REACTION OF N-TRITYLAMINES WITH NITROGEN-CONTAINING HETEROCYCLIC COMPOUNDS

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UDC 547.751'822.7'867.4

Transtritylation occurs during the reaction of N-trityl-N-(β-cyanothethyl)amines with indole, morpholine, and 2- and 4-aminopyridines. The detritylation and transtritylation of the synthesized compounds were studied.

Transtritylation to give, respectively, 3-tritylindole (VI), N-tritylmorpholine (VII), and 2- (VIII) and 4-(tritylamino)pyridine (IX) occurs during the reaction of N-trityl-N-(β-cyanoethyl)amines (I) of the general formula $RN[C(C_6H_5)_3](CH_2CH_2CN)$ with indole (II), morpholine (III), and 2- (IV) and 4-aminopyridine (V). The reagents used for the tritylation of II-V were methyl- (a), isopropyl- (b), butyl- (c), isobutyl- (d), octyl- (e), allyl- (f), benzyl- (g), cyclohexyl- (h), phenyl- (i), and p-tolyl- (j) I.

When VII-IX and N-tritylpyrrolidine (X) and N-tritylpiperidine (XI) are heated with excess methanol, allyl alcohol, ethylene glycol, glycerol, and phenol, transtritylation occurs to give, respectively, methyl trityl ether (XII), allyl trityl ether (XIII), ethylene glycol monotrityl ether (XIV), glycerol α-trityl ether (XV), and p-hydroxytetraphenylmethane. (XVI). When VII-XI are refluxed with acetic acid they give the detritylation product – triphenylcarbinol. In contrast to N-tritylated compounds VII-XI, C-tritylated derivative VI does not form transtritylation and detritylation products with alcohols and acetic acid.

EXPERIMENTAL

3-Tritylindole (VI). A mixture of 1.17 g (10 mmole) of II, 5 mmole of Ia-j, and 40 mmole of glacial acetic acid in 10 ml of dry benzene was refluxed for 10 h. The solvent was removed by vacuum evaporation, and the residue was treated with a dilute solution of 40 mmole of sodium hydroxide. The precipitated VI was washed with water and recrystallized from alcohol.* The yield of VI ranged from 85 to 95%. The product had mp 211-212°C, which was in agreement with the literature data [1, 2].†

N-Tritylmorpholine (VII). This compound was obtained as in the preceding experiment. A 0.87 g (10 mmole) sample of III was used to obtain VII with mp 175-176° (mp 174-176° [3]) in 87-96% yield.

2-(Tritylamino)pyridine (VIII). This compound was obtained as in the preceding experiment. A 0.94 g (10 mmole) sample of IV was used to obtain VIII with mp 151-152° in 90-95% yield. The following melting points are reported in the literature: 150-155° [3], 150-151° [4], and 152-153° [5].

4-(Tritylamino)pyridine (IX). This compound (77-83%) was obtained as in the preceding experiments from 0.94 g (10 mmole) of V. It melted with the evolution of gas bubbles at 109-110°, solidified, and finally melted at 140-142°. Found: N 8.2%. $C_{24}H_{20}N_2$. Calculated N 8.3%.

* Here and elsewhere, in the case of N-tritylamines Ii and Ij, detritylation products – N-(β-cyanoethyl)-aniline (mp 47-48°, in 75-80% yield) and N-(β-cyanoethyl)-p-toluidine (mp 102-103°, in 87-90% yield) – were isolated from the alcohol mother liquor by the addition of water.

† Here and elsewhere, the constants of the tritylation products obtained by means of triphenylchloromethane are presented for comparison. No melting-point depressions were observed for mixtures of the transtritylation products with genuine samples of the corresponding tritylation products.

Vilnius State University. Vilnius State Teaching Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 383-384, March, 1974. Original article submitted February 8, 1973.

Methyl Trityl Ether (XII). A mixture of 3 mmole of VII-XI,* 10 ml of CH_3OH, and 30 mmole of glacial acetic acid was refluxed for 10 h. It was then diluted with ethanol, and water was added gradually to precipitate XII. The yield of XII ranged from 89 to 96%. The product had mp 80-83° (mp 83-84° [6]).

Allyl Trityl Ether (XIII). This compound was obtained as in the preceding experiment. The yield of XII with mp 74-76° (mp 76° [7]) was 88-97%.

Ethylene Glycol Monotrityl Ether (XIV). This compound was obtained as in the preceding experiment. The yield of XIV with mp 96-98° (mp 98-100° [7]) was 80-90%.

Glycerol α-Trityl Ether (XV). This compound was obtained as in the preceding experiment. The yield of XV with mp 95-97° (mp 92-94° [7], 108-109° [8], and 109-110° [9]) was 60-80%.

p-Hydroxytetraphenylmethane (XVI). A mixture of 3 mmole of VII-XI and 5 g of C_6H_5OH was refluxed for 5 h, after which it was treated with aqueous sodium hydroxide solution, and the precipitated XVI was removed by filtration and treated with dilute hydrochloric acid. The yield of XVI with mp 175-280° (mp 280-282° [10] and 284-285° [11]) was 95-100%.

Detritylation of VII-XI. A mixture of 1 g of VII-XI and 10 ml of 75% acetic acid was refluxed for 5-7 min. It was then cooled, and the precipitate was removed by filtration. The yield of triphenylcarbinol with mp 161-162° ranged from 80 to 90%.

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* Compound X was synthesized by the method in [4]. Compound XI was obtained by tritylation of piperidine by means of triphenylchloromethane (the yield of product with mp 135-136° was 78.8%).