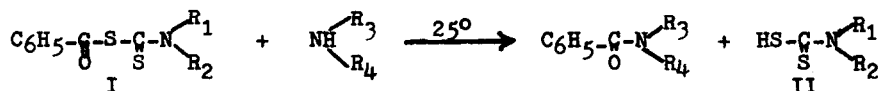


MIXED BENZOIC DITHIOCARBAMIC ANHYDRIDE AS A REAGENT FOR BENZOYLATION

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In the course of our search for new synthetic routes for N,N'-di- and N,N'-trisubstituted thiocarbamides we examined the interaction of mixed benzoic dithiocarbamic anhydrides^{1,2} (I) with primary and secondary amines. Since benzylation was observed instead of the expected thiocarbamylation of amines, we investigated its usefulness as a benzoylating agent.



Benzoic dithiocarbamic anhydride I (R₁=R₂=Me or Et; R₁=H and R₂=Me or Et) was obtained in good yield when an ice cold saturated aqueous solution of the appropriate sodium dithiocarbamate was treated with benzoyl chloride. The anhydride obtained thus was crystallised from a mixture of hexane and diethyl ether. This method gives better yields than the one reported² earlier.

In a typical experiment, benzoic dimethyl dithiocarbamic anhydride (2.25g, 0.01M) in diethyl ether (10ml) was mixed with aniline (0.93g, 0.01M). A rapid reaction occurred at ca 25° and the benzoyl derivative separated. The liberated dithiocarbamic acid (II) and unreacted aniline were removed by washing successively with dilute alkali, acid and water. The residue was almost pure benzanilide (1.6g, 80%).

Similarly other aromatic amines (o-, m-, and p-toluidines, p-chloroaniline, o-, m-, and p-phenylene diamines, o- and p-amino benzoic acids and N-methyl- and N-ethylanilines) and aliphatic amines (ammonia, methyl-, ethyl-, isopropyl-, cyclohexyl-, dimethyl- and diethyl amines, pyrrolidine, glycine and tetrahydro-

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isoquinoline) gave the respective benzoyl derivative in good yield (ca 80%).

The reaction of the anhydride with alcohols and phenols under the same conditions was found to be very sluggish and detectable quantities of esters were obtained only after 24 hours. However, thioalcohols and thiophenols reacted faster with the reagent (in 20 minutes) to give high yields of the corresponding benzoyl derivatives. The reagent reacted rapidly with the bi-functional compounds, o-, p- and m-aminophenols and ethanolamine to give exclusively N-benzoyl derivatives (80-90%).

The anhydride, therefore, appears to be a very effective reagent for benzoylation of amines at room temperature and below (10-25°). It can be used for selective benzoylation of the amino group in presence of alcoholic or phenolic groups if the duration of the reaction is restricted to 15 minutes or less. Elevated temperatures could not be employed as the reagent is known to undergo rapid thermal degradation to benzamide and carbon disulphide^{2,3}. The reaction can be followed spectroscopically. The absorption band of the reagent in the long wave-length region gradually disappears during the reaction.

A similar mixed carboxylic carbonic anhydride has been reported to be effective as an acylating agent for various functional groups⁴⁻⁶. Its preparation is however, tedious and requires strictly anhydrous conditions and low temperatures.

The advantages of the mixed benzoic dithiocarbamic anhydride for benzoylation include operational simplicity, selectiveness and avoidance of alkaline and anhydrous conditions.

References

1. G.W. Watt, CA, 34, 5314 (1940)
2. D.S. Tarbell and R.P.F. Scharrer, J. Org. Chem., 27, 1972 (1962)
3. D.S. Tarbell and E.H. Hoffmeister, Tetrahedron, 21(10), 2857 (1965)
4. D.S. Tarbell and J.A. Price, J. Org. Chem., 22, 245 (1957)
5. T. Wieland, W. Schafer and E. Bokelmann, Ann., 573, 99 (1951)
6. J.R. Vaughan, Jr. and R.L. Osato, J. Am. Chem. Soc., 73, 5554 (1951)