In a typical preparation, a solution of 0.97 g of ferrous sulfate hydrate and 1.39 g of cupric acetate hydrate was prepared in 20 ml of glacial acetic acid and 2 ml of water. The hydroperoxide (0.01 mol) was added under nitrogen at room temperature over a 0.5-hr period. The stirring heterogenous mixture warmed and gradually turned from green to brown and was left overnight. Dissolution in water and extraction to remove acetic acid followed by distillation and/or preparative gas chromatography yielded the olefinic alcohols as well as recoverable alcohols and ketone or aldehyde. These latter materials could, of course, be recycled to increase the yield.

The long-known handleability of primary and secondary hydroperoxides[6] as well as recent methods to produce these materials in very high yield[8] clearly suggest this reaction as a useful relative to the variety of other long-range activating alkoxy radical reactions now extant.[14,15]

(14) See M. M. Green, J. M. Moldowan, and J. G. McGrew, II, *J. Chem. Soc., Chem. Commun.*, 451 (1973), and leading references therein. It could be expected that alkoxy and other hydrogen abstracting radicals formed in other ways would also show this behavior (intervention of Cu^{II}), and we are currently looking into this possibility.

(15) J. W. Wilt, ref 9, Chapter 8.

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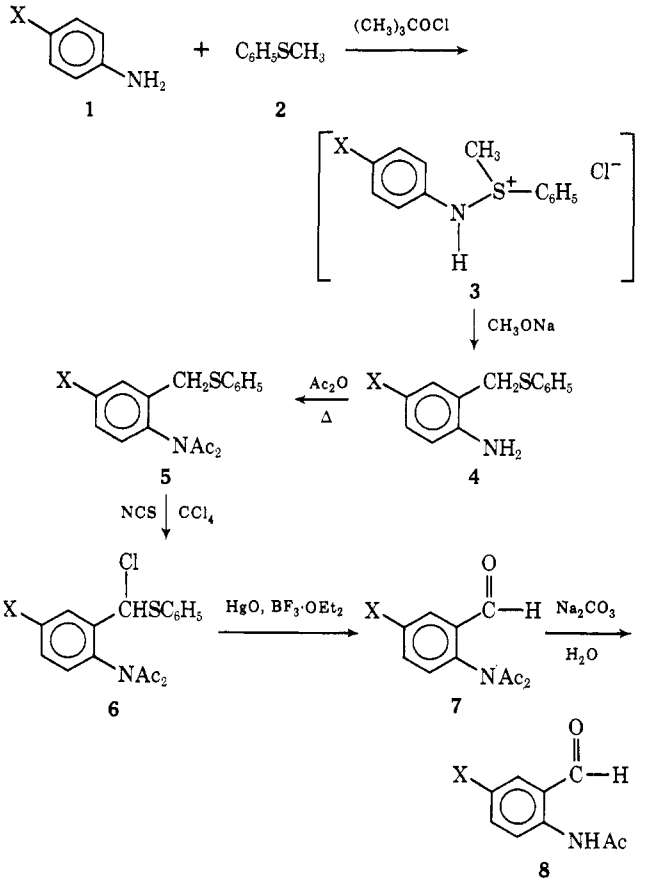


Selective Ortho Formylation of Aromatic Amines

Sir:

Relatively few methods for the formylation of aromatic rings are known. Those which do exist fail to offer very much in the way of selectivity. More specifically, methods for the preparation of derivatives of *o*-aminobenzaldehydes, which have extensive value in the synthesis of certain heterocyclics, are generally limited to the reduction of *o*-nitrobenzaldehydes[1] and the oxidation of *o*-toluidines.[2] We now wish to report two new general methods for the selective ortho formylation of anilines.

Recently, we described a method for the conversion of anilines into *o*-methylthiomethylanilines.[3] In principle, the *o*-methylthiomethyl group is a potential precursor of the aldehyde moiety. In practice, we have found that we could prepare a variety of protected *o*-aminobenzaldehydes in good overall yields by an adaptation of our ortho substitution procedure.

Treatment of a mixture of 1.0 equiv of the aniline (**1**) and 1.6 equiv of thioanisole (**2**) in 3:1 acetonitrile–methylene chloride at −40° with 1.0 equiv of *tert*-butyl hypochlorite gave the azasulfonium salt **3**. These salts were not isolated but were treated with sodium methoxide to yield the phenylthiomethylaniline (**4**) *via* intermediate ylid formation and subsequent intramolecular rearrangement.[3] As shown in Table I the yields of **4** ranged from 58 to 73%.[4]

Table I. Yields Obtained in the Conversion of Anilines into *o*-Aminobenzaldehyde Derivatives

Starting aniline	X	% yield of **4**	% yield of **8** from **4**	Overall % yield of **8** from **1**
1a	CH_3	63	52	33
1b	H	61	73	45
1c	Cl	68	73	50
1d	CO_2CH_3	58	63	37
1e	CN	73	49	36

When **4b** (X = H) was refluxed with excess acetic anhydride for 24 hr, the *N*,*N*-diacetyl derivative **5b** was obtained in 97% yield.[2,5] Treatment of **5b** with 1.1 equiv of *N*-chlorosuccinimide[6,7] in carbon tetrachloride

(1) F. Sachs and R. Kempf, *Chem. Ber.*, **35**, 2704 (1902); F. Sachs and E. Sichel, *ibid.*, **37**, 1861 (1904); F. Mayer, *ibid.*, **47**, 408 (1914); L. I. Smith and J. W. Opie, "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 56.

(2) J. J. Brown and G. T. Newbold, *J. Chem. Soc.*, 4878 (1952); J. J. Brown and R. K. Brown, *Can. J. Chem.*, **33**, 1819 (1955).

(3) P. G. Gassman and G. Gruetzmacher, *J. Amer. Chem. Soc.*, **95**, 588 (1973).

(4) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds for which isolated yields are listed. Infrared and nmr spectral data were consistent with the assigned structures in all cases.

(5) P. G. Gassman and H. R. Drewes, *J. Chem. Soc., Chem. Commun.*, 488 (1973); J. J. Sudborough, *J. Chem. Soc.*, **79**, 533 (1901); A. L. Lumiere and H. Barbier, *Bull. Soc. Chim. Fr.*, **33**, 783 (1905).

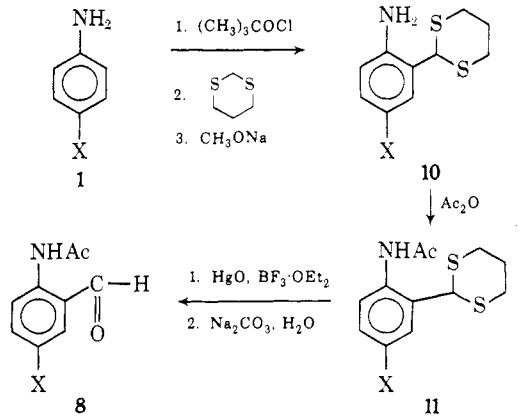
(6) D. L. Tuleen and T. B. Stevens, *J. Org. Chem.*, **34**, 31 (1969); D. L. Tuleen, *ibid.*, **32**, 4006 (1967); D. L. Tuleen and V. C. Marcum, *ibid.*, **32**, 204 (1967); D. L. Tuleen and T. B. Stevens, *Chem. Ind. (London)*, 1555 (1966); G. A. Russell and G. J. Mikol in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, Chapter 3.

(7) For additional discussions of the α-chlorination of sulfides, see G. E. Wilson, Jr., and R. Albert, *J. Org. Chem.*, **38**, 2156, 2160 (1973); H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949); H. Böhme and H. Gran, *ibid.*, **577**, 68 (1952); E. Vilsmaier and W. Sprügel, *ibid.*, **747**, 151 (1971); W. E. Truce, G. H. Birum, and E. T. McBee, *J. Amer. Chem. Soc.*, **74**, 3594 (1952); F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); E. Vilsmaier and W. Sprügel, *Tetrahedron Lett.*, 625 (1972); and R. Harville and S. F. Reed, *J. Org. Chem.*, **33**, 3976 (1968).

at 25° for 1 hr gave a 75% yield of **6b**. Hydrolysis of **6b**, using mercuric oxide and boron trifluoride etherate[8,9] gave the diacetyl derivative **7b**, which was further hydrolyzed with aqueous sodium carbonate to **8b** in 91% yield (based on **6b**). In our general procedure, intermediates **5**, **6**, and **7** were not purified and characterized. For a series of anilines, Table I lists the yields of **8** based on **4** and the overall yields of **8** based on the starting aniline **1**.

As can be noted from the table, the yields for the four-step process for the conversion of **4** into **8** range from *ca.* 50 to 70%. The overall process can tolerate a wide variety of substituents ranging from those which are mildly electron donating to those which are strongly electron withdrawing. Although the overall process for the conversion of **1** into **8** involves several steps, most of the intermediates do not require isolation and purification. Thus, the conversion of anilines into derivatives of *o*-aminobenzaldehydes is readily accomplished. Since the overall yields of purified *N*-acetyl-*o*-aminobenzaldehydes from anilines range from *ca.* 30 to 50%, this process provides an excellent approach to the preparation of these useful synthetic intermediates.

In the procedure described above, the chlorination of **5** to give **6** represents a formal oxidation. In principle, if a more highly oxidized sulfide (*i.e.*, an α-substituted sulfide) were used at an earlier stage, this "oxidation step" could be avoided. In an attempt to accomplish this aim, 1,3-dithiane (**9**) was used as the sulfide in our



process. Thus, various anilines (**1a–1c**) were treated sequentially with (a) *tert*-butyl hypochlorite, (b) 1,3-dithiane, and (c) sodium methoxide. This gave **10** in 25–54% yields. Mixing of **10** with acetic anhydride gave **11**, which on sequential treatment with mercuric oxide–boron trifluoride etherate and aqueous sodium carbonate gave **8**. The yields for the various steps are listed in Table II. As can be seen from Table II, the overall yields of **8** from **1** by the 1,3-dithiane route range from 21 to 44%. In the case of aniline (**1b**) the yields obtained in the two routes were similar. For **1a** and **1c**, the 1,3-dithiane route gave poorer yields. In choosing between these two routes, one has to balance the cost of the 1,3-dithiane and the overall lower yields in the 1,3-dithiane route against the greater number of operations and higher overall yields obtained in the thioanisole route.

(8) E. Vedejs and P. L. Fuchs, *J. Org. Chem.*, **36**, 366 (1971).
(9) For a leading reference to other methods of hydrolyzing sulfides see W. Huurdeman and H. Wynberg, *Syn. Commun.*, **2**, 7 (1972).

Table II. Yields Obtained in the 1,3-Dithiane Route to **8**

Starting aniline	X	% yield of **10**	% yield of **11** from **10**	% yield of **8** from **11**	Overall % yield of **8** from **1**
1a	CH_3	25	90	92	21
1b	H	54	95	85	44
1c	Cl	30	91	88	24

In general, both routes constitute versatile new synthetic procedures. Known methods for the preparation of *o*-aminobenzaldehyde derivatives are limited by the presence of certain functional groups. Thus, **8a**, **8d**, and **8e** and the corresponding aminobenzaldehydes have never been reported. Our methods are very general. Although we illustrated our processes through the use of para-substituted anilines, the processes should be readily applicable to ortho- and meta-substituted anilines[3] and to heterocyclic amines.[10] We are currently investigating these and other applications.

Acknowledgment. We are indebted to the National Cancer Institute of the Public Health Service for a grant which partially supported this investigation.

(10) P. G. Gassman and C. T. Huang, *J. Amer. Chem. Soc.*, **95**, 4453 (1973).
(11) Stauffer Chemical Company Fellow, 1971–1972; Ohio State University Dissertation Fellow, 1972–1973.

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Intramolecular Chelation *via* Imines. A Stereoselective Synthesis of s-Chloro-3-(2-aminoethyl)-1,8-diamino-3,6-diazaoctanecobalt(III) Ion

Sir:

In an earlier paper[1] a facile intramolecular condensation between a ligand containing a reactive carbonyl center and a coordinated ammonia was described. The process was base catalyzed and was presumed to occur by deprotonation of the ammonia to give a coordinated amide ion which then attacked the C=O center to give, after eliminating H_2O, a chelated amine. This type of reaction has now been used for a specially interesting stereospecific synthesis of one isomer of a quinquedentate amine–cobalt(III) complex where the synthesis of the organic ligand is also conducted on the metal ion.

It was anticipated that both possible isomers of $[Co(tren)Cl(NH_2CH_2CHO)]^{2+}$ (tren = tris(2-aminoethyl)amine) could undergo base-catalyzed imine formation leading, after reduction with borohydride ion, to one or more of the four possible isomers of the complex $[Co(trenen)Cl]^{2+}$ (trenen = 3-(2-aminoethyl)-1,8-diamino-3,6-diazaoctane). Syntheses investigated to date, however, have provided but a single isomer of the starting complex which, on the basis of evidence presented below, we assert is the species p-chloro(aminoacetaldehyde hydrate)(tris(2-aminoethyl)aminecobalt(III), p-$[Co(tren)Cl(NH_2CH_2CH(OH)_2)]^{2+}$.[2] (*Anal.*

(1) J. MacB. Harrowfield and A. M. Sargeson, *J. Amer. Chem. Soc.*, **96**, 2634 (1974).
(2) p identifies the coordinated chloride ion as trans to a primary amine group as opposed to trans to the tertiary (t) amine center.