

371. *Isomeric 2-Arylamino-2-cyano-trans-decahydronaphthalenes, and the Condensation of the Cyanohydrin of 3-Methylcyclopentanone with Aniline.*

By R. D. DESAI, R. F. HUNTER, and MEHDI HUSSAIN.

It appeared of interest, in the light of the researches of Hückel and his collaborators (*Annalen*, 1925, **445**, 1; 1927, **453**, 109, 163), to extend the study of the isomeric 1-aryl-amino-1-cyanomethylcyclohexanes (Waheed Bukhsh, Desai, Hunter, and Mehdi Hussain, this vol., p. 1159) to the condensation of the cyanohydrin of *trans*- β -decalone with arylamines. Pairs of isomers, which are evidently related to one another by formulæ (I) and (II) and were characterised by the corresponding 2-arylamino-*trans*-decahydronaphthalene-2-carboxyamides, were obtained from the condensations with aniline, *p*-bromoaniline,



o- and *m*-toluidines, and β -naphthylamine. In the cases of *p*-toluidine and α -naphthylamine, however, only one arylaminocyano-derivative was isolated.

The condensation of the cyanohydrin of 3-methylcyclopentanone with aniline, which might be expected to lead to the formation of a pair of *cis-trans* isomers derived from the uniplanar five-membered ring, was also examined, but only one form of 1-anilino-1-cyano-3-methylcyclopentane was isolated.

EXPERIMENTAL.

2-Anilino-2-cyano-trans-decahydronaphthalene.—A solution of potassium cyanide (4 g.) in water (10 c.c.) was added to a mixture of aniline (5 g.) and *trans*- β -decalone (7.5 g.) in glacial acetic acid (25 c.c.). The product which separated overnight was collected, and the united yield of this with that obtained by dilution of the filtrate with water was recrystallised from benzene. The *A* form separated in needles, m. p. 135° (Found: C, 80.0; H, 8.9. $C_{17}H_{22}N_2$ requires C, 80.3; H, 8.6%), and the mother-liquors deposited fractions melting at 102°, 97°, and 97–98°, which were combined and again recrystallised from the same solvent. The *B* form was deposited in nodules, m. p. 120° (Found: C, 80.2; H, 8.9%), and in nodules embedded with needles of the *A* form, which were separated with the help of a lens and purified by recrystallisation. A mixture of the isomers melted at 107°.

The *amide* of the *A* form was prepared by dissolving the nitrile in cold concentrated sulphuric acid and keeping the mixture overnight. On dilution with water and treatment with ammonia,

1676 *Isomeric 2-Arylamino-2-cyano-trans-decahydronaphthalenes, etc.*

a precipitate formed which crystallised from alcohol in needles, m. p. 158° (Found : C, 74.8; H, 9.0. $C_{17}H_{24}ON_2$ requires C, 75.0; H, 8.8%). The *B form*, prepared in a similar manner from the *B form* of the nitrile, separated from alcohol in small plates, m. p. 141° (Found : C, 74.9; H, 8.9%).

The *A form* of 2-anilino-trans-decahydronaphthalene-2-carboxylic acid was obtained by heating the *A form* of the amide with alcoholic hydrochloric acid for 20 hours, the residue obtained by removal of alcohol being treated with dilute aqueous sodium hydroxide, and the acid recovered from the filtered solution by acidification with acetic acid. It separated from alcohol in small needles, m. p. 198° [Found : C, 74.3; H, 8.7; equiv., 271. $C_{17}H_{23}O_2N$ requires C, 74.7; H, 8.4%; equiv. (monobasic), 273].

The details of the preparation of the compounds described below are similar. The theoretical analytical percentages are given in parentheses.

Compound.	Form.	M. p.	Analysis.	Remarks.
2-p-Bromoanilino-2-cyano-trans-decahydronaphthalene	A	132°	C, 61.2 (61.2); H, 6.2 (6.3)	Needles from benzene.
	B	141	C, 61.6; H, 6.3	Nodules from benzene.
2-p-Bromoanilino-trans-decahydronaphthalene-2-carboxamide	A	180	Br, 58.7 (58.4)	Needles from alcohol.
	B	171	Br, 58.8	Small plates from benzene.
2-o-Toluidino-2-cyano-trans-decahydronaphthalene	A	100	C, 80.5 (80.6); H, 8.9 (8.9)	Needles from benzene.
	B	111	C, 80.4; H, 9.1	Nodules from hexane.
2-o-Toluidino-trans-decahydronaphthalene-2-carboxamide	A	157	C, 75.1 (75.5); H, 9.2 (9.1)	Obtained by keeping the nitrile in conc. H_2SO_4 for 4 months. Small plates from alcohol.
	A	126—127	C, 80.4; H, 8.9	Needles from benzene.
2-m-Toluidino-2-cyano-trans-decahydronaphthalene	B	123—124	C, 80.7; H, 9.0	Hard needles from hexane. M. p. of mixture 106—107°.
	A	122	C, 75.1; H, 9.3	Obtained by keeping the nitrile in conc. H_2SO_4 for 2 months. Needles from hexane.
2-p-Toluidino-2-cyano-trans-decahydronaphthalene		130	C, 80.5; H, 9.1	Needles from benzene.
2-p-Toluidino-trans-decahydronaphthalene-2-carboxamide		166—167	C, 75.3; H, 9.2	Plates from alcohol.
2- α -Naphthylamino-2-cyano-trans-decahydronaphthalene		138	C, 82.6 (82.9); H, 8.1 (7.9)	Rhomboids from benzene.
2- α -Naphthylamino-trans-decahydronaphthalene-2-carboxamide		174	C, 78.0 (78.2); H, 8.3 (8.1)	Small crystals from benzene.
2- β -Naphthylamino-2-cyano-trans-decahydronaphthalene	A	162	C, 82.7; H, 7.7	Thick plates, on repeated recrystallisation from benzene.
	B	160	C, 82.7; H, 8.2	Soft white nodules from benzene.*
2- β -Naphthylamino-trans-decahydronaphthalene-2-carboxamide	A	238	C, 78.0; H, 8.3	Obtained in microscopic plates, purified by trituration with benzene.
	B	221	C, 78.1; H, 8.5	Purified by trituration with benzene.

* A crystalline powder, m. p. 145°, which separated on recrystallisation of the crude condensation product from benzene, was at first mistaken for an individual.

1-Anilino-1-cyano-3-methylcyclopentane.—A solution of potassium cyanide (6.5 g.) in water (15 c.c.) was added to a mixture of aniline (9.3 g.) and 3-methylcyclopentanone (9.8 g.) in glacial acetic acid (50 c.c.) and kept overnight. The oil was separated and cooled in a freezing mixture; the solid obtained had m. p. 43—47°, and a further quantity was isolated after dilution of the filtrate from this with water. On recrystallisation from light petroleum, the anilinocyanoderivative formed soft aggregates of needles, m. p. 49° (Found : C, 77.9; H, 8.1. $C_{13}H_{16}N_2$ requires C, 78.0; H, 8.0%). The *amide*, obtained by keeping a solution of the nitrile in concentrated sulphuric acid overnight, crystallised from benzene in short needles, m. p. 158—159° (Found : C, 71.3; H, 8.5. $C_{13}H_{18}ON_2$ requires C, 71.6; H, 8.3%).