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THE FRAGMENTATION OF 1,3-DIOL MONOESTERS ON ZINC SURFACES

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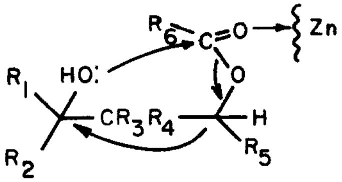
We described (1) the zinc-catalyzed conversion of open-chain vicinal secondary-tertiary and primary-tertiary diol monoacetates into ketones and aldehydes and explained (2) its mechanism by coordination of a donor group with the metal.

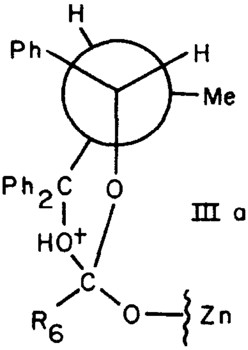
We now report the fragmentation of 1,3-primary-tertiary and secondary-tertiary open-chain diol monoesters when heated with zinc powder or anhydrous zinc acetate:

$$R_1R_2C(OH)\text{-}CR_3R_4\text{-}CHR_5OCOR_6 \xrightarrow[\text{Zn or Zn(OAc)}_2]{\Delta} R_1R_2C{=}CR_3R_4 + $$
$$+ R_5CHO + R_6COOH$$

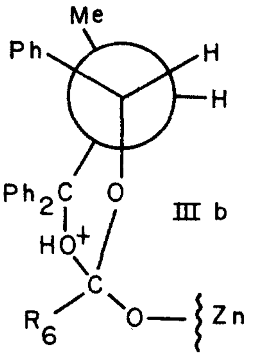
Although the reaction is not limited to the presence of a specific ester group, p-nitrobenzoates were preferable to acetates when R_1 and/or R_2 are alkyl groups. In the latter case zinc acetate is the reagent of choice. Heating of diol monoesters with acids known to cleave 1,3 diols (3a), does not lead to fragmentation. The similarity of results obtained with either Zn_o or $Zn(OAc)_2$ (see Table I) suggested that the reaction is initiated in both cases by electron delocalization due to coordination of the carbonyl oxygen with metal (or metal ion) which leads to hydroxyl displacement and C-C bond cleavage:



The validity of the mechanism involving a six-membered cyclic pathway was supported by results obtained in two cases. Partial conversion of IIIa, of known configuration (3b), showed greater fragmentation rate (61% yield of olefin after heating for 1 hr at 180° with zinc powder, or 56% after heating for 75 min with zinc acetate) than the partial conversion of IIIb (40% yield of olefin with zinc powder and 33% with zinc acetate, under the same conditions), due to less steric hindrance involved in the formation of the cyclic complex from IIIa:



III a



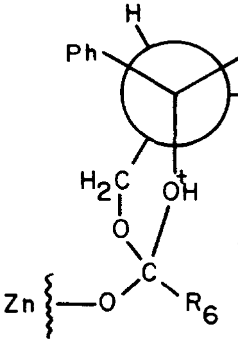
III b

TABLE I

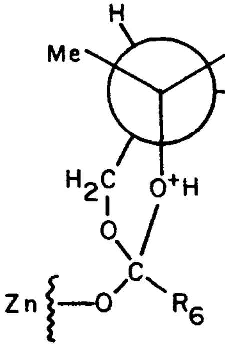
	$R_1R_2C(OH)\text{-}CR_3R_4\text{-}CHR_5OR_6$						Reaction time (hr)	Reaction temperature	Fragmentation yield (%)^{a}
	R_1	R_2	R_3	R_4	R_5	R_6			
(I)	Ph	Ph	H	H	H	Ac	3.5	165°^{d}	69^{b}, 67^{c}
(II)	Ph	Ph	H	H	Ph	Ac	4	165°	78^{b,c}
(IIIa)^{e}	Ph	Ph	H	Me	Ph	Ac	3	182°	80^{b}, 78^{c}
(IIIb)^{e}	Ph	Ph	H	Me	Ph	Ac	3	182°	79^{b}, 76^{c}
(IV)	Ph	Me	H	H	H	Ac	2.5	160°	28^{b,c}
(V)	Ph	Me	H	H	H	PNB	2.5	160°	39^{c}
(VIa)^{e}	Ph	Me	H	Me	H	PNB	1	160°^{d}	59^{c}
(VIb)^{e}	Ph	Me	H	Me	H	PNB	1	160°^{d}	56^{c}
(VII)	Ph	Me	Me	Me	H	PNB	1.5	160°^{d}	60^{c}
(VIII)	Bu	Bu	H	CH_3	H	PNB	2	160°^{d}	34^{c}

[a] Calculated by weight of pure olefin. [b] Reagent: Zn_0. [c] Reagent: $Zn(OAc)_2$. [d] Heating under reduced pressure (25 mm). [e] The corresponding configurations are shown in the text.

The fragmentation of diastereomer VIa (4) afforded only *cis*-2-phenylbutene, whereas VIb provided a



VI a



VI b

mixture of 77% *cis*-olefin and 23% *trans*-2-phenylbutene (5). The latter is thermodynamically less stable (6) but should be the stereochemically expected product from VIb in a synchronous cyclic process; it is assumed therefore that some initial ionisation of VIb takes place, allowing partial equilibration (7). The assumption of a cyclic mechanism does not imply therefore that the cyclic complex always represents accurately the transition state.

The procedure (2) involves heating the reactant, mixed with a 20-fold excess of freshly activated (8) zinc dust or powdered anhydrous zinc acetate, in a glass tube under nitrogen flow or under reduced pressure. The volatile products were collected in a liquid air cooled trap, combined with the products isolated by filtration of the residue (using an appropriate solvent) and chromatographed (9). For the isolation of olefins alone, pentane was used as solvent and the solution passed over a Florisil chromatographic column.

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3. (a) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, *76*, 2285 (1954); (b) *ibid.*, p. 2291.
4. *cf.* Canceill, J. Gabard and J. Jaques, *Bull Soc. Chim. France*, 2653 (1966).
5. As determined by g.l.c. and n.m.r. analysis.

6. D.J. Cram, J. Am. Chem. Soc., 71, 3883 (1949).

7. No equilibration of 2-phenylbutenes occurs under shown reaction conditions.

8. cf. M.B. Rubin and E.C. Blossey, Steroids, 1, 453 (1963).

9. Satisfactory elemental and spectral analysis were obtained for all new compounds and products.