Tetrahedron Letters No. 21, pp. 979-982, 1962. Pergamon Press Ltd. Printed in Great Britain.

SOLVOLYSIS OF BENZHYDRYL THIONBENZOATES

A CRITERION FOR IONIZATION

Stanley G. Smith

The William Albert Noyes Chemical Laboratory

University of Illinois, Urbana, Illinois

(Received 25 July 1962)

CONSIDERABLE evidence has recently become available which indicates that for benzhydryl derivatives the rate of ionization exceeds the rate of solvolysis[1,2,3] or exchange[4,5] by substantial factors. Winstein and co-workers have found that optically active p-chlorobenzhydryl chloride racemizes ca. 30 times as fast as it solvolyzes in acetic acid.[1a] In 80 per cent aqueous acetone racemization exceeds solvolysis by a factor of 3.[1b] In addition Goering and Levy[2] have reported that with carbonyl-^{18}O labeled benzhydryl p-nitrobenzoate oxygen scrambling is 3 times faster than solvolysis in 90 per cent aqueous acetone at 118.6°. Benzhydryl thionbenzoates have now been found to undergo isomerization to the corresponding thiolbenzoates much more rapidly than they solvolyze.

Benzhydryl thionbenzoate, m.p. 68-69°, λ_{max} 418 mμ (ϵ 140, ethanol) MW,

---

[1a] S. Winstein, J.S. Gall, M. Hojo and S. Smith, J. Amer. Chem. Soc. 82, 1010 (1960); [b] S. Winstein, M. Hojo and S. Smith, Tetrahedron Letters (22), 12 (1960).

[2] H.L. Goering and J.F. Levy, Tetrahedron Letters (18), 644 (1961).

[3] Y. Pocker, Proc. Chem. Soc. 140 (1961).

[4a] S. Winstein and J.S. Gall, Tetrahedron Letters (2), 31 (1960); [b] S. Winstein, A. Ledwith and M. Hojo, Ibid. (10), 341 (1961); [c] A. Ledwith, M. Hojo and S. Winstein, Proc. Chem. Soc. 241 (1961).

[5a] A. Iliceto, A. Fava and U. Mazzucato, Tetrahedron Letters (11), 27, (1960); [b] A. Iliceto, A. Fava, U. Mazzucato and O. Rossetto. J. Amer. Chem. Soc. 83, 2729 (1961).

303.2 (calc. 304.40)[6] was prepared from the sodium salt of benzhydrol and thiobenzoyl chloride[7,8] in tetrahydrofuran solvent at 0°. Isomerization of this ester occurs readily in e.g. acetonitrile. Removal of the solvent from an acetonitrile solution of benzhydryl thionbenzoate which had been maintained at 100.0° for 54 hr gave a quantitative yield of the colorless benzhydryl thiolbenzoate, m.p. 91-92°, undepressed by the thiol ester prepared from benzhydrol and thiobenzoic acid.

TABLE 1

Ethanolysis of 0.0210 M Benzhydryl Thionbenzoate at 100.0°

Time (10^{-3} sec)	Titer[a]	A[b]	Fraction solvolysis X 10^2	$10^4 k_1$ (sec^{-1})
-	0.094	0.980	-	-
3.60	0.441	0.628	17.0	1.34
5.40	0.555	0.496	18.7	1.37
8.40	0.694	0.350	16.8	1.36
10.80	0.804	0.269	17.2	1.36
77.40	0.749	0.057	12.3	-

[a] Ml of 0.0198 M NaOMe required per 5.016 ml aliquot.
[b] Absorbance at 418 mμ of a 1.0 ml aliquot diluted with 2.00 ml of ethanol in a 1 cm cell.

The reaction rate of benzhydryl thionbenzoate in ethanol at 100.0° was determined by measuring the rate of disappearance of the 418 mμ band and by potentiometric titration with sodium methoxide of the acid developed in aliquots taken at appropriate times. From these data satisfactory integrated first order rate constants may be calculated as is illustrated in Table 1. The fraction of the reaction which leads to solvolysis product

---

[6] Molecular weight determined on a Mechrolab Vapor Pressure Osometer by J. Nemeth.

[7] H. Staudinger and J. Siegmant, Helv. Chem. Acta 3, 824 (1920).

[8] S.G. Smith, J. Amer. Chem. Soc. 83, 4285 (1961).

is obtained from the ratio of the per cent acid formed to the per cent loss in absorbance, 17 per cent ether and 83 per cent thiol ester being produced.

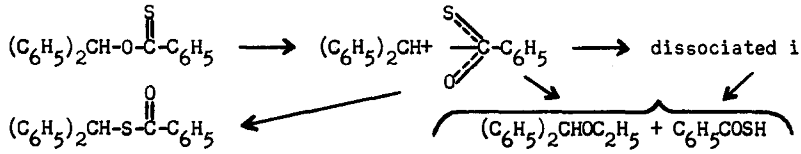
Substituent effects suggest that rearrangement and accompanying solvolysis may be ascribed to an initial ionization. The ethanolysis rate of benzhydryl thionbenzoate and the 4-methyl and 4-chloro derivatives, Table 2, and σ^+ values[9,10] corresponds to a rho of -3.6, a value typical of ionization reactions of benzhydryl compounds.[5,10,11]

TABLE 2

Effect of Substituents on Ethanolysis Rate of Benzhydryl Thionbenzoates at 100.0°

Compound	10^4k_1 (sec^{-1})
p-Methylbenzhydryl thionbenzoate	17.6 ± 0.2
Benzhydryl thionbenzoate	1.36 ± 0.02
p-Chlorobenzhydryl thionbenzoate	0.72 ± 0.01

The unimolecular ionization indicated by the substituent effects would give rise initially to the formation of an ion pair, from which rearranged ester and solvolysis products could arise either directly or from the corresponding dissociated ions. However, when 0.012 M potassium p-methoxythiobenzoate was added to 0.013 M benzhydryl thionbenzoate in ethanol, vapor phase chromatography indicated that no benzhydryl p-methoxythiol-



---

[9] D.E. Pearson, J.F. Baxter and J.C. Martin, J. Org. Chem. 17, 1511 (1952).

[10] Y. Okamoto and H.C. Brown, J. Org. Chem. 22, 485 (1957).

[11] M.S. Silver, J. Amer. Chem. Soc. 83, 404 (1961).

benzoate was formed even though it is easily detected when added to the reaction mixture. Since it is likely that dissociated thiobenzoate and p-methoxythiobenzoate have comparable reactivities this absence of exchange suggests that return from dissociated ions is not an important route for the formation of rearranged products. Apparently at least 83 per cent of the reaction occurs by way of ion pairs. The lack of exchange in this case and complete repression of oxygen equilibration in carbonyl-^{18}O triphenylmethyl benzoate by lithium azide in acetone, recently reported by Swain[12], do not, of course, provide information regarding the possible intervention of more than one variety of ion pair.

The greater nucleophilicity of sulfur compared to oxygen[13,14] as well as the greater stability[8] of thiol esters relative to the thion esters leads to the expectation that ion pair return will give predominately the rearranged thiol ester. If all ion pair return were to result in the formation of rearranged ester then the observed rate of disappearance of thion ester would be identical with the ionization rate. Although some return on oxygen cannot be excluded by the present data, it is likely that the observed rate closely approximates the ionization rate. This isomerization is potentially a more sensitive method for detecting ionization and ion pair return[15] than the equilibration of carboxyl oxygens previously employed.[2]

---

[12] C.G. Swain and G. Tsuchihashi, J. Amer. Chem. Soc. 84, 2021 (1962).

[13] e.g. A. Streitwieser, Jr., Chem. Rev. 56, 571 (1956).

[14] Preliminary experiments indicate that alkylation of potassium thiobenzoate with methyl iodide in acetone at 0° gives less than 1% oxygen alkylation.

[15] J. Petrovich, unpublished work.