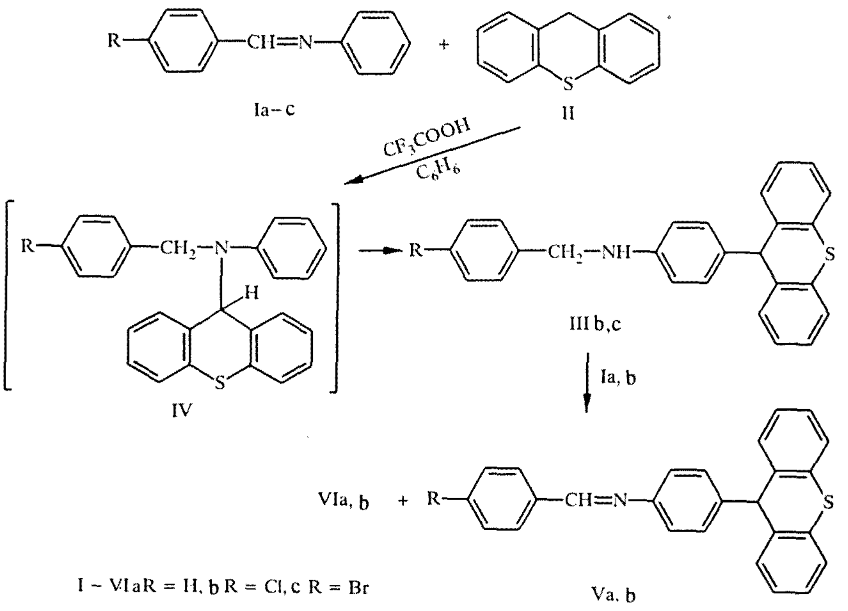
Chemistry of Heterocyclic Compounds, Vol. 31, No. 7, 1995

REDUCTIVE HETARYLATION OF IMINES BY THIOXANTHENE

L. P. Yunnikova

A new approach to the synthesis of hetarylanilines entails the reaction of compounds capable of hydride transfer with imines. Thioxanthene may participate in hydride transfer [1]. The electrochemical oxidation of thiapyran has shown that its dehydrogenation ($-e$, $-H^+$, $-e$) is equivalent to the loss of a hydride ion [2].

We are the first to establish the possibility of hetarylation of imines involving a C—H bond of thioxanthene, which has a labile hydrogen atom. The reaction of imines Ia-Ic with thioxanthene II gave N-arylmethyl-4-(thioxanthen-9-yl)anilines IIIb and IIIc. This reaction probably proceeds through formation of N-arylmethyl-N-(thioxanthen-9-yl)aniline IV as an intermediate. This proposal is based on a study of the mechanism of the electrophilic substitution of xanthylium or thioxanthylium cations by aromatic amines [3]. According to this mechanism, *para*-hetarylanilines are obtained as the result of isomerization of initially formed N-hetarylanilines.



Thus, a solution of 10 mmoles imine Ib or Ic and 5-6 mmoles thioxanthene II in 15 ml CF_3CO_2H and 5 ml benzene was heated at reflux for 8 h. The solvent was removed. The residue was extracted with pentane and neutralized with 20% aqueous NaOH. Ether was added to the oil formed to give:

N-(4-Chlorobenzyl)-4-(thioxanthen-9-yl)aniline (IIIb, $C_{26}H_{20}NClS$) in 41% yield, mp 154-155°C (from ether). IR spectrum (neat): 3400 cm^{-1} (N−H). R_f 0.73 (Silufol UV-254, benzene). PMR spectrum (in $CDCl_3$); 3.76 (1H, br.s, NH), 4.14 (2H, s, CH_2), 5.13 (1H, s, 9-H), 6.30-7.46 ppm (16H, m, arom). This sample was identical to the compound obtained according to Ivanov et al. [4].

D. I. Pryanishnikov Perm Agricultural Institute, 614000 Perm. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1003-1005, July, 1995. Original article submitted December 2, 1994.

N-(4-Bromobenzyl)-4-(thioxanthen-9-yl)aniline (IIIc, $C_{26}H_{20}NBrS$) in 30% yield, mp 160-161°C (from benzene). IR spectrum (neat): 3370 cm^{-1} (N−H). R_f 0.72 (Silufol UV-254, benzene). PMR spectrum (in C_6D_6): 3.08 (1H, br.s, NH), 3.57 (2H, s, CH_2), 5.01 (1H, s, 9-H), 6.27-7.48 ppm (16H, m, arom).

Thioxanthenylimine Va was isolated instead of the expected amine IIIa when imine Ia was used. One explanation for the formation of this product may be the dehydrogenation of amine IIIa formed during the reaction by excess starting azomethine Ia. The formation of a mixture of compounds such as IIIb and Vb is possible in the reaction of imines Ib and Ic with xanthene in the case of superheating of the reaction mixture. The fraction of imine Vb in the mixture of IIIb and Vb increases over time. Indeed, amines IIIa and IIIb obtained by an alternative procedure from thioxanthylium perchlorate and the corresponding N-arylmethylanilines [4] are dehydrogenated by imines Ia and Ib under analogous conditions to give the corresponding thioxanthenylimines Va and Vb. Azomethines Ia and Ib are reduced in this case to the corresponding N-arylmethylanilines VIa and VIb.

Thus, a solution of 20 mmoles N-benzylidenaniline Ia or Ib and 10 mmoles thioxanthene II in a mixture of 25 ml CF_3CO_2H and 25 ml benzene was heated at reflux for 48 h to give:

N-Benzylidene-4-(thioxanthen-9-yl)aniline (Va, $C_{26}H_{19}NS$) in 14% yield, mp 166-167°C (from benzene). PMR spectrum (in C_6D_6): 5.02 (1H, s, 9-H), 6.75-7.76 (17H, m, arom), 7.92 ppm (1H, s, CH=N). A mixed probe of this product with a sample obtained according to a standard procedure [5] did not give a depressed melting point.

N-(4-Chlorobenzylidene)-4-(thioxanthen-9-yl)aniline (Vb, $C_{26}H_{18}NClS$) in 61% yield, mp 171-172°C (from benzene). PMR spectrum (in C_6D_6): 5.03 (1H, s, 9-H), 6.72-7.41 (16H, m, arom), 7.73 ppm (1H, s, CH=N).

N-Benzyl-4-(thioxanthen-9-yl)aniline (IIIa, $C_{26}H_{21}NS$) was obtained according to Ivanov et al. [4], mp 125-126°C (from benzene), R_f 0.67 (Silufol UV-254, benzene). PMR spectrum (in C_6D_6): 2.80 (1H, br.s, NH), 3.72 (2H, s, CH_2), 4.96 (1H, s, 9-H), 6.05-7.26 ppm (17H, m, arom).

A solution of 5 mmoles amine IIIa and 10 mmoles imine Ia in a mixture of 5 ml CF_3CO_2H and 5 ml benzene was heated at reflux for 15 h to give imine Va in 48% yield. The formation of N-benzylaniline (VIa) was detected using PMR spectroscopy.

The elemental analysis data for IIIa-IIIc, Va, and Vb corresponded to the calculated values.

REFERENCES

1. V. A. Izmail'skii, G. E. Ivanov, and Yu. A. Davydovskaya, Zh. Obshch. Khim., **43**, 2503 (1973).
2. N. T. Berberova, A. F. Blinokhvatov, A. S. Archegova, E. S. Klimov, A. V. Shpakova, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 1, 47 (1991).
3. G. E. Ivanov, A. V. Turov, G. V. Pavlyuk, and M. Yu. Kornilov, Ukr. Khim. Zh., **51**, 655 (1985).
4. G. E. Ivanov, A. V. Turov, and M. Yu. Kornilov, Ukr. Khim. Zh., **54**, 78 (1988).
5. Weygand−Hilgetag, Experimental Methods in Organic Chemistry [Russian translation], Khimiya, Moscow (1968), p. 472.