2 : 4 : 6-*Tri-iodophenyl* iso*Cyanate as a Reagent for Hydroxy- and Amino-groups.*

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2 : 4 : 6-Tri-iodophenyl *iso*cyanate gives with many alcohols urethanes which are useful for identification, but it is useless for separation of alcohols from beeswax owing to solubility of the long-chain alkyl derivatives.

THE alcohols of acid-free Benguela beeswax are only partly obtained as hydrogen phthalates when the acid-free wax is treated with phthalic anhydride–pyridine. In an attempt to isolate the alcohols as derivatives insoluble in the esters and hydrocarbons forming the wax residuum, 2 : 4 : 6-tri-iodophenyl *iso*cyanate was chosen as reagent. Though this proved useful for the detection and identification of alcohols, the original purpose remains unfulfilled. Beeswax reacted with the *iso*cyanate in light petroleum, but it was impossible to determine whether the precipitate obtained on concentration and cooling the solution comprised only the 2 : 4 : 6-tri-iodophenylurethanes or contained admixed beeswax esters and/or hydrocarbons; some of the wax compounds also separate under these conditions and recrystallisation was excluded by the nature of the problem.

Methyl and ethyl 2 : 4 : 6-tri-iodocarbanilate were relatively insoluble in cold light petroleum, but, on ascending the homologous series of primary alcohols, the solubility increased in all those solvents, including petroleum, in which beeswax is reasonably soluble. The curve relating melting point with the number of carbon atoms in the normal alkyl chain showed alternation.

Normal and branched purely aliphatic primary alcohols with 2 : 4 : 6-tri-iodophenyl *iso*cyanate readily give crystalline products; primary aralkyl alcohols behave similarly, but, whereas allyl and cinnamyl alcohol formed crystalline products in a few minutes, the unsaturated oleyl alcohol in light petroleum gave only a jelly, as also did 2-hydroxyethyl laurate. Simple alkoxy-ethanols formed the urethanes, but ethanolamine gave *N*-2-hydroxyethyl-*N'*-(2 : 4 : 6-tri-iodophenyl)urea, indicating the greater reactivity of the amino-group towards the reagent. The nature of this derivative was inferred from the high melting point and the insolubility in dilute acid. The derivatives from dimethylamino- and diethylamino-ethanol were of course urethanes, being much lower-melting and soluble in dilute hydrochloric acid.

Simple secondary alcohols react readily, and (—)-menthol gave a derivative on more prolonged heating; ethyl lactate, octan-2-ol, 1-phenylethanol, borneol, and diphenylmethanol failed to react in light petroleum (b. p. 60—80°), though in absence of solvent they gave urethanes in 30 minutes at 150°.

No derivative of a tertiary alcohol has been obtained. Diacetone alcohol at 150° gave a white insoluble solid which appeared to be the diurea.

Phenols react only in the absence of a solvent at 150, the products, in general, being insoluble or, if crystalline, unsuitable for identification of the phenols.

Simple glycols react readily in the absence of a solvent, but the products are very insoluble. Diethylene glycol in light petroleum (b. p. 100—120°) (only a very dilute solution is possible) reacted at 100° to give the diurethane.

*iso*Cyanates often yield the corresponding symmetrically disubstituted ureas when treated with water, some of the amine first formed reacting with the unchanged *iso*cyanate. When 2 : 4 : 6-tri-iodophenyl *iso*cyanate was boiled with aqueous pyridine, 2 : 4 : 6-tri-iodoaniline was obtained. Presumably the insolubility of the amine prevented its reaction with unchanged *iso*cyanate. The diurea was, however, obtained as a by-product in the formation of the *iso*cyanate from 2 : 4 : 6-tri-iodoaniline and carbonyl chloride in toluene, and probably when the *iso*cyanate and 2 : 4 : 6-tri-iodoaniline were heated in toluene for some hours.

Light petroleum solutions of the *iso*cyanate react readily with primary aromatic amines, but the products are not easily crystallised. Secondary amines such as morpholine, piperidine, and diethylamine reacted readily in light petroleum. Diphenylamine appeared to give no product even after 12 hours in this solvent, but gentle heating in absence of a solvent for about three minutes in the molten condition led to the urea.

EXPERIMENTAL

2 : 4 : 6-*Tri-iodophenyl* iso*Cyanate*.—A current of carbonyl chloride was passed through a wide entry-tube into a solution of 2 : 4 : 6-tri-iodoaniline (177 g.) (Hantzsch, *Ber.*, 1903, **36**, 2070; recrystallised from toluene) in toluene (2124 ml.) on a steam-bath, with stirring under reflux, for 6 hr. The solution was left overnight, then heated for 3 hr. The carbonyl chloride and about 1250 ml. of toluene were distilled off, later under reduced pressure, and the *s*-di-(2 : 4 : 6-tri-iodophenyl)urea (20 g.) was filtered off. Evaporating the filtrate to dryness gave crude 2 : 4 : 6-*tri-iodophenyl* iso*cyanate*, which, recrystallised from light petroleum (2·8 l.) (b. p. 60—80°), formed faintly coloured needles, m. p. 129° (147 g., 79%) (Found : C, 16·85; H, 0·5; N, 2·8. $C_7H_2ONI_3$ requires C, 16·9; H, 0·4; N, 2·8%), moderately soluble in toluene and acetone and

Urethanes (*from alcohols and phenols*) *and ureas* (*from amines and hydroxy-amines*).

Alcohol	Formula	M. p.	Solvent *	Found (%)			Calc. (%)		
				C	H	N	C	H	N
MeOH	$C_8H_6O_2NI_3$	209°	Pet B	18·65	1·4	3·0	18·15	1·1	2·65
EtOH	$C_9H_8O_2NI_3$	194	,,	20·2	1·6	2·7	19·9	1·5	2·6
Pr^nOH	$C_{10}H_{10}O_2NI_3$	162	,,	22·0	2·0	2·6	21·5	1·8	2·5
Bu^nOH	$C_{11}H_{12}O_2NI_3$	151	,,	23·4	2·2	2·6	23·1	2·1	2·45
n-$C_5H_{11}{\cdot}OH$	$C_{12}H_{14}O_2NI_3$	120	,,	24·2	2·55	2·5	24·6	2·4	2·4
n-$C_7H_{15}{\cdot}OH$	$C_{14}H_{18}O_2NI_3$	105	,,	27·9	3·1	2·3	27·4	2·9	2·55
n-$C_8H_{17}{\cdot}OH$	$C_{15}H_{20}O_2NI_3$	107	,,	29·1	3·45	2·3	28·7	3·2	2·2
n-$C_9H_{19}{\cdot}OH$	$C_{16}H_{22}O_2NI_3$	105	,,	29·7	3·3	2·35	29·95	3·4	2·2
n-$C_{10}H_{21}{\cdot}OH$	$C_{17}H_{24}O_2NI_3$	108	,,	31·4	3·8	2·4	31·1	3·7	2·1
n-$C_{12}H_{25}{\cdot}OH$	$C_{19}H_{28}O_2NI_3$	112	,,	33·1	4·1	2·1	33·4	4·1	2·05
n-$C_{16}H_{33}{\cdot}OH$	$C_{23}H_{36}O_2NI_3$	108	,,	37·8	5·1	2·0	37·35	4·9	1·9
Bu^iOH	$C_{11}H_{12}O_2NI_3$	140	Pet A	23·2	2·0	2·6	23·1	2·1	2·45
$CHEt_2{\cdot}CH_2{\cdot}OH$	$C_{13}H_{16}O_2NI_3$	77	,,	26·3	2·6	2·4	26·0	2·7	2·3
$CH_2Ph{\cdot}OH$	$C_{14}H_{10}O_2NI_3$	175	Pet B	28·15	1·9	2·5	27·8	1·65	2·3
$CH_2Ph{\cdot}CH_2{\cdot}OH$	$C_{15}H_{12}O_2NI_3$	170	Pet A	29·3	2·2	2·5	29·1	1·9	2·3
$Ph{\cdot}[CH_2]_3{\cdot}OH$	$C_{16}H_{14}O_2NI_3$	135	Pet C	30·7	2·35	2·6	30·3	2·2	2·2
$MeO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$C_{10}H_{10}O_3NI_3$	146	Pet A	21·3	1·9	2·8	20·9	1·7	2·4
$EtO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$C_{11}H_{12}O_3NI_3$	142	Pet B	23·0	2·3	2·5	22·5	2·0	2·4
p-$MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$	$C_{15}H_{12}O_3NI_3$	176	,,	28·7	2·2	2·2	28·3	1·9	2·2
$NMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$C_{11}H_{13}O_2N_2I_3$	115	Pet C	—	—	4·8	—	—	4·8
$NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$C_{13}H_{17}O_2N_2I_3$	131	Pet A	25·8	2·8	4·7	25·4	2·8	4·6
$\overline{O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH}{\cdot}CH_2{\cdot}OH$	$C_{12}H_{12}O_3NI_3$	137	Pet B	24·4	2·1	2·5	24·0	2·0	2·3
$CH_2{:}CH{\cdot}CH_2{\cdot}OH$	$C_{10}H_8O_2NI_3$	178	Pet A	22·1	1·7	2·6	21·6	1·4	2·5
$CHPh{:}CH{\cdot}CH_2{\cdot}OH$	$C_{16}H_{12}O_2NI_3$	190	Pet B	30·9	2·8	2·25	30·4	1·9	2·2
Pr^iOH	$C_{10}H_{10}O_2NI_3$	180	,,	21·8	2·1	2·7	21·5	1·8	2·5
$CHMeEt{\cdot}OH$	$C_{11}H_{12}O_2NI_3$	161	Pet A	23·35	2·2	2·5	23·1	2·1	2·45
$C_6H_{13}{\cdot}CHMe{\cdot}OH$	$C_{15}H_{20}O_2NI_3$	98	Aq. EtOH	28·9	3·4	—	28·7	3·2	—
$C_6H_{11}{\cdot}OH$	$C_{13}H_{14}O_2NI_3$	145	Pet A	26·5	2·8	2·5	26·0	2·7	2·3
$CHPhMe{\cdot}OH$	$C_{15}H_{12}O_2NI_3$	179	Aq. pyridine	29·3	2·3	2·6	29·1	1·9	2·3
Borneol	$C_{17}H_{20}O_2NI_3$	171	Pet B	31·7	3·4	—	31·3	3·1	—
(—)-Menthol	$C_{17}H_{22}O_2NI_3$	143	,,	31·05	3·65	2·4	31·2	3·4	2·1
$CHPh_2{\cdot}OH$	$C_{20}H_{14}O_2NI_3$	195	EtOH	35·2	2·1	2·1	35·2	2·1	2·1
$HO{\cdot}CHMe{\cdot}CO_2Et$	$C_{12}H_{12}O_4NI_3$	154	Pet B	23·5	2·1	2·3	23·4	1·95	2·3
PhOH	$C_{13}H_8O_2NI_3$	181	,,	—	—	2·3	—	—	2·4
$O(CH_2{\cdot}CH_2{\cdot}OH)_2$	$C_{18}H_{14}O_5N_2I_6$	222 †	Anisole	20·1	1·4	2·8	19·6	1·3	2·55
Amine									
NH_2Me	$C_8H_7ON_2I_3$	285—290 †	Aq. pyridine	18·45	1·2	5·45	18·2	1·3	5·3
NH_2Ph	$C_{13}H_9ON_2I_3$	>271	,,	26·4	1·5	4·8	25·4	1·5	4·7
p-$EtO{\cdot}C_6H_4{\cdot}NH_2$	$C_{15}H_{13}O_2N_2I_3$	277 †	,,	28·6	2·1	4·4	28·4	2·05	4·4
o-$MeO_2C{\cdot}C_6H_4{\cdot}NH_2$	$C_{15}H_{11}O_3N_2I_3$	>285	BuOH	27·8	1·7	4·7	27·8	1·7	4·3
$O<(CH_2{\cdot}CH_2)_2>NH$	$C_{11}H_{11}O_2N_2I_3$	262	EtOH	23·1	2·2	—	22·6	1·89	—
$CH_2<(CH_2{\cdot}CH_2)_2>NH$	$C_{12}H_{13}ON_2I_3$	205	,,	24·7	2·4	—	24·7	2·2	—
$NHEt_2$	$C_{11}H_{13}ON_2I_3$	163	Aq. EtOH	23·6	2·6	4·9	23·2	2·3	4·9
$NHPh_2$	$C_{19}H_{13}ON_2I_3$	210	,,	34·65	2·25	—	34·2	1·95	—
$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$C_9H_9ON_2I_3$	260	BuOH	19·5	1·75	5·1	19·4	1·6	5·0

* Pet = light petroleum, b. p.: A = 60—80°; B = 80—100°; C = 100—120°. † Decomp.

soluble to the extent of about 1% in cold and about 5—6% in hot light petroleum (b. p. 60—80°). The ***urea*** was insoluble in all the solvents tried, but, as obtained, formed minute needles unmelted at 300° (Found : C, 16·9; H, 0·6; N, 3·1. $C_{14}H_6ON_2I_6$ requires C, 17·1; H, 0·6; N, 2·9%).

Urethanes.—*General method.* The alcohol in slight excess was added to a hot solution of the *iso*cyanate (0·5 g.) in light petroleum (b. p. 60—80°; 30 ml.) and heated on the steam-bath for 1 hr. In some cases it was necessary to concentrate the solution slightly afterwards in order to isolate the product. Departures from these conditions for secondary alcohols, glycols, and certain amines are mentioned in the theoretical portion. *Products* are tabulated.

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