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REACTIONS OF DIPHENYLDIAZOMETHANE IN THE PRESENCE OF BIS(ACETYLACETONATO)COPPER(II).

MODIFIED DIPHENYLMETHYLENE REACTIONS

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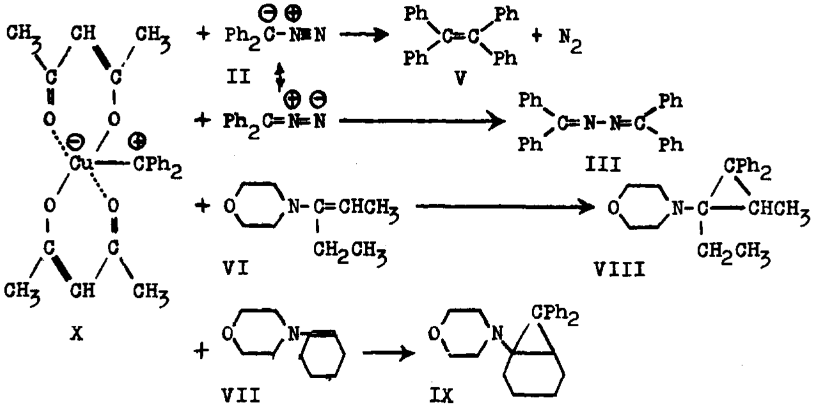
A recent report (1) on the decomposition of diazoacetophenone in alcohols containing bis(acetylacetonato)copper(II) (I), which affords alkoxyacetophenones instead of alkyl phenylacetates, has prompted the publication of independent observation on the reaction of diphenyldiazomethane (II) catalyzed by I.

Thermolysis of II in benzene proceeds slowly to give benzophenone azine (III) (2) and in hydrogen-donating solvents 1,1,2,2-tetraphenylethane (IV) is obtained (2,3). We have now discovered that the copper complex I is an active catalyst for this decomposition and modifies the diphenylmethylene reactions as summarized below.

A homogeneous benzene solution of the diazomethane II containing 0.08 molar equivalent of the copper complex I was heated under reflux for 3 hr., when the smooth nitrogen evolution had ceased. Chromatographic separation of the products on an alumina column afforded tetraphenylethylene (V) in an 86% yield,



besides the azine III (4%). Similar decomposition in cyclohexane yielded III (44%) and V (52%). A trace of the ethane derivative IV was detected among products in cyclohexane. In contrast, however, a poor amount (5-6%) of IV was isolated when the reaction was carried out in ethereal solvents such as tetrahydrofuran, ethyl vinyl ether and styrene oxide (5), in which the reaction proceeded rather sluggishly. Notably, the catalytic action of I was practically suppressed in pyridine solution possibly by coordination (6). Cupric sulphate and copper powder were found to be less favourable catalysts yielding IV along with III and V.

Attempts to obtain diphenylmethylene adducts to ethylenic double bonds by the present catalytic reaction failed with cyclohexene or ethyl vinyl ether as a solvent, while certain enamines afforded the corresponding cycloadducts (7). A solution of the diazomethane II dissolved in excess diethyl ketone morpholine enamine (VI) or cyclohexanone enamine (VII) was added dropwise to a boiling benzene solution of 0.1 molar equivalent (based on II) of the copper complex I, and the mixture was heated under reflux for 3 hr. to afford the respective adducts, 1-ethyl-2-methyl-2-morpholino-3,3-diphenylcyclopropane (VIII), m.p. 132-133° (11%) and 1-morpholino-7,7-diphenylbicyclo[4.1.0]heptane (IX), m.p. 111-112° (62%). By-products were III and V. The adducts were found homogeneous on t.l.c. and the assigned structures were consistent with elemental analyses, mass (8), infrared, ultraviolet (9), and NMR spectra (10).

The striking feature of the aforementioned reactions is the apparent electrophilic nature of the diphenylmethylene carbon and this would reasonably be explained by assuming the intermediacy of a carbene complex X, or an inverse ylide (11) presumably having the structure analogous to those of known pyridine adducts of I (6).

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5. Tetraphenylethane was mostly isolated as a 1:1 molecular complex with the azine III. See ref. 2.

6. For the pyridine adducts of I and related compounds, see (a) D. P. Graddon, J. Inorg. & Nuclear Chem. **14**, 161 (1960); (b) D. P. Graddon and E. C. Watton, J. Inorg. & Nuclear Chem. **21**, 49 (1961); (c) D. Hall, S. V. Sheat and T. N. Waters, Chem. Ind. (London) 1423 (1965).

7. Addition of carbenes to enamines is known: (a) J. Wolinsky, D. Chan and R. Novak, Chem. Ind. (London) 720 (1965); (b) U. Schöllkopf and E. Wiskott, Angew. Chem. **75**, 725 (1963). For electrophilic attack of enamines by bis(iodomethyl)zinc, see (c) G. Wittig and F. Wingler, Chem. Ber. **97**, 2146 (1964).

8. The m/e and assignment of prominent peaks are given. VIII: 321 (molecular peak), 234 (weak, M - 87 (morpholine)), 167 (very strong, benzhydryl or rearranged $C_{13}H_{11}$ cation(s)), and 154 (base peak, M - 167); IX: 333 (molecular peak), 246 (weak, M - 87), 167, and 166 (base peak, M - 167). Isotope abundances also supported the formulas given.

9. In 99% ethanol both adducts showed no maximum above 220 mμ. Shoulders were observed for VIII at 259 mμ (log ϵ 3.10) and for IX at 260 (2.88), 266 (2.81) and 274 mμ (2.55).

10. The spectra were taken in benzene solution on 60 Mc. machine and chemical shifts are given in p.p.m. from internal tetramethylsilane reference. The adduct VIII showed a multiplet of methylene protons adjacent to oxygen at 3.12 (4H), a triplet (J 4.5 c.p.s.) of methylene protons adjacent to nitrogen at 2.59 (4H), a multiplet due to methylene protons

of ethyl group at 2.30-1.65 (2H), a complex multiplet arising both from methine proton of the cyclopropane ring and from methyl protons of the ethyl group at 1.27-0.70 (4H), and a doublet (J 6.5 c.p.s.) of methyl group attached to the cyclopropane ring at 1.00 (3H). Examples of such nonequivalent methylene protons of ethyl group can be found in N. S. Bhacca, D. P. Hollis, L. F. Johnson and E. A. Pier, NMR Spectra Catalog, Spectrum No. 558, 519, etc., Varian Associates, Pallo Alto, Calif., 1963. The adduct IX showed a multiplet at 3.29 (4H) and a triplet (J 4.8 c.p.s.) at 2.37 (4H) both originating from morpholino group, besides two broad signals centering at 1.9 (4H) and at 0.9 (5H) and arising from cyclohexane ring protons. No signal due to ethylenic proton(s) was observed in each spectrum.

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