conditions. Quenching of the intermediate anion with deuterium oxide led to incorporation of deuterium (91% d, $<1\%$ d_2) at C_2 in the product VII.

Complete utilization of the alkenyl or alkyl group attached to copper is permitted by use of 1 equiv of tri-*n*-butylphosphine or pyrrolidine as a solubilizing ligand in contrast to the lithium dialkylcopper reagents which transfer only one of their two alkyl groups to acetylenic esters. The stereospecificity of these alkylations appears to approach 99% with pyrrolidine as ligand.

Analogous alkylations of α,β-acetylenic amides by primary and tertiary alkylcopper reagents have been carried out in this laboratory and will be reported subsequently.

Since neither Grignard nor alkyllithium reagents effect these transformations, the results described above provide a new and useful stereospecific synthesis of trisubstituted olefins from readily available acetylenes.

(14) Efficiency appears to be limited only by the relatively difficulty of forming homoallylic Grignard reagents.

(15) Characterized by bp 118–119° (14 mm); $\nu_{\max}^{\text{film}}$ 1650, 1720 cm^{-1}; nmr (δ, ppm) 1.62 (s, 7-CH_3), 1.69 (s, 7-Me), 2.17 (d, $J = 1.5$ Hz, 3-CH_3), 3.69 (s, OCH_3), 5.11 (m, 6-H), and 5.70 (m, 2-H); mass spectra, *m/e*, 182 (M^+).

(16) Syntex Postdoctoral Fellow, 1967–1968.

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The Effect of Free Radicals on Superconductors. Nitric Oxide on Aluminum

Sir:

In previous work, the idea of "conductive conjugation" has been introduced in theoretical discussions of the possible effects of molecules on the superconductivity of metals.[1-3] The essential point is that under favorable circumstances molecules may interact so strongly with conducting metals that some of the molecular electrons become part of the Fermi sea. Unfortunately, it is difficult to test the conductive conjugation picture experimentally. However, for odd-electron free radicals, the absence of conductive conjugation should manifest itself by a strong depression of the superconducting transition temperature, since localized unpaired spins can break up the Cooper pairs of the superconducting state.[4] This absence of conductive conjugation is demonstrated in the present work for nitric oxide deposited on superconducting aluminum films.

The films were prepared as follows. A 15-20-Å film of silicon monoxide was evaporated onto a quartz crystal held at 4.2°K. The aluminum was then deposited on the silicon monoxide, and the critical temperature (T_c^0) was determined by a four-point resistivity measurement.[5] In these experiments, T_c^0 is defined as that temperature at which the resistance of the pure aluminum film equals one-half of the resistance change observed in the transition. The film was exposed to nitric oxide at a pressure of 6×10^{-8} Torr for a measured period of time, typically 10–60 sec. The new critical temperature, T_c, was measured over a period of 0.25–0.5 hr, and then more nitric oxide was added. This process was repeated until the supply of liquid helium in the cryostat became exhausted.

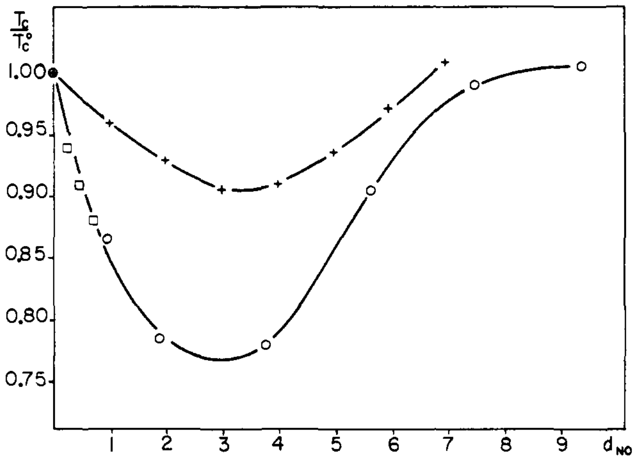

Figure 1. Reduced critical temperature, T_c/T_c^0, *vs.* thickness of nitric oxide, d_{NO}, in monolayers for superimposed aluminum and nitric oxide films. (○) 24-, (□) 28-, and (+) 117-Å aluminum films.

Figure 1 gives the reduced critical temperature, T_c/T_c^0, as a function of the nitric oxide thickness in "monolayers" for 24-, 28-, and 117-Å aluminum films. The initial effect of one monolayer of nitric oxide is to depress the critical temperature by approximately 12–15% for a 24-Å film. The data indicate the absence of conductive conjugation since a fraction of a monolayer also has the effect of sharply depressing the critical temperature. The efficacy of the nitric oxide in depressing the critical temperature is reduced as the thickness of the aluminum is increased. For a nitric oxide thickness of two to four monolayers, the critical temperature attains its minimum value; and, as the nitric oxide thickness is increased, the critical temperature also begins to increase. It returns to or slightly exceeds its original value for a nitric oxide thickness of seven to nine monolayers.

We interpret these results as the product of two competing effects. The first is the depression of the critical temperature due to spin-exchange interaction between the nitric oxide molecule and the metal. The second effect arises from the dimerization of nitric oxide, $2NO \rightarrow (NO)_2$. In this reaction, the unpaired electrons in the nitric oxide molecules become paired in the dimers;[6] an increase of the critical temperature results due to an elimination of the unpaired spins. The former mechanism is predominant for small concentrations of nitric oxide, while the latter dominates for thick nitric oxide films.

In further experiments, a monolayer of nitric oxide was deposted on superimposed films of aluminum and nitro-

(1) H. M. McConnell, B. Hoffman, D. D. Thomas, and F. Gamble, *Proc. Natl. Acad. Sci. U. S.*, **54**, 371 (1965).

(2) B. M. Hoffman, F. R. Gamble, and H. M. McConnell, *J. Am. Chem. Soc.*, **89**, 27 (1967).

(3) H. M. McConnell, F. R. Gamble, and B. M. Hoffman, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1131 (1967).

(4) E. A. Lynton, "Superconductivity," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

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(6) W. J. Dulmage, E. A. Meyers, and W. N. Lipscomb, *J. Chem. Phys.*, **19**, 1432 (1951).

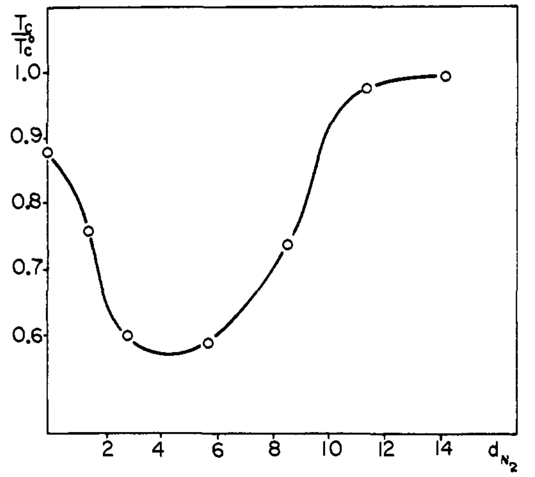

Figure 2. Reduced critical temperature, T_c/T_c^0, *vs.* thickness of nitrogen, d_{N_2}, in monolayers for superimposed 25-Å aluminum–nitrogen–one monolayer of nitric oxide films.

gen. A 25-Å film of aluminum was deposited on silicon monoxide which was then exposed to nitrogen at a pressure of 1×10^{-7} Torr for periods of 30–300 sec. Figure 2 gives the reduced critical temperature as a function of the nitrogen thickness in "monolayers"[7] for a 25-Å aluminum–nitrogen–one monolayer of nitric oxide sandwich. For increasing nitrogen thicknesses, the critical temperature is reduced more than if no nitrogen were present. At three to five monolayers of nitrogen, the critical temperature reaches a minimum at approximately 60% of its original value. Additional nitrogen causes the critical temperature to increase until the nitric oxide causes essentially no reduction beyond 15 monolayers of nitrogen.

These results again reflect two competing mechanisms: one which decreases the critical temperature and one which returns it to its original value. First, a thin nitrogen film inhibits nitric oxide dimerization on the aluminum surface, so that a lower critical temperature can be produced for a given amount of nitric oxide. The subsequent increase in the critical temperature after the minimum has been attained can be explained by complete surface coverage by nitrogen.[7]

A simultaneous codeposition of nitric oxide and aluminum at 4.2°K produces an enhancement in the critical temperature. In this case, there may well be conductive conjugation, although the observed enhancement may be due to a "softening" of the aluminum lattice.[8]

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(7) Our "monolayer" of nitric oxide is defined as that amount which adheres to the surface after an exposure of 46 sec to a nitric oxide partial pressure of 6×10^{-8} Torr. It is estimated to be 3.4 Å. One "monolayer" of nitrogen is similarly defined to be produced after an exposure of 21 sec to a nitrogen partial pressure of 1×10^{-7} Torr and corresponds to 3.6 Å. An accommodation coefficient of unity is assumed in both definitions.

(8) F. R. Gamble and E. J. Shimshick, *Phys. Letters*, **28A**, 25 (1968).

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Inefficiency in the Photosensitized Dimerization of Indene

Sir:

Although photochemical cyclodimerization reactions are widely known,[1] the details of many of these reactions have not been studied. Hammond[2] has suggested that photosensitized dimerization reactions proceed by an energy transfer mechanism (eq 1–5). Schenck[3] and

$$\text{sensitizer} + \text{light} \rightarrow {}^1\text{sen}^* \rightarrow {}^3\text{sen}^* \qquad (1)$$

$$ {}^3\text{sen}^* \rightarrow \text{sen} \qquad (2)$$

$$ {}^3\text{sen}^* + \text{indene} \rightarrow {}^3\text{indene}^* + \text{sen} \qquad (3)$$

$$ {}^3\text{indene}^* \rightarrow \text{indene} \qquad (4)$$

$$ {}^3\text{indene}^* + \text{indene} \rightarrow \text{dimer} \qquad (5)$$

Metzner,[4] on the other hand, have suggested that the photosensitized dimerization of indene proceeds through a diradical sensitizer–indene complex. In this paper it

$$\begin{array}{l} \text{sen} + \text{light} \rightleftarrows \text{sen}^* + \text{indene} \rightleftarrows \\ \qquad\qquad \bullet\text{sen–indene}\bullet + \text{indene} \rightarrow \text{sen} + \text{dimer} \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad \text{sen} + \text{indene} \end{array}$$

will be shown how quantum yield measurements on the dimerization of indene limit the possible choice of mechanisms.

The quantum yields[5] of dimerization of indene were measured as a function of the concentration of indene. The results are given in Table I. If reactions 1–5 occur, the reciprocal of the quantum yield of dimer formation will be given by expression A.

$$\phi^{-1} = (1 + k_4/k_5[\text{indene}])(1 + k_2/k_3[\text{indene}]) \qquad (A)$$

The data of Table I have been plotted in Figure 1. The plots are linear, indicating that k_2 is much smaller than k_3[indene], just as expected. The most striking feature of these plots is that the intercepts are all greater than five, instead of unity as predicted by expression A. Since the intercepts correspond to infinitely concentrated indene solution, only reactions involving indene will be important. *The results require an energy-wasting step involving ground-state indene.* Such a reaction could be either (6) or (7). In order to distinguish between reactions

$$ {}^3\text{sen}^* + \text{indene} \rightarrow \text{sen} + \text{indene} + \text{heat} \qquad (6)$$

$$ {}^3\text{indene}^* + \text{indene} \rightarrow 2\text{indene} + \text{heat} \qquad (7)$$

6 and 7, an equimolar mixture of indene and *trans*-stilbene was irradiated with either benzophenone or Michler's ketone as the sensitizer. It was found that the quantum yield of stilbene isomerization was unchanged by the presence of indene and that indene dimer formation was completely quenched. If it is assumed that energy transfer is diffusion controlled from the sensitizer to

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(1) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 739.

(2) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

(3) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962).

(4) W. Metzner, Dissertation, University of Bonn, 1966.

(5) Filtered 3660-Å light was used. The actinometer was the benzophenone-sensitized isomerization of *trans*-stilbene. The dimers formed were measured by gas chromatography. Measurement of the disappearance of indene showed there were no side reactions. Other tests showed the products of the reaction were stable to the analytical conditions.