295. *Arylamides of β-Arylaminocrotonic Acids. Part I.*

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Arylamides of β-arylaminocrotonic acids should result from a reaction between one molecule of ethyl acetoacetate and two molecules of arylamine, $CMe(OH){:}CH{\cdot}CO_2Et + 2RNH_2 = CMe(NHR){:}CH{\cdot}CO{\cdot}NHR + H_2O + EtOH$. β-1-Naphthylaminocrotono-1-naphthylamide was prepared by Gibson, Harihan, Menon, and Simonsen (J., 1926, 2247), who found that it was easily hydrolysed by dilute acid, giving acetoacet-α-naphthalide. Jadhav (*J. Indian Chem. Soc.*, 1930, **7**, 669) prepared the β-, *m*-, and *p*-nitroanilinocrotononitroanilides, which are easily hydrolysed by acid to the corresponding acetoacetnitroanilides. He also claims to have prepared β-arylaminocrotonarylamides from *p*-anisidine, *p*-phenetidine, certain xylidines, and from *o*-, *m*-, and *p*-chloroanilines: these compounds were found not to be hydrolysable even by boiling concentrated hydrochloric acid. Since such stability is unexpected, we decided to investigate this point.

Jadhav's work was therefore repeated and compounds which corresponded in melting points to those described by him were obtained in poor yields. We have shown that the compounds described by him as β-arylaminocrotonarylamides obtained from *p*-anisidine, *p*-phenetidine, certain xylidines, *o*-, *m*-, and *p*-chloroanilines are really the corresponding *s*-diarylureas: the reason for the stability of these compounds to hydrolysis is therefore evident. We have confirmed our conclusions in each case by a full analysis of the substance and by a comparison with an authentic specimen of the *s*-diarylurea. It has already been shown by other investigators (*e.g.*, Knorr, *Annalen*, 1886, **236**, 69; Hurst and Thorpe, J., 1915, **107**, 937) that *s*-diarylureas may be produced if the reaction between ethyl acetoacetate and the arylamine is carried out at a high temperature.

In connexion with the xylidines, Jadhav's nomenclature is inconclusive and it is not possible to state definitely which xylidines he used. In repeating this section of the work we employed *p*-xylidine and a *m*-xylidine ($NH_2 : Me : Me = 1 : 2 : 4$) and obtained the corresponding *s*-diarylureas. In a later paper (*J. Indian Chem. Soc.*, 1931, **8**, 681) Jadhav also uses this indefinite nomenclature: his *m*(1 : 4 : 5)-xylidine is probably *p*-xylidine, his *m*(1 : 3 : 4)-xylidine cannot be identified from our results and the results of his later paper.

We intend to attempt the preparation of β-arylaminocrotonarylamides derived from *p*-anisidine, *p*-phenetidine, xylidines, chloroanilines, and other arylamines in order to study their stability to hydrolysis.

EXPERIMENTAL.

The micro-analyses were carried out by Schoeller of Berlin, the macroanalyses by one of us (J. K. T.). For purpose of comparison, the *s*-diarylureas derived from *p*-anisidine, *p*-phenetidine, the xylidines, *o*-, *m*-, and *p*-chloroanilines were prepared by adding carbonyl chloride in toluene solution (20%) to excess of the arylamine diluted with a little of the same solvent. The solids were washed with water and alcohol and finally crystallised from glacial acetic acid. In every case the m. p. of the diarylurea was the same as the m. p. of the product obtained from ethyl acetoacetate and the arylamine; the m. p. of the mixture showed no depression. The reaction between ethyl acetoacetate and the arylamine was carried out as described by Jadhav, but in many cases the time of heating necessary before the appearance of product was longer than that given by him.

s-*Di*-p-*anisylurea.* 6½ Hours' heating were required; needles, m. p. 234—235° (Jadhav gives 1 hour; needles, m. p. 235—236° [Found (micro.): C, 66·3; H, 6·2; N, 10·3. $C_{15}H_{16}O_3N_2$ requires C, 66·2; H, 5·9; N, 10·3%].

s-*Di*-p-*phenetylurea.* 1½ Hours; m. p. 232—233° (Jadhav gives 45 minutes; m. p. 230—231°; literature gives m. p. 225—226° [Found (micro.): C, 68·2; H, 6·7; N, 9·2. Calc. for $C_{17}H_{20}O_3N_2$: C, 68·0; H, 6·7; N, 9·3%].

s-*Di*-(2 : 4-*dimethylphenyl*)*urea.* The ester (13 g.) and *m*-xylidine (NH_2 : Me : Me = 1 : 2 : 4) (12 g.) were heated for about 1 hour; solid then began to separate. After heating for a few minutes longer, the solid was collected, washed with alcohol to remove oil, and crystallised from acetic acid, forming needles, m. p. 263—265° [Found (micro.): C, 76·1; H, 7·5; N, 10·8. $C_{17}H_{20}ON_2$ requires C, 76·1; H, 7·5; N, 10·4%].

s-*Di*-(2 : 5-*dimethylphenyl*)*urea.* The ester (13 g.) and *p*-xylidine (12 g.) were refluxed for about 1 hour; decomposition with separation of a solid then suddenly commenced. This solid, after trituration and washing with alcohol, crystallised from much acetic acid in fine needles, m. p. 285° (closed tube) [Found: C (macro.), 75·9; H, 7·6; N (micro.), 10·5%]. Jadhav describes his two β-xylidinocrotonoxylidides as melting above 275°.

s-*Di*-o-*chlorophenylurea.* After 2 hours' refluxing, only a very small amount of needles separated on cooling and scratching; a further quantity was obtained by heating for 2 hours more. The needles melted at 238—239° (Jadhav gives 1½ hours, m. p. 236°) [Found (micro.): C, 55·6; H, 3·7; N, 9·9; Cl, 24·9. $C_{13}H_{10}ON_2Cl_2$ requires C, 55·5; H, 3·6; N, 10·0; Cl, 25·2%].

s-*Di*-m-*chlorophenylurea.* 3 Hours; needles, m. p. 245—246° (Jadhav gives 2 hours; needles, m. p. 240—241°) [Found (micro.): C, 55·2; H, 3·7; N, 10·1; Cl, 25·0%].

s-*Di*-p-*chlorophenylurea*. After heating for 2 hours, no solid separated on cooling; on heating for 4 hours longer, the whole mass solidified. It crystallised in needles melting in a sealed hard-glass tube at 306—307°; in soft-glass tubes the m. p. was much lower and was accompanied by obvious decomposition (Jadhav gives 2 hours; needles, m. p. above 275°) [Found: C (micro.), 55·4; H, 3·6; N (macro.), 10·1; Cl (macro.), 25·1%].

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