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VICINAL PHENYL GROUP SHIFT IN THE LEAD TETRAACETATE AND RELATED OXIDATIONS OF 5,5,5-TRIPHENYL-1-PENTANOL[1]

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Abstract—In the lead tetraacetate and heavy metal-bromine oxidations of 5,5,5-triphenyl-1-pentanol **1d**, the major cyclization product obtained was the rearranged 2,2,3-triphenyltetrahydro-2*H*-pyran **11d**, resulting from homolytic and heterolytic 1,2-phenyl group shift (the latter only in the lead tetraacetate reaction) in the respective intermediate species with electron deficient δ-carbon **4d** and **6d**.

The conversion of conformationally mobile alcohols **1** to 5-membered cyclic ethers **7** by means of lead tetraacetate (LTA) is considered to involve species **2–6** as intermediates (Scheme 1, pathway A).[2,3] The amount of positive charge at C(δ) in **6**, as reflected by carbonium ion reactions other than internal ether ring closure to **7** (such as adjacent proton elimination, external nucleophile addition, alkyl group migration, etc.), appears to be low when this carbon is primary (**a**) or secondary (**b**),[2–4] and even when the δ-CH$_2$ group forms part of a neopentyl-type system (**c**), rearranged products resulting from heterolytic 1,2-Me shift in **6c** are obtained in only 8–10% yield.[1]

We have now studied the LTA reaction (in refluxing benzene) of 5,5,5-triphenyl-1-pentanol **1d**, and have found (Scheme 2) that the normal 5-membered cyclic ether, i.e. 2-(triphenylmethyl)tetrahydrofuran **7d**, was formed in only 5.5% yield, whereas the major cyclization product, isolated in 59% yield, was the rearranged 6-membered cyclic ether, i.e. 2,2,3-triphenyltetrahydro-2*H*-pyran **11d**.[b] In this case the phenyl group can undergo 1,2-shift both homolytically (in the δ-carbon radical **4d**)[5] and heterolytically (in the δ-carbocation **6d**)[6] (in contrast to alkyl groups which migrate solely as anions[1,5,6]), to give the respective rearranged intermediates **8d** and **10d** (Scheme 3, pathway A).

Heavy metal salts (mercuric oxide or silver carbonate) and bromine (in *n*-pentane or carbon tetrachloride at room temperature) were less efficient in effecting cyclization of alcohol **1d** (Scheme 2);[c] however, here also both cyclic ethers **7d** and **11d** were obtained, but the relative amount of the rearranged product **11d** was somewhat lower than in the LTA reaction.

Since, according to available evidence,[7,8] this type of ether ring closure reaction (the "hypobromite reaction") does not proceed via the ionic species **6** (Scheme 1), but involves (pathway B) the intermediates **2–5** and finally direct internal displacement of Br by the OH-oxygen in the δ-bromo-alcohol **5**, the 1,2-shift of the phenyl group in the course of the heavy metal salt-bromine oxidation of alcohol **1d** (Scheme 3, pathway B), leading via the rearranged ε-bromo-alcohol **9d** to **11d**, can occur only by a homolytic mechanism (**4d** → **8d**). Therefore, by comparing the results of the LTA and heavy metal salt-bromine oxidations of alcohol **1d** (Scheme 3, pathways A and B, respectively), it can be inferred that in the LTA reaction (pathway A) vicinal phenyl group migration (leading to **11d**) takes place both at the δ-carbon radical stage (**4d** → **8d**) and at the δ-carbocation stage (**6d** → **10d**).

EXPERIMENTAL[d]

NMR spectra. Varian spectrometer A-60A (60 MHz); CCl$_4$ soln and TMS as internal standard were used (chemical shifts in δ units; s, singlet; t, triplet; q, quartet; m, multiplet; b, broad; ca, complex absorption). IR spectra: Perkin–Elmer Grating spectrophotometer, Model 337 (in CCl$_4$). Silica gel (0.05–0.2 mm) was used for column chromatography. The separation and purity of products was checked by TLC on silica gel G (Stahl) with pentane–benzene–diethyl ether (2:1:1), detection being effected with 50% H$_2$SO$_4$. Light petroleum refers to the fraction boiling at 40–60°.

Alcohol **1d** was prepared from triphenylmethyl bromide, Mg and THF,[9] and recrystallized from cyclohexane, m.p. 116–118°.[9,10]

The *lead tetraacetate oxidation* was carried out in the usual way,[2] by using 6.33 g (0.02 mol) of **1d**, 9.31 g (0.02 mol + 5% excess) of LTA, 2.2 g (0.02 mol + 10% excess) of dry CaCO$_3$ and 150 ml of Na-dried benzene. The mixture was refluxed until disappearance of Pb^{IV} (about 5 h), worked up (as previously described[2]) and the reaction products were chromatographed on silica gel. Elution with light petroleum afforded 3.71 g (59%) of **11d**, m.p. 142–143° (from light petroleum); IR: ν_{max} 1600, 1500, 1460, 1080, 1050 (d), 1040, 890, 710, 650, 600 cm^{-1}; NMR: δ 1–2.2 (H$_2$C-4 and H$_2$C-5, bm), 3.25–4.2 (HC-3 and H$_2$C-6, ca), 6.8–7.65 (three C$_6$H$_5$, ca). (Found: C, 88.04; H, 7.34. C$_{23}$H$_{22}$O requires: C, 87.86; H, 7.05%).

Elution with pentane–benzene (9:1) gave 0.35 g (5.5%) of **7d**, m.p. 110–111° (from MeOH); IR: ν_{max} 1600, 1500, 1460, 1080, 1040, 890, 705, 640 cm^{-1}; NMR: δ 0.95–2.2 (H$_2$C-3 and H$_2$C-4, bm), 3.55 (H$_2$C-5, q), 5.38 (HC-2, t, $J = 7$ Hz), 7.25 (three C$_6$H$_5$, m). (Found: C, 87.83; H, 7.16. C$_{23}$H$_{22}$O requires: C, 87.86; H, 7.05%).

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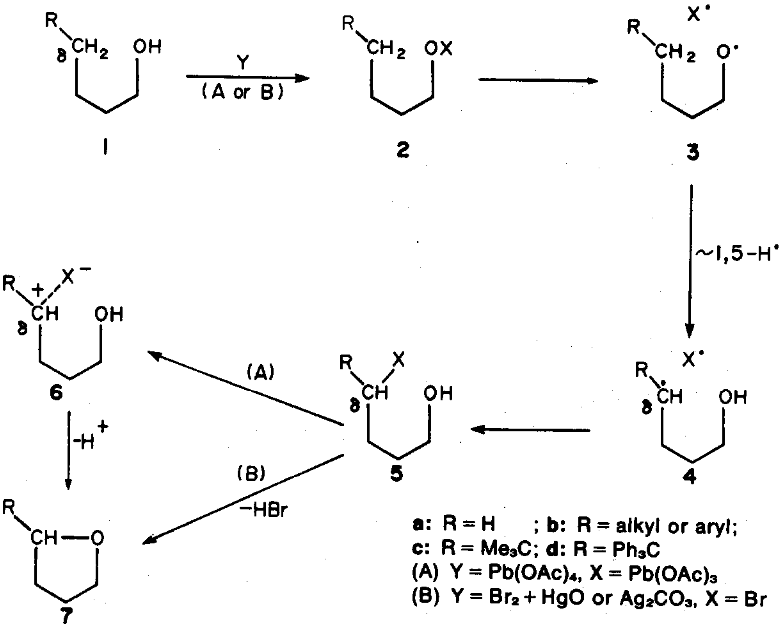
[b] Other products in this reaction were unchanged **1d** (8%) and its acetate (12–15%).

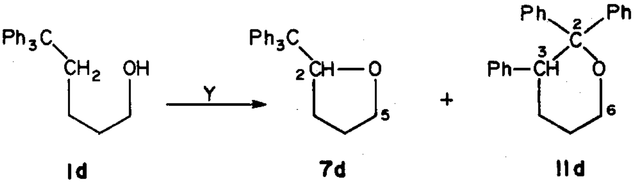
[c] Other products isolated in these reactions were unchanged **1d** (12–16%), 5,5,5-triphenylpentanal (30–35%) and bromine containing material (not further investigated).

[d] Spectral measurements were performed in the Laboratories for Instrumental Analysis (directed by Prof. D. Jeremić), and elemental microanalyses in the Microanalytical Laboratory (Dr. R. Tasovac) of the Chemistry Department.



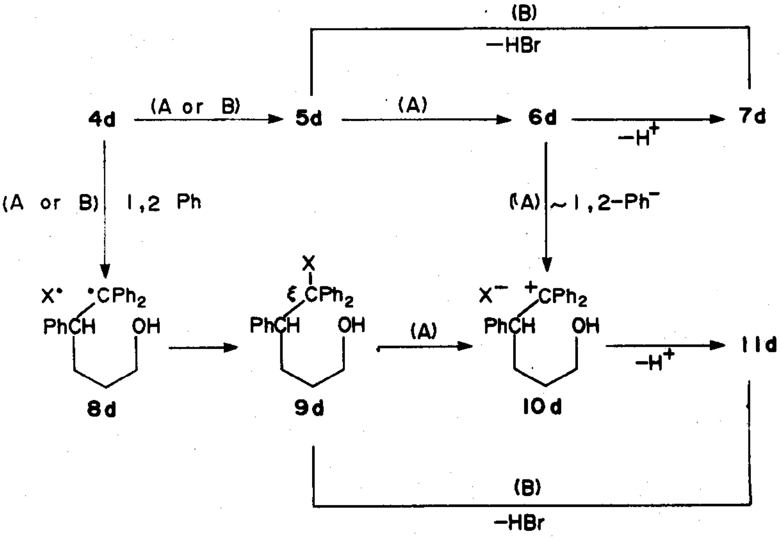
a: $R = H$; b: R = alkyl or aryl;
c: $R = Me_3C$; d: $R = Ph_3C$
(A) $Y = Pb(OAc)_4$, $X = Pb(OAc)_3$
(B) $Y = Br_2 + HgO$ or Ag_2CO_3, $X = Br$

Scheme 1.



		7d	11d
$Y = Pb(OAc)_4$	:	5.5%	59%
$Y = HgO + Br_2$	:	6 %	33%
$Y = Ag_2CO_3 + Br_2$	:	4 %	19%

Scheme 2.



(A) $X = Pb(OAc)_3$; (B) $X = Br$

Scheme 3.

By gradually increasing the proportion of benzene in the pentane–benzene eluent pair (up to 1:1), the acetate of **1d** was isolated (1.07 g, 15%), and compared to authentic 5,5,5-triphenyl-1-pentyl acetate prepared from **1d** and Ac_2O in dry pyridine, in the usual way. Elution with MeOH afforded 0.51 g (8%) of unchanged **1d**.

The *hypobromite reactions* were performed with 10 mmoles of alcohol **1d** and 20 mmoles of metal salt (HgO or Ag_2CO_3) in 40 ml of solvent (pentane or CCl_4), in dim light at 20°.[7] Br_2 (20 mmoles) was added in the course of 30 min to the stirred suspension, followed by stirring for another 60 min. The mixture was filtered and the filtrate washed with $Na_2S_2O_3$aq, $NaHCO_3$aq and H_2O, and dried (Na_2SO_4). The residue, upon removal of solvent, was subjected to column chromatography as described above. The yields of cyclic ether products **11d** and **7d**, obtained in these reactions, are given in Scheme 2.

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