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STUDIES ON THE ORIGIN OF ALLYLIC C-H "INSERTION" PRODUCTS IN ADDITIONS OF DIMETHYL DIAZOMALONATE TO OLEFINS. THERMOCATALYTIC REACTION OF DIAZOMALONATE WITH DICYCLOPROPYL ETHYLENE

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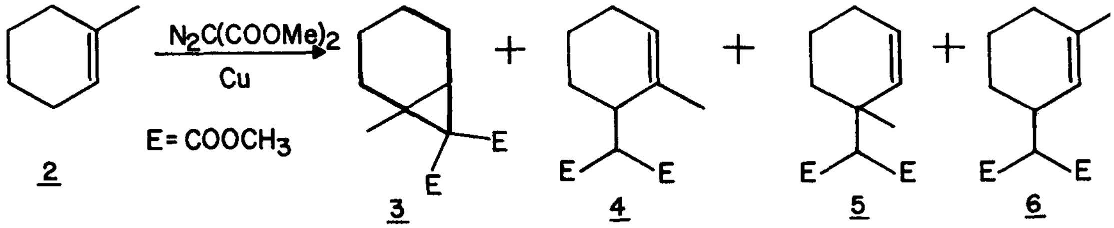
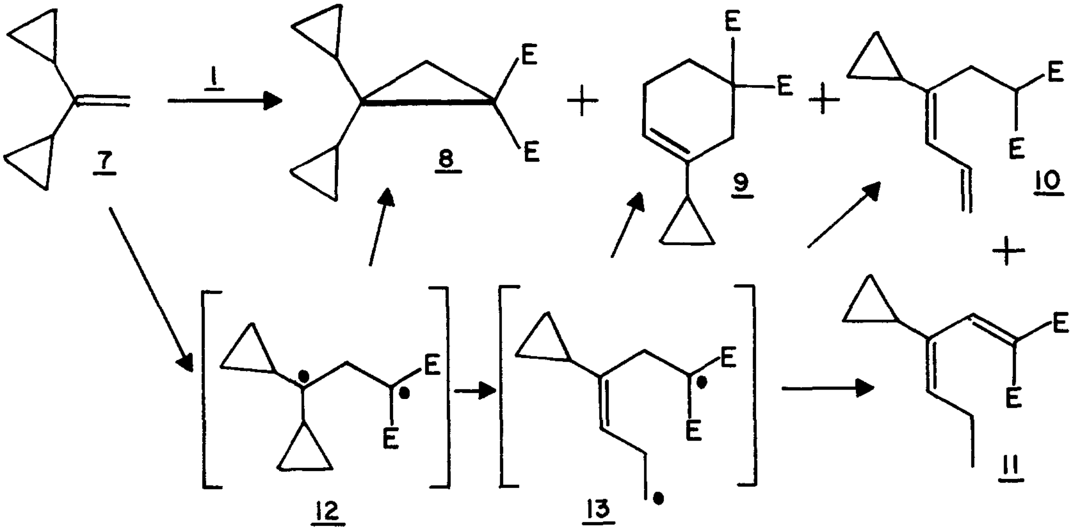
The copper catalyzed reaction of methyl diazomalonate with dicyclopropyl ethylene gives only the 1+2 adduct in up to 88% yield. No rearrangement compounds are produced. Thermolysis of this adduct furnishes the product of cyclopropane ring disconnection only without rearrangement.

When alkyl diazoacetates are exposed to a wide variety of alkenes in the presence of copper salts at 60 - 150° cyclopropanes usually result along with little or no C-H insertion or rearrangement products[1]. Conversely, diazomalonic esters furnish an assortment of compounds under the same conditions whose origin has not been well established[2]. The production of variable amounts of diesters <u>4</u> - <u>6</u> during the copper catalyzed addition of methyl diazomalonate <u>1</u> to 1-methylcyclohexene[2,3] prompted us to investigate the mechanisms entailed in their formation, since these have been briefly described either as a direct allylic C-H insertion process of a partly triplet-like copper carbenoid species or as C-H insertion at the most highly substituted position with concomitant rearrangements of unspecified nature[3,4]. More recently the participation of copper hydrocarbenoid or copper hydride species paired to an allylic carbocation obtained as a consequence of the formation of only one new carbon-carbon bond in the cyclopropanation reaction has been postulated on the basis of relative product distribution in additions of <u>1</u> to a limited number of cyclohexenes to account for the generation of cyclopropanes and formal allylic C-H insertion products from a common intermediate[4b,5]. Nevertheless, the possible participation of electron transfer processes and diradical intermediates[6] was not evaluated. Below we report the outcome of experiments addressed to this issue.

The substrate employed in the present study, dicyclopropyl ethylene, allows for the intermediacy of diradical species, hence the presence of a triplet-like carbenoid, to be detected[7] during the copper catalyzed addition of <u>1</u> and the thermolysis of the cyclopropane adducts derived therefrom, by virtue of the fast decomposition of cyclopropylcarbinyl free radicals[8] whereby compounds <u>9</u>, <u>10</u>, and <u>11</u> would be formed. Furthermore, actual allylic C-H insertion product <u>14</u> and compound <u>15</u> obtained *via* homo-1,5-hydrogen shift[8a,9] would readily be identified.


N₂C(COOMe)₂
Cu
E= COOCH₃
2
3
4
5
6
E


1
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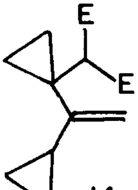

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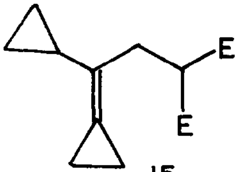

15


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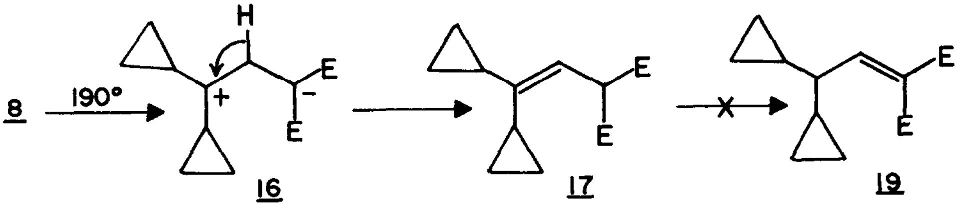
8
190°
H
+
−
E
16
17
19

Bis(acetoacetonato)copper(II) catalyzed decomposition of 1 in excess 7 and benzene (80°, 24 h) gave only dicyclopropyl cyclopropane diester 8 which was isolated from the reaction mixture by vacuum distillation {bp 129-30°(bath)/0.25 Torr}; ir (neat) C=O 1730 (s), C-O 1250 (s) cm^{-1}; nmr (CCl_4) δ 0.28-0.75 (m, 8, $4CH_2$ of cyclopropanes), 0.90-1.18 (m, cyclopropyl methynes), 1.18 (s, 2, CH_2 of cyclopropane), 3.69 (s, 6, OCH_3) ppm. Analysis: Calcd. for $C_{13}H_{18}O_4$: C,65.51; H,7.62; O,27.87; Found: C, 65.37; H, 7.52; O, 27.11. Neither rearrangement compounds 9, 10, and 11, nor C-H insertion product 14, nor tetramethoxycarbonyl ethylene -diazomalonate carbene dimer- were detected in the crude reaction mixtures. Changes in diazocompound/catalyst ratio (see Table I) and in type of catalyst did not alter the product composition.

These results can best be interpreted by the assumption that, on the one hand, either a singlet-like copper carbenoid or a diazo copper complex is involved in the addition step, and not a triplet-like carbenoid as contended before[3]. Also, the participation of diradical intermediates may be ruled out for this reaction while the contribution of polar species or a concerted 1 + 2 addition are probably dominant. On the other hand, the absence of formal C-H insertion products such as 14 casts doubt as to whether Wulfman's proposition[4b] on the abstraction of an allylic hydrogen to furnish a hydrocarbenoid is generally tenable, although C-H insertion reactions of cyclopropane hydrogens are expected to be more difficult than those of allylic C-H bonds of aliphatic compounds.

TABLE I

EFFECT OF CATALYST $\{Cu(AcAc)_2\}$/DIAZOCOMPOUND MOLAR RATIO ON PRODUCT DISTRIBUTION IN THE ADDITION OF METHYL DIAZOMALONATE TO DICYCLOPROPYL ETHYLENE AT ca. 80° FOR 24 HOURS.*

CATALYST/ 1 (molar ratio) X 10^3	Compound 8** (%)	Unreacted 1*** (%)
6.12	29	61
12.23	67	15
24.46	83	--
44.04	88	--

*) Product composition was determined by GC-mass spectrometry analysis using a 5 ft 10% SE-30 column at 110°C.

**) Yield of isolated product.

***) Yield of recovered methyl diazomalonate.

When the reaction of 1 with 7 was performed for prolonged periods of time (over 36 hours) olefinic material became apparent in the crude mixture. This product was identified as compound 17 on the basis of its spectral data (*vide infra*). In order to account for this phenomenon, pure dicyclopropylcyclopropane diester 8 was thermolyzed in the liquid phase at 190°. As much as 50%

conversion to 17 {nmr (CCl_4) δ 0.10-0.80 (m, 8, $4CH_2$ of cyclopropanes), 1.15-1.70 (m, 2, cyclopropane methyne), 3.72 (s, 3, OCH_3), 3.77 (s, 3, OCH_3), 4.50 (d, 1, J= 6.0 Hz, allylic methyne), 5.42 (d, 1, J= 6.0 Hz, vinyl methyne)}[10] was observed after 60 minutes[11]. Rearranged compounds were not obtained suggesting that for 18-type trimethylene derivatives, cyclopropane bond disconnection does not take place via diradical intermediates in the liquid phase as suggested previously[8a,12], but rather via an ionic process in agreement with other work[13]. Sequence 8→16→17 provides a feasible explanation of this occurrence. It is noteworthy that migration of the double bond in 17 to the thermodinamically more stable α,β-unsaturated diester 19 was not witnessed

REFERENCES AND NOTES

1) V. Dave and E.W. Warnhoff, Org. React., 18, 217 (1970).

2) a) B.W. Peace and D.S. Wulfman, Synthesis, 137 (1973) and ref. cited.
b) Apparent allylic C-H insertion products have also been reported in reactions of methyl diazomalonate with vinyl ethers; see: E. Wenkert, M.E. Alonso, B.L. Buckwalter, and K.J. Chou, J. Am. Chem. Soc., 99, 4778 (1977).

3) D.S. Wulfman, B.W. Peace, and E.K. Steffen, J.C.S. Chem. Commun., 1360 (1971)

4) Care must be excersised in the design and interpretation of experiments directed towards the elucidation of the mechanisms of metal-salt catalyzed carbenoid additions to olefins. The available data at the present time is clearly insufficient. For an enlightening review on this subject see: a) D. S. Wulfman, Tetrahedron, 32, 1231 (1976); b) D.S. Wulfman, R.S. McDaniel, Jr. and B.W. Peace, ibid., 32, 1241 (1976); c) D.S. Wulfman, B.W. Peace, and R.S. McDaniel, Jr., ibid., 32, 1251 (1976).

5) This hypothesis, however, does not explain the absence of sterically favored exocyclic C-H insertion products in additions to 1-methyl cyclohexene and 1,2-dimethyl cyclohexene. See reference 2.

6) a) R.A. Firestone, J. Org. Chem., 41, 2212 (1976); b) W. Kirmse, Carbene Chemistry, 2nd Edit., Academic Press, New York 1971.

7) a) N. Shimitzu and S. Nishida, J.C.S. Chem. Commun., 389 (1972); O.M. Nefedov, I.E. Dolgü, I.B. Sheredova, and R.N. Shafan, Izv. Akad. Nauk SSSR. Ser. Khim., 1885 (1972) {Chem. Abstr., 77, 164071 (1973)}.

8) The rearrangement of a cyclopropyl methyl radical at 30° is 10^3 times faster than the 1,5-hydrogen shift at 370°; see: J.J. Gajewski, R.J. Weber, R. Braun, M.L. Manion, and B. Hymen, J. Am. Chem. Soc., 99, 816 (1977); b) D.J. Carlsson and K.U. Ingold, ibid., 90, 7047 (1968).

9) W. Ando, Tetrahedron Lett., 929 (1969).

10) This nmr spectrum was identical to the one observed when the reaction mixture was heated for long periods of time.

11) Neither conversion of 8 to 11[7a] nor transformation of 8 into 15 was observed.

12) P.H. Mazzocchi and H.J. Tambourin, J. Am. Chem. Soc., 97, 555 (1975).

13) S. Danishefski and G. Rovnyak, J. Org. Chem., 40, 114 (1975) and ref. cit.

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