HgOAc)] could conceivably arise from a normal oxymercuration adduct of the type 3 (M=Hg, x = 2) which however prefers stabilization by a 1,3-elimination (AcOH).

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6 Yield is 80% based on recovered longicyclene.

7 No resonance above 2.30 ppm.