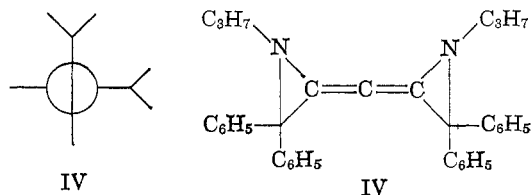


Stereochemical considerations indicate that four isomers of IIIa or IIIb should exist as a result of different orientations of the aziridine rings with respect to each other.

Reaction of C₃ with N-diphenylmethyleisopropylamine would be expected to produce one allenic product



(IV). Evidence for formation of this product is an allenic absorption in the infrared and an *m/e* peak at 241 in the mass spectrum of the crude reaction mixture.

No products attributable to reaction of monatomic carbon with the imines used were definitely found, though many components appeared in the chromatograms of the crude reaction mixtures. Such products might be expected since reaction of carbon vapor with alkenes leads to formation of spiropentanes.³

Acknowledgment. This work was partially supported by a National Science Foundation institutional grant.

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 Received October 9, 1965

The Chlorination of Anilines. Proof of the Existence of an N-Chloro Intermediate

Sir:

An aniline, being an ambident¹ nucleophile, might be expected to react with a chlorinating agent chiefly on nitrogen because this atom constitutes the most highly nucleophilic site of the molecule. Ultimate carbon-chlorine covalency formation would then be attributable to the instability of this N-chloroaniline intermediate.²

We report here conclusive evidence that N-chloro-N-methylaniline is the intermediate in the chlorination of N-methylaniline by calcium hypochlorite in carbon tetrachloride.

When 10 equiv. of calcium hypochlorite³ is stirred with 1 equiv. of N-methylaniline in carbon tetrachloride at 0°, removal of a filtered aliquot after 30 min. indicates the presence of almost 1 equiv. of active chlorine⁴ in the solution. The infrared spectrum of this solution reveals a degree of disappearance of the N-H stretching band (at 3415 cm.⁻¹) which closely parallels the titra-

(1) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

(2) This suggestion has been made by numerous authors, e.g., F. D. Chattaway and K. J. P. Orton, *J. Chem. Soc.*, **79**, 462 (1901). The most recent use of this hypothesis has been made by R. S. Neale, R. G. Schepers, and M. R. Walsh [*J. Org. Chem.*, **29**, 3390 (1964)], who attribute the high *ortho:para* ratios which they observed to such N-chloro intermediates.

(3) J. T. Baker, Purified Powder, 30-35% available chlorine; our analysis just before use indicates 12.6% active chlorine.

(4) Measured by addition of solution to an excess of potassium iodide and titration with sodium thiosulfate. Stirring calcium hypochlorite in carbon tetrachloride in the absence of N-methylaniline, followed by filtration and titration of the carbon tetrachloride filtrate, produces a zero titer (certainly less than 1%) of active chlorine.

tion value (see Table I). Further substantiation that this is indeed a solution of N-chloro-N-methylaniline is the fact that analysis of the sample which has been treated with potassium iodide and sodium thiosulfate reveals it to consist mainly of N-methylaniline.⁵

Table I. Assay of N-Chloro-N-methylaniline Solution by Titration, by Infrared, and by the Nature of the Compounds Recovered on Treatment With Potassium Iodide

Time, min.	% yield of N-chloro compd. by		% recovered N-methylanilines Unsubstituted	<i>o</i> -Cl	<i>p</i> -Cl
	Titration	Infrared ^a			
10	57.5	54.3	93.5	5.2	2.3
30	88.5	85.4	81.0	10.3	5.8

^a Yield = (1.00 - [absorbance at time *t*/absorbance at start])100.

On the other hand a filtered aliquot, removed after 30 min. but not treated with KI, was found after standing for 24 hr. to contain 66.7% *o*-chloroaniline, 3.1% *p*-chloroaniline, ~16.5% dichloroaniline, and no unreacted N-methylaniline. This proves that the N-chloro-N-methylaniline is indeed the *intermediate* in the reaction producing ring-chlorinated N-methylanilines.

Two additional observations appear to be of particular interest. (1) The *ortho:para* ratios differ significantly when the final products are formed in the presence of the inorganic chlorinating agent (*ortho:para* ~2) and when they are formed in a solution containing the N-chloro intermediate as the sole chlorinating agent (*ortho:para* >3.4).⁶ (2) N-Chloro-N-methylaniline, though it rearranges in the course of hours to ring-chlorinated materials, is reasonably stable.⁷ This raises hopes of the possibility of using such reactive intermediates as starting materials for other reactions. Work on these last two points is in progress.⁸

(5) *I.e.*, C₆H₅N(Cl)CH₃ + 2KI + CH₃CO₂H = C₆H₅NHCH₃ + I₂ + KCl + CH₃CO₂K. The fact that some of this recovered material is already ring chlorinated suggests that some (less than 7.5% after 10 min.) of the N-chlorinated material, as assayed by both titration and infrared, may be *o*- and *p*-chloro-N-chloro-N-methylaniline.

(6) In fact this *ortho:para* ratio is the highest reported. Neale, *et al.*, ref. 2, obtained *ortho:para* 2.2 for N-methylaniline.

(7) In 0.02 M carbon tetrachloride solution the rate at which the N-H band in the infrared increased was quite slow; *e.g.*, it did not increase noticeably in the first 10 min.

(8) Support of this work by a grant from the U. S. Public Health Service (AM 06834) is gratefully acknowledged.

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 Received August 30, 1965

Allylbenzene Isomerization Catalyzed by Deuteriocobalt Tetracarbonyl

Sir:

When an excess of a 1-olefin is treated with cobalt hydrocarbonyl (HCo(CO)₄) at room conditions under a nitrogen atmosphere, olefin isomerization occurs very rapidly.¹ Two mechanisms² have been proposed to explain the isomerization: (a) allylic exchange involving hydrogen donation from the metal hydride to

(1) G. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

(2) R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 1549 (1963).