374. *The Preparation of Symmetrical Aromatic Triamines and Triïsocyanates.*

By J. E. Gill, R. MacGillivray, and J. Munro.

Catalytic reduction of symmetrical aromatic trinitro-compounds in ethyl acetate solution, using Raney nickel as catalyst, has been shown to be a convenient method for the preparation of symmetrical aromatic triamines. The corresponding tri*iso*cyanates, triurethanes, and triureido-derivatives have also been prepared.

The preparation and isolation of *s*-aromatic triamines have in the past proved difficult, and before the present work the only amines of this type reported have been 2 : 4 : 6-triaminotoluene (Hein and Wagner, *Ber.*, 1935, **68**, 856) and 2 : 4 : 6-triaminoanisole (Damschroder and Shriner, *J. Amer. Chem. Soc.*, 1937, **59**, 931). These workers had trouble in isolating the amines, which they prepared by catalytic reduction of the corresponding nitro-compounds in ethyl alcohol solution, and all their manipulations had to be carried out in an oxygen-free atmosphere.

Aliphatic alcohols are not good media for the reduction of polynitro-compounds as they are poor solvents for the nitro-compounds but, when diluted with the water formed during reduction, they are very active solvents for the amines produced, and isolation is correspondingly difficult. Ethyl acetate is employed as solvent in the following hydrogenation method, with Raney nickel as catalyst, and a number of new *s*-triamines has been isolated without difficulty and in good yield. The success of ethyl acetate as solvent depends on (*a*) its good solvent power for aromatic nitro-compounds, (*b*) its relatively poor solvent power for the corresponding amines which therefore crystallise readily at the end of the reaction, and (*c*) the fact that the water formed during reduction of the nitro-groups is miscible with this solvent at the concentrations used. [The solubility of water in ethyl acetate is 4—5% between 50° and 60° (Merriman, *J.*, 1913, 1774).] Methyl acetate may also be used, but the miscibility of the higher homologues with water is too low to permit them to be used successfully. Hydrogen pressures around 40 lbs. per sq. in. have given the optimum rates of reduction, but reaction can be effected even at atmospheric pressure if the solution is heated during reduction. The method is also applicable to the preparation of mono- and di-amines.

The reaction of phosgene with the hydrochlorides of these amines suspended in a phosgene-inert solvent appears to be a general method for the preparation of symmetrical aromatic tri*iso*cyanates.

EXPERIMENTAL.

s-Aromatic Triamines.—An ethyl acetate solution of the *s*-trinitro-compound (5% concentration or 3% in the case of *s*-trinitrobenzene) is shaken with hydrogen at about 40 lbs. per sq. in. initial pressure and Raney nickel catalyst (15% of the weight of the nitro-compound) (*Org. Synth.*, 1941, **21**, 15). The temperature is allowed to rise unchecked. At the end of the reduction the solution should be colourless or faintly pink. The reaction time varies from 30 to 80 minutes depending on the quantity of materials used and the efficiency of shaking. The amine is obtained in crystalline form by filtering off the spent catalyst and leaving the ethyl acetate solution to cool.

The properties of several of these triamines are indicated in Table I.

Table I.

s-Triamine of	M. p.	Yield, %.	Analyses, %.							Benzoyl derivative, m. p.
			Formula.	Found: C.	H.	N.	Requires: C.	H.	N.	
Benzene	84° * 108—112 †	76	$C_6H_9N_3,H_2O$	51·08	7·66	29·15	51·06	7·80	29·79	356—357°
Toluene	121—122	60	—		—			—		—
Ethylbenzene	73—74 *	60	$C_8H_{13}N_3,H_2O$	57·10	8·83	24·80	56·81	8·87	24·84	292—293
Chlorobenzene	97	60	$C_6H_8N_3Cl$	45·81	5·33	26·20	45·71	5·08	26·66	261
					(Cl, 22·19)			(Cl, 22·54)		
Anisole	117—118	80	—		—			—		232
Phenetole	124—125	94	$C_8H_{13}ON_3$	57·40	8·15	24·70	57·49	7·79	25·15	206—207
Phenyl iso*butyl ether*	b. p. 184—185/2 mm.	80	$C_{10}H_{17}ON_3$	61·00	8·42	21·50	61·54	8·72	21·54	235—236
Diphenyl ether	145	74	$C_{12}H_{13}ON_3$	67·06	6·04	20·23	66·99	6·05	19·54	258—259
Phenylethanol	131—132	55	$C_8H_{13}ON_3$	57·10	7·74	25·80	57·49	7·79	25·15	293—294
Phenylethyl acetate	106—107	71	$C_{10}H_{15}O_2N_3$	—	—	19·60	—	—	20·10	—

* Hydrated. † Anhydrous.

All the amines have been obtained as colourless needles which darken slowly on being left in air, but they have been kept for periods of up to 2 months without appreciable change in colour when stored under vacuum over phosphoric oxide. Chemically they are all very similar, being very soluble in water and alcohols and in mineral acids with salt formation. They are less soluble in the lower saturated aliphatic esters and only slightly soluble in hydrocarbon solvents. They are not soluble in ether and petroleum. The benzoyl derivatives are prepared with benzoyl chloride and aqueous alkali.

The hydrochlorides can be prepared in quantitative yields by saturating with dry hydrogen chloride the ethyl acetate solutions obtained on reduction of the nitro-compounds.

Stable amines could not be prepared by reduction of the following compounds under the above conditions; picric acid, *s*-trinitrobenzoic acid, methyl *s*-trinitrobenzoate, *s*-trinitroaniline, *s*-trinitroacetanilide, *s*-trinitrophenylmethylnitroamine or 1-bromo-, 1-iodo-, and 1-fluoro-*s*-trinitrobenzenes.

s-*Aromatic Tri*iso*cyanates*.—Carbonyl chloride is passed into a suspension of the appropriate amine hydrochloride (1 part) in chlorobenzene (10 parts) under anhydrous conditions and the temperature is raised to 110—120° and maintained there until the solid passes into solution as the tri*iso*cyanate and hydrogen chloride ceases to be liberated. At the end of the reaction excess of carbonyl chloride is removed by blowing a stream of dry nitrogen through the mixture, and the solution is filtered, if necessary, from any insoluble material. The solvent is then removed under reduced pressure, and the tri*iso*cyanate purified by distillation under reduced pressure.

TABLE II.

s-Tri*iso*-cyanate of	M. p.	Yield, %.	Formula.	Analyses, %. Found:			Required:			Urethane, m. p.	Urea, m. p.
				C.	H.	N.	C.	H.	N.		
Benzene	84—85°	50	$C_9H_3O_3N_3$	53·61	1·50	21·00	53·73	1·49	20·89	191—192°	>350°
Toluene	78—79	73	$C_{10}H_5O_3N_3$	55·80	2·42	19·90	55·82	2·33	19·54	199—200	306—307
Ethylbenzene	48—49	78	$C_{11}H_7O_3N_3$	57·70	3·20	18·29	57·65	3·06	18·34	225—226	289—291
Chlorobenzene	93·5—94·5	67	$C_9H_2O_3N_3Cl$	46·20	1·10	18·00	45·85	0·85	17·83	154—155	288—289
Anisole	83—83·5	78	$C_{10}H_5O_4N_3$	51·90	2·24	18·22	51·95	2·16	18·18	114—115	283—284
Phenetole	49—49·5	71	$C_{11}H_7O_4N_3$	53·59	3·15	16·94	53·88	2·85	17·14	134—135	263—264
Diphenyl ether	78—78·5	61	$C_{15}H_7O_4N_3$	61·99	2·41	14·46	61·44	2·39	14·33	liquid	271—272

All the tri*iso*cyanates examined are fairly low-melting solids which crystallise as colourless needles. They react readily with moisture and have to be stored under anhydrous conditions. Aromatic hydrocarbons and chlorinated hydrocarbons are good solvents and the tri*iso*cyanates may be recrystallised from them.

The triurethanes are readily prepared by dissolving the tri*iso*cyanates in hot ethyl alcohol and allowing the solutions to cool. The triureido-compounds are obtained by adding ether containing excess of dry ammonia gas to ethereal solutions of the tri*iso*cyanates. They can be recrystallised from water. Table II indicates the properties of several of these compounds.

RESEARCH DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES LTD.,
NOBEL DIVISION, STEVENSTON, AYRSHIRE.

[*Received, December* 30*th*, 1948.]