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The Reaction of Dicyclopentadiene with Ethyl Diazoacetate

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The reaction of *endo*-dicyclopentadiene (**1**) with ethyl diazoacetate (**3**) was carried out in the presence of several copper compounds. Two patterns of reaction were observed, depending on the type of copper compound used; the following schemes were proposed for the two reactions. I: The reaction proceeds through a coordination of the olefinic group to copper to form an olefin-copper complex, followed by an attack of the diazo compound on the complex. II: The reaction proceeds through a coordination of the diazo compound to copper to form an inversed ylide (**11**), followed by an electrophilic attack of the carbonium-ion center in **11** on the olefin to form a three-membered cyclic transition state, **12**.

It has been believed that the copper-catalyzed reactions of aliphatic diazo compounds with olefins involve copper-carbene-olefin complexes in the final stage of the reaction.[1] The scheme has been confirmed by the stereochemical relation of products with the variation in the electronic and steric factors of the ligands in the catalyst,[2] and by the introduction of chirality into the products in the reaction catalyzed by the chiral copper compounds.[3] With a view to clarifying how copper compounds participate in the transition state in these reactions, the reaction of *endo*-dicyclopentadiene with ethyl diazoacetate was carried out under several conditions.

Results

When *endo*-dicyclopentadiene (**1**) or its copper(I) chloride complex (**2**) was reacted with ethyl diazoacetate (**3**), compounds **4**—**8** were obtained in the yields shown in Table 1. Compound **9** was obtained when the reaction was carried out in the presence of triethyl phosphite (**10**). The yields were obtained by gas-chromatographic analysis, and the product identifications for new compounds were carried out as follows.

The structures of **6** and **7** were speculated to have a cyclopropane ring fused to a cyclopentane ring, judging from the IR bands characteristic of the double bond in a strained norbornene system,[4] which appeared at 1570 cm^{-1} for **6** and at 1574 cm^{-1} for **7**. The struc-

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[1] For a recent review, see V. Dave and E. W. Warnhoff, "Organic Reactions", Vol. 18, ed. by W. G. Dauben, John Wiley & Sons, Inc., New York, N. Y. (1970), p. 217.

[2] W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135, 1141 (1969).

[3] H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

[4] B. W. Cook, R. Miller, and P. Todd, *J. Organometal. Chem.*, **19**, 421 (1969).

TABLE 1. REACTION CONDITIONS AND PRODUCT DISTRIBUTIONS IN THE REACTION OF **1** OR **2** WITH **3**[a)]

Reaction	Substrate	Copper compound[b)]	Solvent[c)]	Temp(°C)	**4**	**5**	**6**	**7**	**8**	**8**/(**6**+**7**) Ratio
1	**1**	CuCl	AN	20—21	2.3	0.7	0.1	0.3	17.9	41.6
2	**2**		D	17—19	7.2	1.4	trace	trace	55.3	great
3	**1**	$\text{CuCl}_2\cdot 2\text{H}_2\text{O}$	D-W	40—50	4.3	1.1	1.1	0.6	8.6	5.1
4	**1**	CuSO_4	D-W	55	1.2	1.2	0.2	0.6	6.9	8.1
5	**2**		DMSO	15—17	16.3	12.5	0.2	0.6	3.0	3.8
6	**1**	Cu(acac)_2[d)]	D	65	4.4	5.4	5.3	27.9	34.5	1.0
7	**1**	**2**[d)]	D	67	9.9	10.8	1.0	4.3	5.6	1.1
8[e)]	**1**	**10**·CuCl	D	40	—[f)]	2.3	2.0	5.0	7.0	1.0

a) No account was taken of the low-boiling fractions (for instance, ethyl chloroacetate).
Although the mass balance of the reaction is not satisfactory, we consider the ratio **8**/(**6**+**7**) represented in this table is still meaningful, because the ratio is independent of the reaction conditions (reaction time or length of induction period) in a respective reaction, while the actual yields of products are more or less influenced.
b) Unless otherwise stated, equimolar amount to substrate was used.
c) AN: acetonitrile; D: dioxane; D-W: dioxane-water (1:1).
d) One-tenth equivalent was used.
e) **9** (8.5%) was also obtained.
f) The peak on the gas chromatogram overlapped with that of a phosphorus-containing substance.

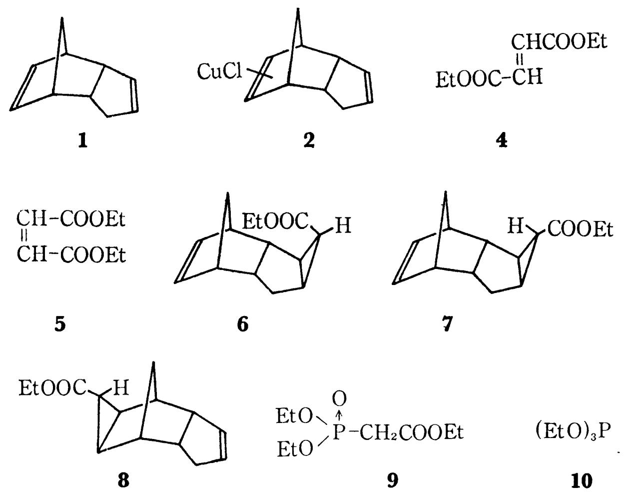

Chart 1

tures were also supported by the deformation bands of C–H in a cyclopropane ring fused to a cyclopentane ring,[5] which appeared at 999 cm^{-1} for **6** and at 1011 cm^{-1} for **7**. The *exo*-configuration of the cyclopropane ring was tentatively assigned on the basis of the steric consideration that the alternative configuration would result in an enormous nonbonded steric repulsion.[5] Since the steric repulsion created by the ethoxycarbonyl group and the hydrogen atoms in the norbornene system would be more serious in **6** than in **7**, the structure **7** was assigned to the major product.

The structure of **8** was supported by the elemental analysis and by an IR band at 1612 cm^{-1}, characteristic of the double bond in a cyclopentene ring, and a band at 1026 cm^{-1}, the deformation band of C–H in a cyclopropane ring fused to a norbornane system.[5] The stereochemistry of the cyclopropane ring and the ethoxycarbonyl group was assigned in a similar way.

The structure of **9** was assigned on the basis of the elemental and spectroscopic analyses. The IR spectrum showed an ester carbonyl band at 1745 cm^{-1}. The NMR spectrum showed a doublet at δ 2.73 (2H, J=20 Hz) for $-\text{CH}_2-\text{P}$, besides signals corresponding to three ethyl groups.

Discussion

Referring to the ratio of **8**/(**6**+**7**), we can classify the reactions into three groups: Class I (Reactions 1—2) with higher ratios, Class II (Reactions 3—5) with intermediate ratios, and Class III (Reactions 6—8) with lower ratios. This fact suggests that more than one mode of the participation of copper in the reaction is present. We assume that the diversity arises from the different ability of copper catalysts to coordinate to a double bond. It has been established that an olefinic ligand coordinates to a metal more readily when the metal is in a low oxidation state than when it is in a high oxidation state.[6] The rationale behind this might be that a metal with a lower valency, because of its formal abundance of electrons, back-donates its electrons into the antibonding orbital of the ligand more efficiently than does the same metal with a higher valency, thus providing a further stabilization for the metal-olefin complex. The donation and back-donation between the metal and the olefin might result in a net excitation of electrons from bonding to antibonding orbitals in the olefin, hence stabilizing the complex, particularly when the original olefin has much I-strain.[7] Actually, it has been established that, in the copper(I) complex of **1**, the copper atom coordinates selectively to the double bond in the strained norbornene ring, as is shown in **2**.[4] It may be suggested that, in Reaction 1, the catalyst participates in the reaction in the state of copper(I) with a strong coordinative power. The preferential formation of **8** over **6** and **7** can be explained by assuming an initial coordination of the strained double bond to the copper(I) atom, followed

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[5] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964).

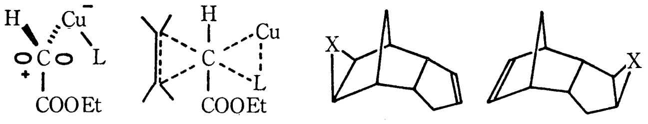
[6] M. L. H. Green, "Organometallic Compounds," Vol. 2, ed. by G. E. Coates, M. L. H. Green, and K. Wade, Methuen & Co. Ltd., London, (1968), p. 19.

[7] Ref. 6, p. 21.

by the attack of the diazo compound on the complex. That the reaction occurred in the near vicinity of the copper atom is evident from the fact that the complex **2** reacted with ethyl diazoacetate to form **8** predominantly (Reaction 2).

In reactions of Class III, on the other hand, both double bonds in **1** are involved in the reaction to a similar extent, thus indicating that the coordination of the metal has not played any important role in the reaction. Unlike the reactions in Class I, reactions in this class exhibit an induction period: the reactions proceeds smoothly at 40—65 °C only after the reaction has started at a higher temperature with the addition of one-third of the total amount of diazo compound. This indicates that the catalyst as such is not the actual species catalyzing the reaction. Although the exact state of this species is uncertain, we consider that copper is involved in the reaction in a state with a poor coordinative power. This consideration is consistent with the fact that the ratio (**8**/(**6**+**7**)) is quite low in Reaction 8, where the copper compound has been coordinatively saturated with the phosphorus ligand, although we observed no induction period.

Both reaction schemes (with strong and poor coordinative power of the metal) seem to occur competitively in reactions in Class II. This seems reasonable in view of the fact that copper(II) chloride is reduced partly to copper(I) chloride by ethyl diazoacetate.[8] Probably the same situation is also found with copper(II) sulfate. Furthermore, the reaction pattern of **2** (Reaction 2) was altered from Class I to Class II when the solvent was changed from dioxane to DMSO (Reaction 5). It is conceivable that a strongly coordinative solvent might partly expel copper from the complex, **2** thus providing a reaction pattern typical of reactions in Class III.



11 **12** **13** **14**

a: X=O **b**: X=CH$_2$

Chart 2

We feel that Moser's model,[2] which places emphasis on the coordination of copper to a double bond, is not suitable to explain the results we have presented thus far; we propose the following scheme for the reactions in Class III: the diazo compound attacks the copper compound to form an inversed ylide, **11**, and then the carbonium-ion center in **11** undergoes an electrophilic attack on the olefin to form a three-membered cyclic transition state, **12**. A three-membered cyclic transition state was proposed in view of the general belief[9] that a norbornene double bond should react in preference to a cyclopentene double bond as long as the reaction proceeds through a four-, five-, or six-membered cyclic transition state. In a separate experiment, we observed that the epoxidation of **1** with peracid, which has been confirmed to proceed through a three-membered cyclic transition state,[10] afforded **13a** and **14a** in a ratio of 1.3 (**13a**/**14a**), while epoxidation through a radical mechanism, which involves the double-bond opening,[11] afforded **13a** in preference to **14a** by a factor of 9.5.[12] Moser[2] proposed a copper-containing four-membered cyclic transition state rather than a three-membered cyclic transition state such as **12** for the present type of reaction, because no interaction causing the observed steric effects of ligands can be expected with the latter model. We are, however, of the opinion that the reaction scheme through the transition state **12** could also be susceptible to the steric effects, since the size of ligands in the copper compound **11** would sterically control the mode of approach of **11** to an olefinic group. Moreover, we consider that a transition state in which steric interaction between the reagent and the substrate are effective *to only a minor extent* is preferable in view of the following facts. The selective additions of dichlorocarbene[13] and dichloroketene[14] to the cyclopentene ring of **1** have been reported, and the unusual behavior in these cases has been interpreted in terms of the steric interaction between reagents and the hydrogen atoms in the norbornene system. Apparently, if the reaction between **1** and **3** proceeded through a transition state in which a considerable ligand effect can be expected, the formations of **6** and **7** would predominate, in contrast with the observed results. A good example favoring the present transition state, **12**, which is basically the same as that proposed for the Simmons-Smith reaction, has been provided by the observation[5] that the Simmons-Smith reaction of **1** afforded **13b** and **14b** in 12 and 11% yields respectively, as well as 63% of the diadduct.

Experimental

The IR spectra were obtained on JASCO IRS and Hitachi EPI-G3 spectrometers. The NMR spectra were measured on a JEOL MH-60 (60 MHz) spectrometer; the chemical shifts are represented in δ values relative to the internal TMS standard. The mass spectra were measured on a Hitachi RMS-4 mass spectrometer.

endo-*Dicyclopentadiene-copper(I) Chloride Complex (2).* This complex was prepared from **1**, CuCl$_2$·2H$_2$O, and SO$_2$ in 95% ethanol by the method used for the preparation of the 1,5-cyclooctadiene-CuCl complex reported by Baird.[15] Mp 112 °C (decomp.). Lit[4]: mp 115 °C (decomp.).

Triethyl Phosphite-copper(I) Chloride Complex. This complex was prepared according to the method reported by

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[8] T. Saegusa, Y. Ito, T. Shimizu, and S. Kobayashi, This Bulletin, **42**, 3535 (1969).

[9] R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry," Wiley-Interscience, London, (1971), p. 306; J. Rocek, *J. Amer. Chem. Soc.*, **91**, 991 (1969).

[10] D. Swern, "Organic Peroxides," Vol. II, ed. by D. Swern, Wiley-Interscience, New York, N. Y. (1971), p. 472.

[11] S. J. Moss and H. Steiner, *J. Chem. Soc.*, **1965**, 2372.

[12] T. Sato and E. Murayama, unpublished results.

[13] L. Ghosez, P. Laroche, and L. Bastens, *Tetrahedron Lett.*, **1964**, 3745.

[14] L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

[15] W. C. Baird, Jr., *J. Amer. Chem. Soc.*, **85**, 1009 (1963).

Arbusoff.[16)]

*Reactions of **1** with* **3**. A solution of **1** (1.32 g) and copper compounds (specified amounts shown in Table 1) in 25 ml of a solvent was kept at an appropriate temperature. A solution of **3** (1.14 g) in 5 ml of the corresponding solvent was then added dropwise over a period of 2 hr. In cases where no nitrogen evolution was observed, the reaction mixture was heated to 70—80 °C after one-third of the total amount of diazo compound had been added. After the nitrogen evolution had been observed (usually in 20—90 min), the reaction mixture was cooled to the original temperature and the remainder of the diazo compound was added. The reaction mixture was poured into cold hydrochloric acid (200 ml of ice water containing 20 ml of concentrated hydrochloric acid) and shaken with ether. Ether was then removed, the residue was distilled under a vacuum, and the distillate was analyzed by gas chromatography. The six fractions, in the order of retention time, were as follows:

4 and **5**: Their retention times on gas chromatography and NMR and IR spectra were identical with those of authentic samples.

9: IR (CCl_4): 1745 (vs), 1275—1255 (b, s) and 1060—1020 cm^{-1} (b, s); NMR (CCl_4): δ 4.3—3.7 (m, 6H), 2.73 (d, J=20 Hz, 2H) and 1.4—1.1 (m, 9H).

Found: C, 43.1; H, 7.8%. Calcd for $C_8H_{17}O_5P$: C, 42.9; H, 7.6%.

6: MS: *m/e* 218 (M), 189 ($M-C_2H_5$), 173 ($M-OC_2H_5$), and 152 (base peak, $M-C_5H_6$); IR (CCl_4): 2940 (vs), 1730 (vs), 1570 (w), 1145 (b, vs) and 999 cm^{-1} (m).

7: MS: *m/e* 218 (M), 189 (very weak, $M-C_2H_5$), 173 ($M-OC_2H_5$), 153 (base peak, $M-C_5H_5$) and 152 (M-C_5H_6); IR (CCl_4): 2960 (vs), 1730 (vs), 1574 (w), 1160 (b, vs), and 1011 cm^{-1} (m); NMR (CCl_4): δ 6.15—6.0 (m, 2H), 3.95 (q, 2H), 2.9—2.6 (m), 1.7—1.0 (m), and 1.2 (t).

8: MS: *m/e* 218 (M), 189 ($M-C_2H_5$), 173 (M-OC_2H_5) and 152 (M-C_5H_6); IR (CCl_4): 2930 (vs), 1728 (vs), 1612 (w), 1170 (b, vs) and 1027 cm^{-1} (m); NMR (CCl_4): δ 5.8 (q, 2H), 4.2 (q, 2H), 2.7—2.2 (m), 1.7—0.9 (m), and 1.25 (t).

Found: C, 76.8; H, 8.5%. Calcd for $C_{14}H_{18}O_2$: C, 77.0; H, 8.5%.

*Reactions of **2** with* **3**. A solution of **2** (2.3 g) in 25 ml of a solvent was kept at an appropriate temperature. A solution of **3** (3.2 g) in 10 ml of the corresponding solvent was then added drop by drop over a period of 2 hr, after which the mixture was stirred for an additional hour. The reaction mixture was then worked-up in the way described above.

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16) A. Arbusoff, *Ber*. **38**, 1171 (1905).