Studies in Stereochemical Structure. Part X. Optically Active Desyl Chloride.*

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[Reprint Order No. 4426.]

Although racemisation occurs under most conditions, (+)-desyl chloride is obtained by slow addition of thionyl chloride to (—)-benzoin in pyridine at —40° to —30°.

(—)-BENZOIN was first isolated by McKenzie and Wren (*J.*, 1908, **93**, 309) by the action of phenylmagnesium bromide on (—)-mandelamide. This method has remained the principal and easiest for preparation of the optically active benzoins although resolution has been achieved by classical methods (Wilson and Hopper, *J.*, 1928, 2482; Preiswerk and Erlenmeyer, *Helv. Chim. Acta*, 1934, **17**, 329). Furthermore, (±)-mandelic acid is readily resolved by (—)-ephedrine (Roger, *J.*, 1935, 1544).

McKenzie and Wren (*J.*, 1910, **97**, 473) warmed (—)-benzoin with thionyl chloride and obtained completely inactive desyl chloride [confirmed by one of us (R. R.); cf. Preiswerk and Erlenmeyer, *loc. cit.*]. Ward (*J.*, 1929, 1544) improved the preparation of (±)-desyl chloride by adding thionyl chloride to the solid complex formed by heating equimolecular proportions of benzoin and pyridine, but this also gave only the (±)-chloride from (—)-benzoin. Roger and McGregor (*J.*, 1934, 1545), however, found that in the formation of the solid benzoin–pyridine complex optical activity was lost completely. Further attempts at room temperature had no better result. Gerrard has studied the action of thionyl chloride on hydroxylated compounds and the part played by bases in such actions (*J.*, 1939, 99; 1940, 218), and, finally, on consideration of all the data we adopted the following simple procedure: thionyl chloride was added slowly to (—)-benzoin in pyridine at —40° to —30°, and (+)-desyl chloride ($[\alpha]_{5461}$ +168° in acetone) emerged. The yield was not particularly good, some unchanged benzoin being always recovered, and further experiments under differing conditions yielded desyl chlorides of various degrees of optical purity. Table 1 shows the marked effect of temperature and small variations of conditions on the yield and optical purity of the resultant chloride.

TABLE 1.

Reactants (mols.) [a]			Desyl chloride (recryst.)			Benzoin recovered (recryst.)	
$SOCl_2$	C_5H_5N	Conditions	G.	$[\alpha]_{5461}$ [b]	M. p.	G.	$[\alpha]_{5461}$ [b]
2·5	1	$SOCl_2$ all added at once	1·5	0°	64—64·5°	—	—
1	1·25	$SOCl_2$ added slowly; mixture kept at —60°	0·2	+140	71—72	1·2	—130°
2·5	1	Kept at —30° to —10°........	0·6	+108	64—75 [c]	0·4	—134
2·5	1	Very slow addn. at —40°	0·62	+168	75—75·5	0·1	—130
2·5	1	Very slow addn. at 0°	0·8	+118·1	68—70	0·4	—115

[a] (—)-Benzoin used = 2 g. (1 mol.). [b] In acetone. [c] Low rotation of (+)-desyl chloride and spread of m. p. indicates a mixed crop of (+)-desyl chloride and (—)-benzoin.

Some rotation dispersions of (+)-desyl chloride are recorded in the Experimental section. For acetone solution this is best expressed by a modified two-term Drude equation,

$$[\alpha]_\lambda = 12{\cdot}42/(\lambda^2 - 0{\cdot}1297) + 27{\cdot}3/\lambda^2$$

in the visible spectrum (see Table 2). Other solvents gave similar results. This offers an interesting comparison with the dispersion of (—)-benzoin in acetone which Roger and McGregor (*loc. cit.*) found was best fitted by a similar type of equation, from which it would seem that the optical character of the fragment Ph·$\overset{\bullet}{C}$H·COPh is not materially affected by substitution of the more negative Cl for OH.

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* Part IX, 1939, 108.

EXPERIMENTAL

Preparation of (+)-*Desyl Chloride from* (−)-*Benzoin*.—To a mixture of (−)-benzoin (2 g., 1 mol.; $[\alpha]_{5461}$ −148° in acetone) and pyridine (0·75 c.c., 1 mol.), cooled to between −40° and −30°, thionyl chloride (refluxed with sulphur for some time and then fractionally distilled twice) (1·5 c.c., 2·5 mols.) was added drop by drop with constant shaking : cloudiness developed after about half of the addition. Next day the mixture was cooled to −10° and ice added to decompose the brown solid which had separated overnight. After lixiviation with ether some solid remained undissolved and on recrystallisation from alcohol separated as colourless needles, m. p. 132—133° alone or mixed with authetic (−)-benzoin.

The ether extract was washed with sodium hydrogen carbonate solution, then water, dried (Na_2SO_4), and evaporated. Addition of light petroleum to the residue caused crystallisation of (+)-desyl chloride which, recrystallised from light petroleum, formed colourless needles, m. p. 75—76° [(±)-desyl chloride has m. p. 65—66°], $[\alpha]_{5461}$ +168·4° (*c* 0·618 in acetone) (Found : C, 72·8; H, 4·8; Cl, 15·2. Calc. for $C_{14}H_{11}OCl$: C, 72·9; H, 4·8; Cl, 15·4%). Other rotatory data are given in Table 2.

TABLE 2. $[\alpha]_D$ *of* (+)-*desyl chloride* ($l = 2$) (*values calc. from the Drude equation in parentheses*).

			λ (Å)				
Solvent	Concn. (*c*)	Temp.	6234	5893	5780	5461	4358
Acetone	0·4145	16°	118·2°	136·3°	142·3°	165·2°	349·7°
			(118·2)	(135·7)	(142·5)	(165·3)	(350·1)
EtOH	0·453	17·4	122·6	134·7	142·4	167·8	347·7
Dioxan	0·465	18	131·2	139·7	159·2	180·6	365·6
C_6H_6	0·444	16·8	139·6	153·1	171·2	186·9	389·5
$CHCl_3$	0·473	18·6	113·1	126·9	131·1	154·4	323·4
CCl_4	0·421	19·8	71·3	73·6	77·2	87·9	168·7

We thank the Department of Scientific and Industrial Research for a maintenance grant to one of us (R. W.) which has rendered this study possible.

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[*Received, June* 24*th*, 1953.]