

CCCXX.—*The Action of Substituted Aromatic Amines on Camphoric Anhydride. Bromo- and Iodo-camphoranilic Acids and Camphoro-bromo- and iodo-phenylimides.*

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WHEN a substituted aniline is condensed with camphoric anhydride, a camphoranilic acid and the corresponding imide are formed, the relative quantities depending on the nature of the substituent (R)

and its position in the amine (Singh and Singh, J., 1927, 1994; see also J., 1925, 127, 1966). The order in which the *o*-, *m*-, and *p*-substituted amines affect the yield of the camphorimide is, however, not consistent for R = Cl, Br, I, Me, and CO₂H.

The results obtained from the condensation products of camphoric anhydride with bromoanilines and iodoanilines are now reported. Table I gives the approximate percentage yields of the respective camphorimides, formed together with carboxy-, methyl-, chloro-, bromo-, and iodo-camphoranilic acids.

TABLE I.
Percentage yields of the imides.

	CO ₂ H.	Me.	Cl.	I.	Br.
<i>p</i>	Nil	Traces	15—20	25—30	40
<i>m</i>	„	—	6	31	25
<i>o</i>	„	—	5	—	5—10

Except for the position of chlorine, the order for the *p*-substituted amines corresponds to the order which indicates the relative influence of the substituents on the nitration of a monosubstituted benzene. The ratio acid/imide produced is also dependent on the temperature at which the reaction is carried out, though the order in which the substituents affect the ratio is the same as that given in Table I. All the condensations except that of *o*-iodoaniline (*vide infra*) were carried out at a temperature between 145° and 150° and the reaction mixture was heated for 3—4 hours.

With regard to the optical rotations of these compounds, (a) the *o*-bromo- and *o*-iodo-acids give negative values in acetone and methyl ethyl ketone; (b) the *p*-isomeride has in all cases the maximum rotation, which is in accordance with Frankland's rule (J., 1896, 69, 1583). These observations also support Cohen's rule (Frankland, J., 1912, 101, 667) "that the rotatory effect of the ortho-grouping differs more from that of the phenyl than do those of the meta- and para-groupings"; (c) the molecular rotatory powers of the acids do not follow the order of the dielectric constants of the solvents used.

Table II gives the molecular rotatory powers of camphoranilic acid and some of its 2'-substituted derivatives in methyl alcohol, ethyl alcohol, acetone, and methyl ethyl ketone.

As regards their effect in diminishing the molecular rotatory power in acetone and in methyl ethyl ketone, the order of the substituents is that of their effect on the optical activity of menthyl and *sec*.-β-octyl esters of monosubstituted acetic acids and benzoic acids (Rule and Smith, J., 1925, 127, 2188; Rule and Mitchell, J., 1926, 3202; Rule and collaborators, this vol., p. 178). This

TABLE II.

Substit.	[M] _D .			
	MeOH.	EtOH.	Me ₂ CO.	MeEtCO.
H	+150°	+131°	+101°	—
CO ₂ H	-584	-574	-551	-390°
Me	+146	+144	+ 98	+ 90.75
I	- 50.9	—	- 82.8	- 70.17
Br	- 36.0	+ 21.9	- 61.1	- 31.96
Cl	+ 57.8	+ 35.6	- 40.3	- 28.5
OMe*	- 29.6	+ 27.6	- 16.3	- 9.55

* Private communication.

corresponds to the relative polarity of the groups as deduced from molecular inductive capacities. For methyl- and ethyl-alcoholic solutions there is a small displacement in the order of the substituents.

It is remarkable that the above order of substituents is followed when the solvents are ketones and not when they are alcohols. The substances examined by Rule and his collaborators (*loc. cit.*) were all liquids and the question of the effect of solvents did not arise. The authors have not been able to find in the literature mention of any series of optically active, ortho-substituted substances examined in ketonic solution with a view to correlating the molecular rotation with the nature of the *o*-substituent. It seems probable that such optically active substances show the same relative changes in rotatory power in ketonic solvents and in the pure state. Work is in progress to determine whether the effect on the optical activity of substituents in the ortho-position follows the above order only when the substances are dissolved in ketones.

For the meta- and the para-substituted derivatives the effect of the substituents accords with what Rule and others (*loc. cit.*) have called their general effect, *i.e.*, CO₂H > halogens > Me > H.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Bromo- and Iodo-anilines.—The method was that described for the condensation of *o*-chloroaniline (J., 1927, 1995). Sodium carbonate was used to separate the camphoranilic acid from the imide. They can also be separated by fractional crystallisation from alcohol.

Camphoro-*o*-bromophenylimide crystallised in short needles, m. p. 142° (Wootton, J., 1910, 97, 415, gives 139—140°) (Found : Br, 23.9. Calc. : Br, 23.85%), and the *m*-bromo-isomeride in silky needles, m. p. 190° (Wootton gives 184—185°) (Found : Br, 23.9%).

2'-Bromocamphoranilic acid crystallised in silky needles, m. p. 168°, [M]_D - 61.1° in acetone (Wootton gives m. p. about 78°,

$[M]_D - 41.1^\circ$ (Found: Br, 22.8; equiv., by titration with NaOH, 353.3. Calc.: Br, 22.6%; equiv., 354). The 3'-bromo-acid crystallised in prisms, m. p. 224° after shrinking at 220° (Wootton, 215—217°) (Found: Br, 22.8%; equiv., 353.4).

4'-Bromocamphoranilic acid crystallised in stout needles, m. p. 206—207° (Found: Br, 22.7%; equiv., 352.5), and camphoro-*p*-bromophenylimide in prismatic needles, m. p. 182.5° (Found: Br, 23.9%).

The condensation of camphoric anhydride and *o*-iodoaniline was carried out at 115° ; at higher temperatures a viscous oil was obtained and the yield of the acid was seriously diminished. The alcoholic solution of the condensation product was precipitated with water, and the acid dissolved by addition of dilute aqueous ammonia. The residue was probably unchanged material containing a small quantity of camphoro-*o*-iodophenylimide, which could not be separated and purified. The ammoniacal solution was acidified, yielding an amorphous spongy mass, which was redissolved and reprecipitated several times. 2'-Iodocamphoranilic acid was thus

TABLE III.

Rotations of Bromo- and Iodo-camphoranilic Acids and Camphoro-bromo- and -iodo-phenylimides ($l = 2$).

Temp. 33° (25° for values marked *).

Camphoranilic Acids.

Solvent.	Conc. (g./25 c.c.). $[a]_D$.		Conc. (g./25 c.c.). $[a]_D$.		Conc. (g./25 c.c.). $[a]_D$.	
	2'-Bromo-.		3'-Bromo-.		4'-Bromo-.	
MeOH	0.2823	+10.18°	0.3046	+44.3°	0.2654	+51.3°
EtOH	0.2820	+ 6.2	0.2870	+37.7	0.2806	+46.7
Me ₂ CO	0.3029	-17.3	0.2902	+31.4	0.2776	+35.4
MeEtCO	0.3043	- 9.03	0.3067	+37.4	0.3012	+42.3
	2'-Iodo-.		3'-Iodo-.		4'-Iodo-.	
MeOH	0.2660	+12.7°*	0.2788	+41.69°	0.2887	+44.16°
EtOH	—	—	0.2950	+35.60	0.1954	+42.20*
Me ₂ CO	0.3539	-20.2*	0.2906	+29.60	0.3061	+36.30
MeEtCO	0.1849	-17.5*	0.3006	+31.60	0.3015	+41.80

Camphorohalogenophenylimides.

	<i>o</i> -Bromo-.		<i>m</i> -Bromo-.		<i>p</i> -Bromo-.	
	MeOH	0.2616	+15.77°	0.3036	+17.70°	0.3056
EtOH	0.2669	+13.37*	—	—	—	—
Me ₂ CO	0.2858	+ 9.26	0.3012	+14.10	0.2826	+15.87
MeEtCO	0.2906	+10.70	0.3048	+ 9.84	0.2998	+16.67
			<i>m</i> -Iodo-.		<i>p</i> -Iodo-.	
MeOH			0.2570	+15.56°	0.2810	+10.67°
EtOH			0.2606	+21.58	—	—
Me ₂ CO			0.3045	+10.2	0.2853	+ 7.88
MeEtCO			0.3054	+12.27	0.2996	+ 9.59

obtained as a somewhat sticky powder, which was dried in a vacuum desiccator for 48 hours; m. p. 147—149° (Found : I, 31.2; equiv., 400. $C_{16}H_{20}O_3NI$ requires I, 31.7%; equiv., 401).

Camphoro-m-iodophenylimide crystallised as a light fluffy mass, m. p. 172° (Found : I, 33.0. $C_{16}H_{18}O_2NI$ requires I, 33.2%), and *3'-iodocamphoranilic acid* in light prismatic needles, m. p. 226—227° (Found : I, 31.7%; equiv., 402, 406).

Camphoro-p-iodophenylimide crystallised in needles, m. p. 197° (Found : I, 33.1%), and *4'-iodocamphoranilic acid* in short needles, m. p. 221° (Found : I, 31.8%; equiv., 399).

In general, the preceding imides are readily soluble in acetone and methyl ethyl ketone, fairly readily soluble in methyl alcohol, and sparingly soluble in ethyl alcohol, and the acids are soluble in the common organic solvents.

4'-Methylcamphoranilic acid (compare Wootton, *loc. cit.*; Singh and Puri, J., 1926, 504) and only a trace of the imide were obtained by the general method.

The rotatory power of 2'-methoxycamphoranilic acid was determined in methyl ethyl ketone for comparison : 0.1989 g. dissolved in 25 c.c. gave $\alpha_D - 0.50^\circ$, whence $[M]_D - 90.75^\circ$.

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