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REACTION OF 4,4′-DIMETHOXYDIPHENYLMETHANIMINE WITH CARBON DISULFIDE*

H. B. WILLIAMS,† K. N. YARBROUGH, K. L. CROCHET and D. V. WELLS
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

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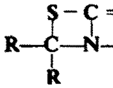
Abstract—The reaction of 4,4′-dimethoxydiphenylmethanimine with carbon disulfide in bromoform was studied at temperatures of 40°, 50°, and 60° in sealed tubes, The products from this reaction are 4,4′-dimethoxythiobenzophenone and 4,4′-dimethoxydiphenylmethaniminium thiocyanate. The proposed mechanism postulates primary attack on the carbon atom of carbon disulfide by the imine nitrogen leading to a resonance stabilized intermediate followed by ring closure with formation of a 4-membered ring,



$$\begin{array}{ccccc} & S & - & C & =S \\ & | & & | & \\ R- & C & - & N & -H \\ & | & & & \\ & R & & & \end{array}$$

which is unstable and decomposes to form thioketone and isothoicyanic acid. Supporting evidence for the proposed mechanism was drawn from kinetic studies, NMR studies, the effect of copper on the reaction system and the reaction of the benzyl substituted imine N-benzyl-4,4′-dimethoxydiphenylmethanimine (Schonberg's Reagent) with carbon disulfide at 43°. The formation of benzyl isothiocyanate in the system was inferred from the presence of N,N-dibenzylthiourea. The presence of benzyl isothiocyanate in the *substituted* imine–CS_2 system suggests that the initial decomposition product from the four membered ring intermediate in the imine–CS_2 system is HNCS.

The work suggests that dithiocarbamic acids in oxidizing metallic copper may not react through a dithiocarboxyl group in a classical sense but through a zwitterionic form of the molecule where the hydrogen is attached to the nitrogen atom.

SEVERAL investigations,[1] stemming from the reaction of N-benzyl-4,4′-dimethoxydiphenylmethanimine, $(CH_3OC_6H_4)_2C{=}NCH_2C_6H_5$, with elemental sulfur[2] led to the isolation and identification of 4,4′-dimethoxydiphenylmethanimine.[3] It was shown that this imine reacts with H_2S and with CS_2 to form the blue 4,4′-dimethoxythiobenzophenone[4] and that the reaction gives well-defined products in reproducible reactions. We have experimentally established the fact that diphenylmethanimine also reacts to produce the corresponding thioketone, presumably a characteristic reaction of diarylmethanimines. Apparently, the corresponding reaction does not occur however when there are two hydrogen atoms on the carbon alpha to the azomethine linkage.[5] In such cases there are formed equilibrium mixtures of β-alkylaminodithiocarbamic acid and the corresponding di-sulfhydryl imino compound.

RESULTS AND DISCUSSION

The reaction of 4,4′-dimethoxydiphenylmethanimine (I) with carbon disulfide gave 4,4′-dimethoxythiobenzophenone (II) and isothiocyanic acid (III) as products. The HNCS could not be isolated since it readily forms an isomeric mixture with IV and

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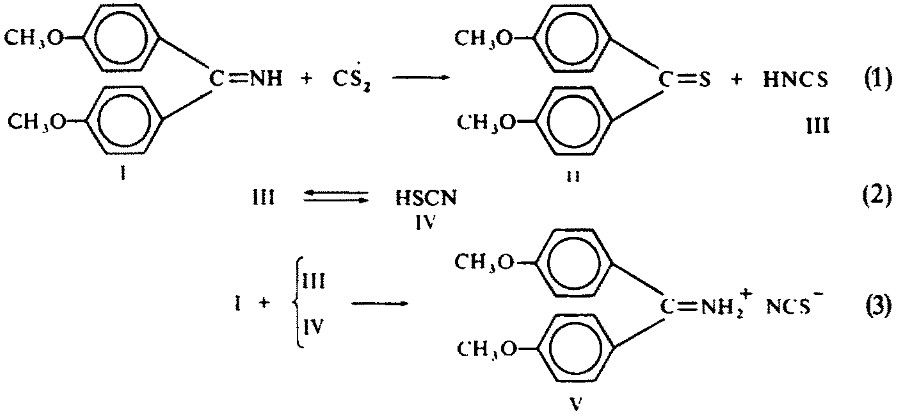
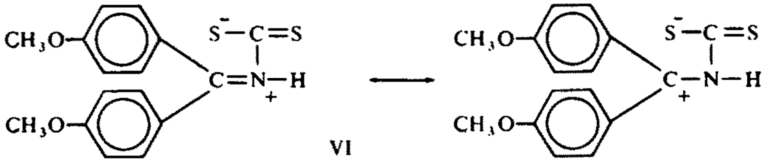
† To whom correspondence should be addressed.

both may react with I to form 4,4′-dimethoxydiphenylmethaniminium thiocyanate (V).

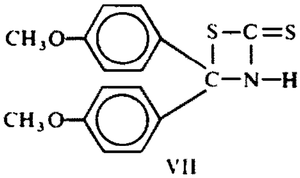


The NMR spectrum of the imine, I, includes an absorption at 8·9δ (NH), and that of the salt, V, includes one at 10·6δ ($\overset{+}{N}H_2$). In the NMR spectrum of a mixture of I and V, however, both of these absorptions are replaced by an intermediate one, signaling rapid proton exchange. During the course of reaction between I and CS_2 a downfield drift of the NH peak was observed. This change in chemical shift, which extended to 112 Hz after 150 minutes at 60° and to 60 Hz after 530 min at 40°, was a measure of the progress of the reaction. The resistance of a saturated solution of V in $CHBr_3$ was measured. In a cell of cell constant 0·014 cm^{-1} the solution resistance was 2·5 megohms, indicating an undissociated salt or intimate ion pair.

We propose two intermediates in the mechanism of the reaction between CS_2 and imine to form thioketone. The first results from electron-donating attack on the carbon atom for CS_2 by the imine nitrogen, and the second from closure, to form a molecule containing a four membered ring.



VI



VII

Both VI and VII should have been forming since the early stages of the reaction and might also undergo proton exchange in the system. Efforts to follow NH proton peak by NMR when the imine was reacted with CS_2 in the absence of bromoform of other solvent resulted in only an apparent slight upfield drift of the order of 2–3 Hz. Failure to observe a downfield drift was attributed to the fact that V is completely insoluble in carbon disulfide and in fact crystallized from the solution being investigated.

Attempts were made to achieve mass balances for I reacting with CS_2 in bromoform at 40°, 50°, and 60°C. Within experimental error, moles of II and V were the same at all times. Imine (I) was determined by absorbance at 887 CM^{-1}.

At 40° mass balance was apparently maintained throughout the reaction with the amount of imine reacted being accounted for within experimental error. The observation indicated that, at 40°C and for the 520 min during which the reaction was followed, the concentration of intermediate did not reach a level detectable by this method even though the products II and V were formed in appreciable amounts. At 50° and 60°, mass balance was not achieved in the early stages of the reaction, a fact which we attribute to a buildup of the intermediate(s), VI and/or VII. Apparently a rise in temperature enhanced the rate of the initial reaction between I and CS_2 to a greater extent than it increased the rate of decomposition of VII to form II. The data indicate that the rate of formation of the intermediate(s) was greater than its rate of decay, and that maximum intermediate concentration occurred after about 50 min at 60°.

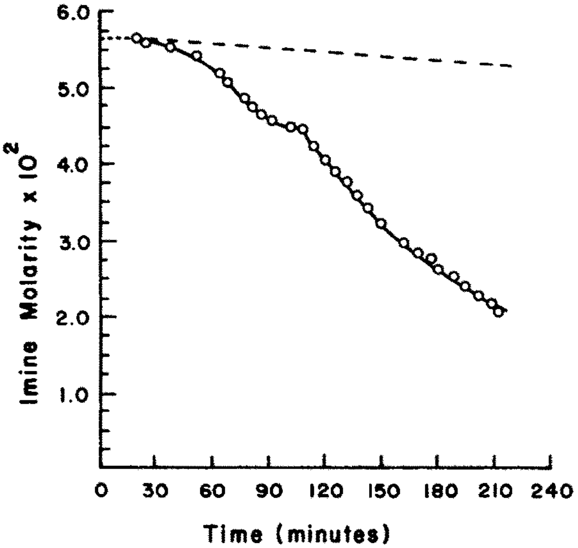
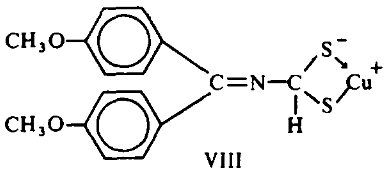


FIG. 1. Rate of disappearance of I in CS_2 at 40° in presence of copper metal.

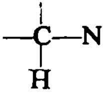
The influence of metallic copper and certain other metals on the reaction is an effect which we have only begun to study and which we encountered accidentally when infrared cells were used which utilized spacers composed of a copper containing alloy. Fig. 1 shows the rate of disappearance of imine in CS_2 solution under this condition. When the imine was dissolved in CS_2 under identical conditions as above except that no metal was present, the imine concentration decrease was approximated by the dashed line in Fig. 1. The rate of disappearance of imine in CS_2 solution at 40° was roughly ten times greater, and the disappearance of thioketone was about 50 times greater, in the presence of copper metal (cell spacers) than in the absence of copper for a

210 min time of reaction. The reaction of I with CS_2 in the presence of copper metal produces II, V and a copper containing compound, VIII.



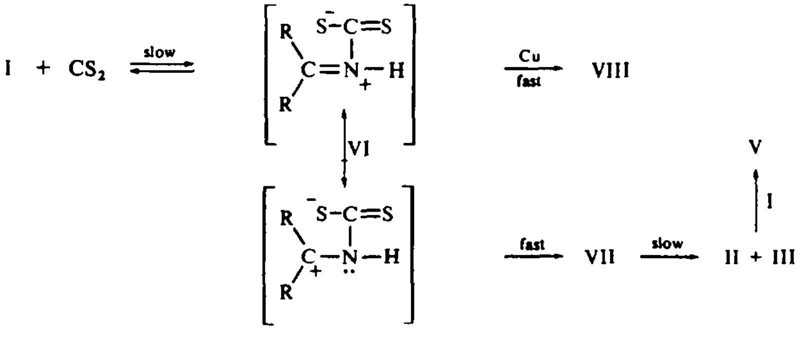
VIII

The rate of disappearance of I was more rapid in the presence of copper and the rates of formation of II and V were also greater. It is possible that copper may have catalyzed one reaction (step) and functioned as a reactant in another. Evidence that VIII contains CU I was obtained from EPR, NMR and magnetic balance studies. The compound is not paramagnetic and is, in fact, slightly diamagnetic. The empirical formula of VIII was confirmed by analysis.

None of the known reactants or products react individually with copper metal under the conditions of these reactions, yet the reaction mixture readily attacks copper and without the liberation of hydrogen. We interpret the reaction of imine in CS_2 with copper metal to be indicative of the presence of the zwitterionic intermediate (VI) and that it oxidizes copper metal to produce VIII or a tautomeric compound possessing a  $-\underset{H}{\overset{|}{C}}-N{=}\dot{C}$ moiety. A four-center mechanism by which VII is formed directly from CS_2 and I thus appears to be unlikely. Compounds similar to VIII are known.[6-8] It is also possible that the copper surface functions catalytically to provide sites for the imine (I) and CS_2 to interact and form intermediate VI or sites which enhance the conversion of VI to intermediate VII.

Reaction mechanism: Consistent with the experiments and our interpretation of the observed phenomena, the mechanism indicated in Scheme I is proposed to be the most suitable for the present reaction.[*] One effect of copper being in contact with the

SCHEME 1



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[*] To test for radical occurrence, the reaction between CS_2 and 4,4′-dimethoxydiphenylmethanimine was carried out in both the presence and absence of granular metallic copper in solutions containing α,α-diphenyl-β-picrylhydrazine. The presence of the picrylhydrazine caused no apparent reduction in the rate of production or total quantity of thioketone. No picrylhydrazyl radical was observed.

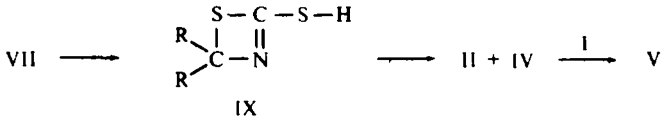
system is the conversion of some of VI to VIII. The rate of conversion of VI to VII is fast and compares with the rate of formation of VIII. The formation of VII presumably is not reversible. Birum and Matthews[9] report a cycloaddition of CS_2 and triphenyl-phosphoranylideneketene with loss of COS and formation of triphenylphosphoranylidenethioketene. The thioketene group of this product, $R_3\overset{+}{P}{-}C{=}C{=}S$, is isoelectronic with the isothiocyanate function of $H{-}N{=}C{=}S$.

Although reactions have been reported between dialkylthiuram-disulfides and copper bronze[10] to form copper dithiocarbamate complexes we have been unable to find any accounts of reactions between dithiocarbamic acids and copper. However, we have experimentally established that diethyldithiocarbamic acid reacts with copper and without the evolution of hydrogen gas. Our work dealing with the imine–CS_2–copper system suggest that for dithiocarbamic acids reacting with copper the oxidation product retains the acid hydrogen in the molecule. It further implies, not that a dithiocarbamic acid is necessarily present in the imine–CS_2 system, but that the species which oxidizes copper in an established dithiocarbamic acid system is perhaps similar to our proposed intermediate VI.

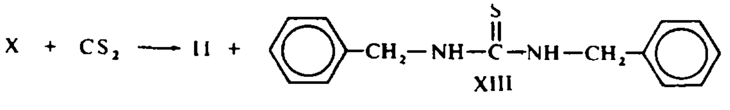
We have no data that settle the manner by which the presence of copper enhances the formation of thioketone; however, it seems probable that VI becomes associated with the copper surface where it can react either with copper directly or, from its new orientation, be converted more readily to VII than it is in solution in the absence of the copper surface.

An altermate path for our system would involve rearrangement of VII with the formation of IX, Scheme 2. Compound IX would give II and thiocyanic acid (IV) as products.

SCHEME 2.

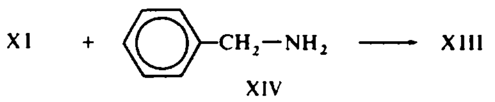


Scheme I leads to the formation of isothiocyanic acid. Since these compounds readily isomerize, no choice can be made between the two schemes on the basis of product formation from unsubstituted imine. In an attempt to distinguish between the two possibilities, we studied the reaction between the benzyl substituted imine N-benzyl-4,4,-dimethoxydiphenylmethanimine $(CH_3OC_6H_4)_2C{=}NCH_2C_6H_5$, X and carbon disulfide to determine if either benzyl isothiocyanate ($C_6H_5CH_2NCS$, XI or benzyl thiocyanate ($C_6H_5CH_2SCN$, XII) was a product. XI would result from Scheme 1 and XII from Scheme 2. The products from this reaction at 43° were thioketone (II), and N,N′-dibenzylthiourea (XIII) and some 4,4′-dimethoxybenzophenone, presumably formed by the reaction of the thioketone with oxygen in the presence of light. The transient existence of XI was inferred from the formation of XIII, which probably occurred by reaction of XI with benzylamine, XIV (equation 5). Benzylamine would have resulted form the reaction of XI with small amounts of moisture in the system. A



(4)

further suggestion that XI was in the reaction mixture was the appearance of an absorption band at 2100 cm^{-1} during the course of the reaction. Though this absorption frequency is characteristic of isothiocyanates,[11, 12] we were unable to isolate the responsible species.



(5)

Since the likelihood of the isomerization of benzyl thiocyanate to the isothiocyanate is extremely slight under the condition of this experiment,[13–15] the presence of XIV in the substituted imine–CS$_2$ system suggests that the initial decomposition product from VI is III and that the reaction follows the mechanism given in Scheme I. Although we may not exclude a sulfur protonated species as a form present in the mixture it is excluded as a necessary reactant.

EXPERIMENTAL

M.ps were taken on a Thomas–Hoover apparatus and are uncorrected. Visible spectra were obtained with a Beckman DB spectrophotometer. Standard KBr techniques were used for solids, and matched NaCl cavity cells were used for solns. NMR spectra were obtained with a Varian Associates A-60A o HA-100 spectrometer using TMS as the internal standard. Conductivity measurements were made with a model RC 16 conductivity bridge (Industrial Instruments, Inc.) using a 50 ml cell with Pt electrodes and a cell constant of 0·0140 cm^{-1}. An "alga" micrometer syringe was used for quantitative reaction mixture preparation. Temperature control during reactions was maintained with a Sargent water bath. Reaction temperatures within the NMR sample cavity were controlled by a constant stream of N$_2$ passed over a nichrome filament heater. Elemental analyses were performed by Galbraith Laboratories of Knoxville, Tennessee.

Materials. Compound X, 4,4′-dimethoxybenzophenone, reagent grade CS$_2$ and Cu metal were commercial materials used as received. CHBr$_3$ was obtained commerically and used after distillation. 4,4′-dimethoxythiobenzophenone was prepared as described previously.[4]

4,4′-Dimethoxydiphenylmethanimine (I). To 81 g (0·335 mole) 4,4′-dimethoxybenzophenone was added 100 g (0·84 mole) SOCl$_2$. The reaction mixture was refluxed 3 hr, left overnight, and excess SOCl$_2$ was removed under vacuum. The residue or red, crystalline dichloride was dissolved in 500 ml CHCl$_3$. In a 2-1. Flask, which was fitted with a solid CO$_2$–acetone filled condenser, was condensed 500 ml of ammonia. To this were added 15·3 g of Na in small pieces and 0·2 g ferric nitrate. The CHCl$_3$ soln of dichloride was then added dropwise. The CO$_2$–acetone condenser was replaced by a water condenser and the mixture was stirred for 2 hr. The mixture was filtered and the NM was washed with CHCl$_3$. Dry HCl was passed through the filtrate to adjust the pH to 6. solid NH$_4$Cl was filtered off and the filtrate was concentrated to 200 ml by passing a stream of dry N$_2$ through it. The addition of 800 ml ice-cold ligroin caused crystallization of crude I (77g, 0·32 mole, 95% yield), m.p. 130·5–131·5°.

The IR spectrum of the crude imine showed absorption at 1650 cm^{-1} due to the presence of 4,4′-dimethoxybenzophenone. Purification was accomplished by extracting the imine from ether solution into cold (blow 10°) dil HCl, adjusting the pH of the aqueous soln to 9 with concentrated NaOH soln (temp kept below 10°), and extracting the free imine repidly into ether. The ether extract was dried over Na$_2$CO$_3$ and most of the ether was evaporated with a stream of dry N$_2$. The remaining ether was decanted from the resulting crystals of I, m.p. 131–131·5°. About one-half of the yield of I was lost in the purification process. The IR spectrum of the product was identical to that of an authentic sample of I[1a, 3] and showed no carbonyl absorption at 1650 cm^{-1}.

4,4′-Dimethoxydiphenylmethaniminium thiocyanate (V). V was prepared by reacting I with CS$_2$ in CHBr$_3$. V is soluble in water and CHBr$_3$ but insoluble in CS$_2$. An aqueous soln of V gives a positive thiocyanate test with Fe(III). I can be recovered from an aqueous soln of V by the addition of base.

Recrystallization of V by dissolving it in $CHBr_3$ and adding CS_2 gave needles, m.p. 152–163° (dec); IR 2070 cm^{-1} (—SCN)[16]. Found: C, 63·84; H, 5·27; N, 9·21; S, 10·80. Calcd. for $C_{16}H_{16}N_2O_2S$: C, 64·00; H, 5·38; N, 9·36; S, 10·70%).

Reaction of N-*benzyl-4,4′-dimethoxydiphenylmethanimine* (X) *with Carbon Disulfide*. A soln of 0·1 g (3×10^{-4} mole) of X in 2 ml CS_2 was heated in a stoppered tube at 43° for 28 days. The reaction mixture changed from colorless to yellow to green to blue, and crystals precipitated from the mixture. At the end of the heating period the reaction mixture was filtered. Removal of CS_2 from the filtrate gave 0·040 g of blue crystals indentified by visible and IR spectra as a mixture of II,[4] XV, $\nu_{C=O}$ 1645 cm^{-1} and a trace of an oil with absorption at 2100 cm^{-1}. This yellow oil was removed under vacuum. When the blue-white crystals (0·083 g), were washed with benzene, a blue filtrate and white crystals were obtained. Removal of benzene from the filtrate gave blue crystals (0·064 g) which were identified by spectra as a mixture of II and XV. The IR spectrum of the white crystals was identical with that of XIII.[17] The yield of XIII was 0·012 g ($4·7 \times 10^{-5}$ mole, 31%), m.p. 147–148° (lit,[18] m.p. 148°); NMR $\delta_{TMS}^{CDCl_3}$ 7·25 (—C_6H_5, 10H), 6·08 (—NH, 2H, broad), 4·60 (C_6H_5—CH_2—N—, 4H). Differential thermal analysis gave a single, sharp, endothermic peak at 151°. The actual yield of XIII was higher than that reported since it is somewhat soluble in both CS_2 and benzene. XV was present in the reaction mixture as a result of the photodecomposition of II in dilute solns in the presence of O_2.

Procedure for the preparation and isolation of the copper bearing compound, VIII. Freshly prepared 0·1 M solns of I in CS_2, with 2·5 g fresh Cu turnings per 10 ml of solns were mechanically-shaken and reacted for 35 min, and then partially immersed in an acetone–solid CO_2 bath to retard the decomposition of VIII to II. The reaction mixture was then filtered through a fine paper. The filtrate was diluted with cold EtOH, 70 ml per 10 ml filtrate, and subjected to aspiration until most of the Cs_2 had been removed. Compound VIII was then removed by filtration and maintained in the dark in a dry state. The yield of VIII was 0·114 g ($3·0 \times 10^{-3}$ mole, 10·0%, based on imine). Found: (duplicate analyses) C, 50·63; H, 3·89; N, 3·60; S, 16·65; Cu, 16·53; C, 50·36; H, 3·96; N, 3·55; S, 16·87; Cu, 16·77. Calcd. for $C_{16}H_{15}O_2NS_2Cu$: C, 50·44; H, 3·97; N, 3·68; S, 16·83; Cu, 16·68%).

Procedures for analytical measurements of products from reaction of CS_2 *with* I *in* $CHBr_3$. The reactions between CS_2 and I were carried out in sealed glass tubes of 6 ml volume. To 0·282 g (0·0013 mole) of I in a test tube was added 0·850 ml $CHBr_3$. Then 0·015 ml CS_2 was added with maintenance of the liquid interface. The tube was equilibrated under dry N_2 at 25° and sealed with a torch. Twelve tubes were used for each run. The sealed tubes were brought to reaction temp with a minimum of interface disturbance, vigorously shaken by hand and returned to the thermostat. Reaction time was counted from the time of shaking. On removal from the thermostat, the reaction mixtures were quenched at −18° and stored in a freezer at −7° until analyzed.

Analysis for V *isolated from reaction*. Individual tubes were warmed to 25° and opened. The contents were dissolved in 20 ml CS_2 and cooled to 10°. Those samples in which crystals formed were filtered through weighed fritted crucibles. The crystals were washed with CS_2, dried and weighed a V. The wash from V was added to the filtrate, and it was diluted to 25·0 ml with Cs_2 for further analyses.

Analysis for soluble V. A small amount of V did not precipitate from soln and was analyzed as thiocyanate ion. A 10·00 ml protion of the diluted filtrate was extracted with two 20 ml portions of 0·5% KOH and further treated by standard methods for the spectrophotometric determination of ferric thiocyanate at 461 mμ. Beer's Law obedience was demonstrated at these concentrations of CNS^-.

Analysis for unreacted I IR spectra were taken of the diluted filtrate at 887 cm^{-1}, a wavelength at which neither CS_2 nor $CHBr_3$ absorbs. Beer's Law behavior was established in the concentration range studied, and a molar extinction coefficient of 311 (absorbance cm^{-1} mole—1) was determined.

Analysis for II. The diluted filtrate was further diluted with CS_2 to give a concentration of II where beer's Law behavior was demonstrated (0·0004 to 0·0018 M) Visible spectra were taken at a wavelength of 593 m. Molar extinction coefficients for II in various solvents were cited in an earlier publication.[4]

Procedure for analytical NMR work. Glass sample tubes furnished by Varian were used. CS_2 was added to a solution of I in bromoform at the reaction temp. The tube was sealed with a cork, vigorously shaken and placed in the thermostated NMR probe. Reaction time was counted from the time of the tube's placement into the probe.

Preparation of diethyldithiocarbamic acid and its reaction with copper metal. Approximately sodium diethyldithiocarbamate was dissolved in 10 ml water and 10 ml CCl_4 was added. To the water phase was added sufficient 6M HCl to produce the white flocculent diethyldithoicarbamic acid which was extracted into the CCl_4 phase with shaking. The water phase was separated from the organic phase and Cu turnings were added to the latter. There resulted a rapid reaction with the production of a burnt amber color in the CCl_4 soln and a noticeable brightening of the copper surface.

As a check on the above the same visible results were obtained by adding diethyl amine to a test tube containing Cu turnings covered with chilled CS_2. Neither the amine nor the CS_2 produced the observed reaction when singly placed in contact with Cu.

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