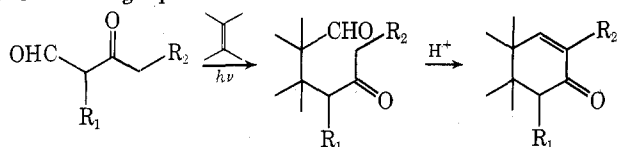


acyclic α -formyl ketone which is enolized toward the aldehyde carbonyl. Because the photoproducts can only undergo aldolization in a single sense, a fourfold simplification in the overall annelation sequence has resulted, compared with the analogous reactions with β diketones. In terms of net structural change, the reaction can be summarized by the following equation.



The single remaining point of ambiguity, orientation of the photoaddition with unsymmetrical alkenes, is currently under investigation. Based on preliminary findings we expect our studies to result in a general cyclohexenone synthesis which complements existing methods.¹³

References and Notes

- (1) (a) We wish to thank the U.S. Public Health Service for financial support (Grant No. 1 R01 GM20780-01). (b) A portion of this work was presented at the 168th National Meeting of the American Chemical Society, Sept 8-13, 1974, Atlantic City, N.J., Orgn 100. (c) We are indebted to Dr. David Rosenthal and Mr. Fred Williams of the Research Triangle Institute for Mass Spectrometry (supported by NIH Grant RR 00330) for mass spectral determinations.
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- (7) NMR spectra were determined in CCl_4 solution at ambient temperature; only slight deviations were noted relative to solvolysis conditions (pentane solutions at -20°). The NMR absorption for the "aldehyde" hydrogen (δ 7.6-7.9) was used to calculate the position of the rapid equilibrium ($A \rightleftharpoons B$) assuming extreme values of δ 6.7 and 9.2 for tautomers A and B, respectively.^{6a} The ratio concentrations of the tautomers A:B for **1a**, **1b**, and **1c** are 52:48, 52:48, and 64:36, respectively.
- (8) New compounds gave satisfactory elemental and spectral analyses. Although the yields of the reactions reported here have not been optimized, they are generally in the range of 60-100% for the photolysis and 60-90% for the aldol cyclization.
- (9) Careful analysis of the aldehyde region of the NMR spectra of the crude photoproducts permitted the assignment of structure **3 vs. 5**. These results are in accord with a similar analysis of the cyclized material, **4 vs. 6**. For instance, **3b** exhibited a singlet at δ 9.64 while **4b** showed a singlet at δ 6.05. Compounds **5b** and **6b** would be expected to show a triplet and double doublet, respectively, for the same two protons. Because we could detect no trace of the alternate absorptions, we feel justified in assigning a conservative value of >95% for the enol specificity in the photochemical cycloadditions.
- (10) The location of the carbonyl group at C-2 of **8a**, and thus the specificity of this photoaddition, was verified by mass spectral determination of the extent of deuterium exchange in the dihydro derivative of **8a**.
- (11) The identity of **8c** was verified by independent synthesis.
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- (13) The photolyses reported here were performed with an excess of alkene using a Hanovia 450-W medium-pressure lamp through Correx or Pyrex. The reactor was cooled to -20 to -30° during irradiation, a condition which afforded increased efficiency in product formation as well as cleaner reaction mixtures. Reaction times were generally between 1 and 2 hr for the complete conversion of 2-4 g of formyl ketone.

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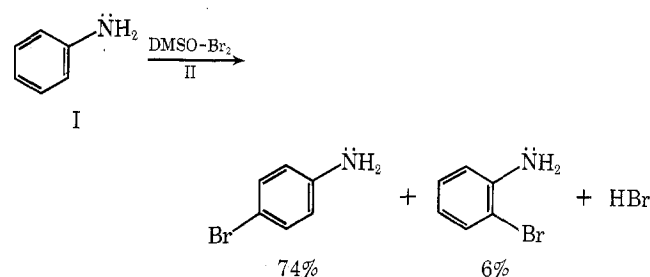
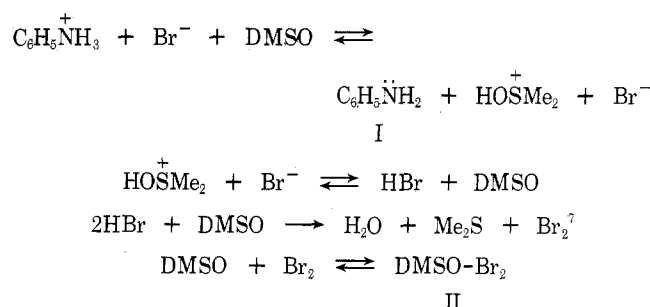
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Indirect Bromination by Reaction of Aniline Hydrobromide with Dimethyl Sulfoxide

Summary: Indirect bromination of aniline can be achieved by reaction of the aniline hydrobromide salt with dimethyl sulfoxide to afford *p*-bromoaniline and *o*-bromoaniline in a 12:1 ratio. This simple indirect bromination proceeds with a high degree of regioselectivity to afford predominantly *p*-bromoaniline.

Sir: Fletcher and coworkers¹ have reported that 2-amino-3-bromofluorenone is obtained from the reaction of *tert*-butyl bromide and 2-aminofluorenone in dimethyl sulfoxide and from the reaction of 2-aminofluorenone with 48% HBr in dimethyl sulfoxide. We wish to report that the reaction of aniline hydrobromide with dimethyl sulfoxide at an elevated temperature (refluxed for 45 min) afforded predominantly the *p*-bromoaniline in 74% yield and only 6% *o*-bromoaniline. This indirect bromination process is summarized in Scheme I which depicts the DMSO-Br₂ adduct² II as the active brominating species.

Scheme I



The process depicted in Scheme I illustrates the selective indirect bromination of aniline by way of its hydrobromide salt to yield almost exclusively *p*-bromoaniline.³ This result is somewhat surprising since direct bromination^{3b} of aniline in most instances yields di- and trisubstituted derivatives.

Although the DMSO-Br₂ adduct has been depicted in Scheme I as the brominating species we have no direct evidence of its constitution. A second possible brominating agent is the Me₂S-Br₂ adduct;⁴ dimethyl sulfide formed in the oxidation of hydrogen bromide could complex with free bromine. However the formation of both of the bromine adducts would be expected to be reversible processes, and it would be anticipated that the reaction conditions would favor the formation of the DMSO-Br₂ adduct (provided that the thermodynamic stabilities of the two adducts are not vastly different), since the reaction is normally carried out in the presence of a large excess of DMSO.

***p*- and *o*-Bromoaniline.** Aniline hydrobromide (13.05 g, 0.075 mol) was added to 100 ml of dimethyl sulfoxide⁵ and the resulting mixture was refluxed for 45 min. The reaction was allowed to cool to room temperature and poured into a dilute solution of sodium

hydroxide (3.0 g in 750 ml of H₂O). The resulting mixture was extracted with two 150-ml portions of a 5:1 Skelly B:ethyl ether solution. The extracts were combined, washed with 100 ml of H₂O, dried over anhydrous sodium sulfate, and filtered. Concentration of the organic phase and distillation of the resulting oil afforded 10.1 g (80%) of a semisolid, bp 76–80° (0.5 mm); GLC analysis showed that the mixture consisted of ~74% *p*-bromoaniline and 6% *o*-bromoaniline. Recrystallization of the semisolid from aqueous ethanol afforded 8.7 g (67%) of pure *p*-bromoaniline, mp 62.4–64° (lit.^{3a,6} mp 66–66.5°).

References and Notes

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