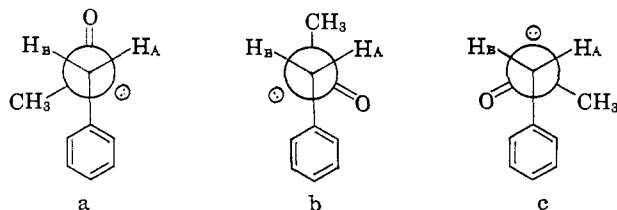


energy ( $E_a = 28.1$  kcal./mole) the rate constant at  $15.0^\circ$  is calculated to be  $9.3 \times 10^{-8}$  l.  $M^{-1}$  sec. $^{-1}$  for a single hydrogen. The much smaller reactivity of the methyl hydrogens is evident.

Due to the pyramidal configuration of the sulfoxide group,<sup>16</sup> benzyl methyl sulfoxide is asymmetric and, indeed, the optically active compound can be prepared in a state of high optical purity.<sup>17</sup> The nonequivalence of the methylene hydrogens in an asymmetric acyclic compound has been shown to be mainly due to conformational preference.<sup>18</sup> Therefore, considering only one enantiomer of benzyl methyl sulfoxide, the n.m.r. spectrum indicates that the conformations a, b, and c are unequally populated under the conditions of exchange on the methylene group.



In an attempt to derive the principal conformation the dipole moment of benzyl methyl sulfoxide has been determined. The measured<sup>19</sup> value, 3.86 D. (benzene), is unfortunately too close to that of the sulfoxide group itself (3.90 D.<sup>20</sup>) for inference to be made. *p*-Chlorobenzyl methyl sulfoxide has a dipole moment of 3.66 D.<sup>19</sup>

It must be concluded from the n.m.r. and rate data that the hydrogen exchange process is stereospecific. It follows then that the carbanion must be protonated from the side of the departing proton.<sup>21</sup> Yet the carbanionic center must be nearly flat because of the observed effect of phenyl on the rates.

Which of the methylene hydrogens is preferentially exchanged should become known from studies, now in progress, with benzyl methyl sulfoxide of known absolute configuration.<sup>17,24</sup> An intriguing speculation is that a hydrogen to be exchanged must be *trans* to the unshared pair on sulfur.<sup>25</sup> It will also be of interest to examine similarly optically active  $\alpha$ -deuterio-

(16) P. W. B. Harrison, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 2079 (1926).

(17) K. Mislow, M. M. Green, and M. Raban, *J. Am. Chem. Soc.*, 87, 2761 (1965).

(18) G. M. Whiteside, D. Holtz, and J. D. Roberts, *ibid.*, 86, 2628 (1964). However, for a different interpretation of this phenomenon, see H. S. Gutowsky, *J. Chem. Phys.*, 37, 2196 (1962).

(19) We thank Mr. Brian F. Scott, University of Toronto, for this measurement.

(20) L. E. Sutton in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1965, p. 395.

(21) Similar conclusions have been drawn regarding protonation of sulfonyl anions.<sup>22,23</sup>

(22) D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, 85, 1100 (1963).

(23) E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, 13, 793, 803 (1965).

(24) A. Streitwieser, Jr., J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron*, 6, 338 (1959).

(25) It has been suggested<sup>22</sup> that the most stable conformation of sulfonyl and sulfinyl carbanions would have the anionic charge oriented *trans* to the sulfur oxygen(s). While this situation is plausible for the sulfonyl case (see however ref. 23, for an opposing view), the conformational preference of oxygen of thiane oxides to the axial position<sup>26</sup> as well as other evidence<sup>26</sup> suggests that in the sulfoxide case it is the unshared electron pair that may have dominating influence.

(26) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, 86, 2935 (1964); J. C. Martin and J. J. Uebel, *ibid.*, 86, 2936 (1964).

benzyl methyl sulfone, in view of the evidence<sup>22</sup> that sulfonyl anions are superior to sulfinyl and phosphinoxy in configuration-holding capability.

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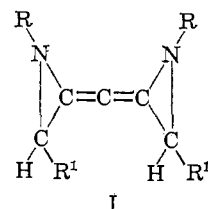
Received September 13, 1965

## Reaction of Carbon Vapor with Imines

Sir:

Recent investigations of the reactivity of carbon vapor has involved reaction of monatomic and triatomic carbon vapor, produced in a carbon arc, with alkenes,<sup>1-3</sup> monatomic carbon, produced by nuclear techniques, with alkenes,<sup>4,5</sup> and thermally produced carbon atoms with benzene.<sup>6</sup> Skell and co-workers report the addition of  $C_3$  to alkenes producing substituted bisethanoallenes.<sup>1,2</sup> The stereospecific nature of the addition of  $C_3$  to olefins has indicated that the ground state of  $C_3$  is singlet,<sup>2</sup> a conclusion consistent with analysis of spectra of carbon vapor.<sup>7</sup> Wolfgang and co-workers have reported insertion reactions of monatomic carbon into alkenes producing allenes<sup>4</sup> as well as many other products.<sup>5</sup>

We report here the reaction, occurring on a surface cooled to  $-196^\circ$ , of carbon vapor with imines, producing previously unknown compounds having what we believe to be structure I.



The apparatus employed, shown in Figure 1, was similar to that used by Skell, *et al.*<sup>2</sup> Graphite electrodes were threaded into brass rods which were sealed into the vacuum system by rubber O rings. Alternating current was supplied by a transformer (output 17 v., 100 amp. maximum; input 230 v.). Graphite rods,  $5/16$  in. diameter, were National Carbon Co. spectroscopic quality carbons. The carbons were outgassed at  $800^\circ$  in hydrogen atmosphere prior to use. The apparatus shown in Figure 1 was connected directly to an oil diffusion pump by 32-mm. glass tubing. The vacuum system was capable of pumping to  $10^{-6}$  mm. pressure. In a typical experiment, 2-3 ml. of imine in the lower flask was cooled with Dry Ice. The apparatus was evacuated and the cold finger cooled with liquid  $N_2$ . The arc was operated on a 3 sec. on-27 sec. off

(1) P. S. Skell and L. D. Wescott, *J. Am. Chem. Soc.*, 85, 1023 (1963).

(2) P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, *ibid.*, 87, 2829 (1965).

(3) P. S. Skell and R. R. Engel, *ibid.*, 87, 1135 (1965).

(4) M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, 86, 4741 (1964).

(5) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, 86, 4747 (1964).

(6) J. L. Sprung, S. Winstein, and W. F. Libby, *ibid.*, 87, 1812 (1965).

(7) A. E. Douglas and K. Clusius, *Can. J. Phys.*, 32, 319 (1954).

cycle while the imine was distilled from the lower flask onto the cold finger over a 20–40 min. period. When the imine was completely distilled, the lower flask was again cooled with Dry Ice. After waiting 20–30 min. for the electrodes to cool, the cold finger was warmed to room temperature. Products and unreacted imine were collected in the lower flask. The condensed material was stored under nitrogen at  $-78^{\circ}$ . A difficulty with this arrangement is that imine vapor can contact the hot carbons with resultant pyrolysis.

Imines were prepared by direct reaction of aldehydes or ketones with amines.<sup>8</sup> N-Diphenylmethylenisopropylamine was prepared by reaction of benzophenone dichloride with isopropylamine.

Analysis of products was carried out by infrared spectroscopy, gas chromatography (20% fluorosilicone oil on Chromosorb W, both supplied by Chrom-Line Laboratories, Kansas City, Mo.), and mass spectrometry.

*Reaction of Carbon Vapor with N-Benzylideneisopropylamine.* Infrared analysis of the mixture collected in the lower flask showed an absorption at  $4.65\text{--}4.7\ \mu$ . The mass spectrum showed a peak at  $m/e$  330. Gas chromatography (at  $125^{\circ}$ , He carrier at 40 ml./min.) showed three peaks, the heights of which were in a ratio of 1:1:2, and retention times, respectively, of 1 min. 39 sec., 1 min. 49 sec., and 2 min. 0 sec. Additional peaks of equal heights appeared at 2 min. 20 sec., 3 min. 9 sec., 3 min. 25 sec., and 4 min. 30 sec.

*Reaction of Carbon Vapor with N-Diphenylmethylenisopropylamine.* Infrared analysis of the mixture collected in the lower flask showed absorption at  $4.65\ \mu$ . Gas chromatographic analysis showed one major component in addition to starting material and several minor products. This component was collected, and its mass spectrum showed a peak at  $m/e$  241. Since the mass spectrometer used had an  $m/e$  upper limit of 400, the anticipated parent peak of 482 was not observed. This component also showed infrared absorption at  $4.65\ \mu$ .

Estimation of yields for either reaction is difficult since we have been unable to isolate pure products. Approximately 0.10 g. of graphite was vaporized during a typical experiment, but this includes fragmentation of small carbon particles from the electrodes. The infrared spectrum of the crude mixture taken after 3 or 4 days indicated a decrease in intensity of the absorption band at  $4.65\text{--}4.7\ \mu$ .

*Reaction of Carbon Vapor with Other Imines.* Although the crude mixtures from the reaction of carbon vapor and N-benzylideneisopropylamine, N-isopropylideneisopropylamine, N-ethylideneisopropylamine, and isopropylideneisopropylamine showed infrared absorption bands in the  $4.6\text{--}4.7\ \mu$  region, the gas chromatographs showed nothing but peaks corresponding to starting material as well as many minor components.

These results are consistent with reaction of carbon vapor and N-benzylideneisopropylamine forming bis(N-benzylideneisopropylamino)allene (II).<sup>9</sup> Stereochemi-

(8) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Am. Chem. Soc.*, **66**, 82 (1944).

(9) Infrared absorption at  $4.65\text{--}4.70\ \mu$  for the strained allene II is at somewhat shorter wave length than for the substituted bisethanoallenes ( $4.85\text{--}4.90\ \mu$ ) reported by Skell.

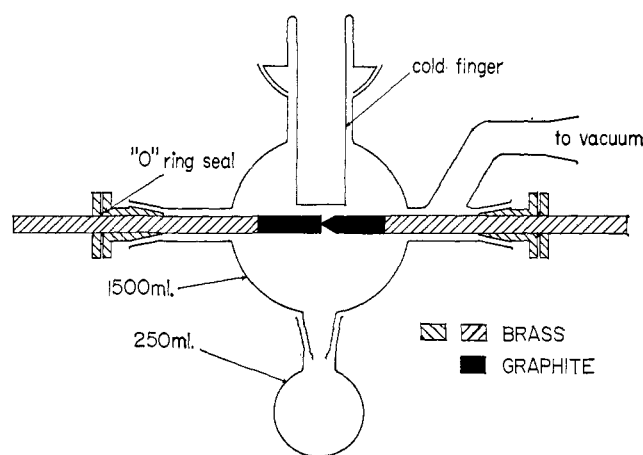
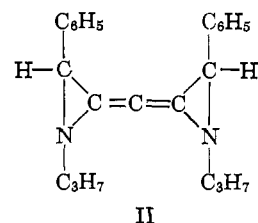
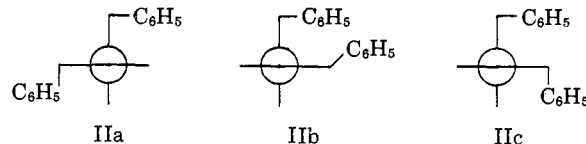


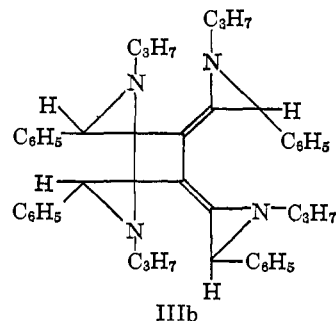
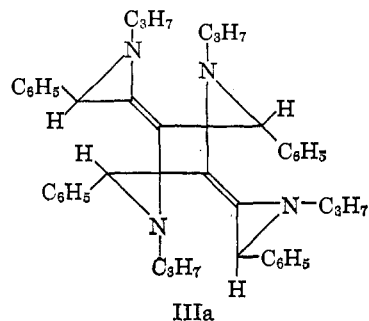
Figure 1. Reaction chamber diagram.



cal considerations predict that the pair of enantiomers designated IIa should be formed in equal amount as IIb and in half the amount of IIc. The presence of four



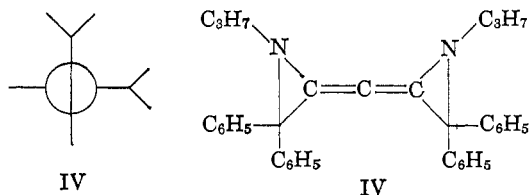
additional components, each present in equal amount, remains unexplained. A possibility is that II dimerizes under less severe conditions than allene,<sup>10</sup> forming compounds with the cyclobutane structure IIIa or IIIb.



(10) J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4269 (1959).

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 C<sub>3</sub> 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.<sup>3</sup>

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

Sir:

An aniline, being an ambident<sup>1</sup> 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.<sup>2</sup>

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 hypochlorite<sup>3</sup> 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 chlorine<sup>4</sup> in the solution. The infrared spectrum of this solution reveals a degree of disappearance of the N-H stretching band (at 3415 cm.<sup>-1</sup>) 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.<sup>5</sup>

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	<i>o</i> -Cl	<i>p</i> -Cl
	Titration	Infrared <sup>a</sup>			
10	57.5	54.3	93.5	5.2	2.3
30	88.5	85.4	81.0	10.3	5.8

<sup>a</sup> 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).<sup>6</sup> (2) N-Chloro-N-methylaniline, though it rearranges in the course of hours to ring-chlorinated materials, is reasonably stable.<sup>7</sup> 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.<sup>8</sup>

(5) I.e., C<sub>6</sub>H<sub>5</sub>N(Cl)CH<sub>3</sub> + 2KI + CH<sub>3</sub>CO<sub>2</sub>H = C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> + I<sub>2</sub> + KCl + CH<sub>3</sub>CO<sub>2</sub>K. 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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### Allylbenzene Isomerization Catalyzed by Deuteriocobalt Tetracarbonyl

Sir:

When an excess of a 1-olefin is treated with cobalt hydrocarbonyl (HCo(CO)<sub>4</sub>) at room conditions under a nitrogen atmosphere, olefin isomerization occurs very rapidly.<sup>1</sup> Two mechanisms<sup>2</sup> 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).