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SOME REPRESENTATIVE CYCLOADDITIONS OF VINYLCYCLOPROPANE. AN EVIDENCE FOR THE TWO-STEP PROCESS IN THE DONOR-ACCEPTOR TYPE CYCLOADDITION

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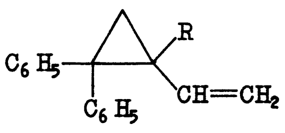
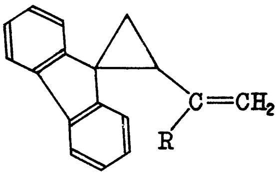
Reaction of 1,1-diphenyl-2-vinylcyclopropane with 2,3,4,5-tetrachlorocyclopentadienone ethylene ketal proceeded smoothly to give a diene adduct quantitatively, whereas its reaction with tetracyanoethylene gave unexpected adducts after rearrangements. These results evidence that the latter donor-acceptor type cycloaddition proceeds via a zwitterionic intermediate.

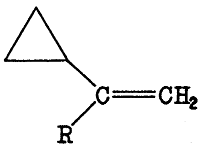
During the course of our study to develop a new substrate to investigate radical cycloadditions,[1] we prepared 1,1-diphenyl-2-vinylcyclopropane (1a)[2] as a challenging substrate possessing a larger k(cyclopropylcarbinyl-allylcarbinyl rearrangement) than k(diradical cyclization), and examined its reactions. In the present communication, we wish to report the results of cycloadditions of 1a, and related 1b—1f, with 2,3,4,5-tetrachlorocyclopentadienone ethylene ketal (2) and tetracyanoethylene (3). The results described below indicate that 1a could in fact be such a substrate as anticipated, which in turn provide an evidence that the reaction between 1 and 3 takes a two step process.[3]



1a : R = H
1b : R = CH_3

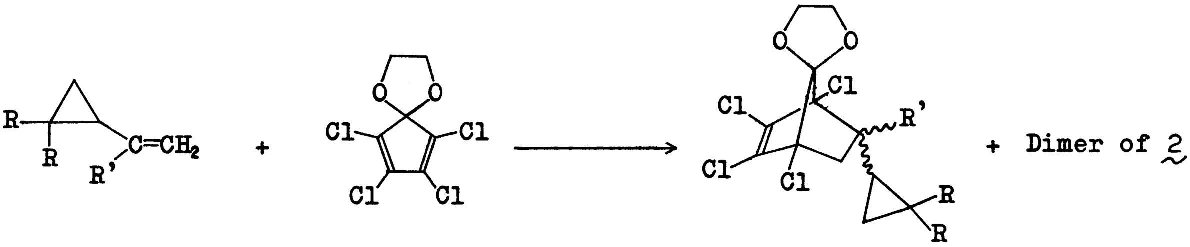


1c : R = H
1d : R = CH_3



1e : R = H
1f : R = cyclo-C_3H_5

Diels-Alder Reaction. Irrespective of the structural variation, the reaction of **1a**, **1e**, or **1f** with **2** proceeded smoothly at 110-190°C to give a diene adduct **4** quantitatively.[4] The fact that the change in the solvent polarity brought no effect both on the rates of reaction and on the course of reaction indicates that the present reaction reserves the characteristics of the Diels-Alder reaction.[5]



1a : R = R = C_6H_5 , R' = H

1e : R = R = R' = H

1f : R = R = H, R' = cyclo-C_3H_5

2

4a : R = R = C_6H_5 , R' = H (mp 197-198°C)

4e : R = R = R' = H (bp 130-135°C at 0.07 mm)

4f : R = R = H, R' = cyclo-C_3H_5 (mp 97.5-98°C)

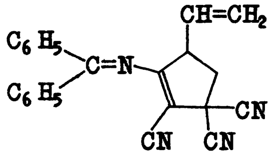
Reaction of **1** with Tetracyanoethylene (**3**). Contrary to the Diels-Alder reaction, the reaction of **1** with **3** takes two distinct routes depending on the structure of the olefin **1**.

The reaction of **1f** with **3** gave a 2 + 2 cycloadduct **5f** in a quantitative yield.[6] It was true even in the reaction at 147°C; no adduct other than **5f** was detected at a high temperature as well. The reaction of **1e** with **3** also yielded **5e**,[6] although the reaction was more sluggish than that of **1f**.

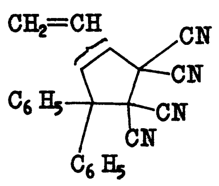
The reaction of **1a** (435 mg, 1.98 mmol) with **3** (253 mg, 1.98 mmol) in 1,2-dichloroethane (100 ml) at room temperature gave yellow needles (total 357 mg) and colorless plates (50 mg) after two months (with 157 mg recovery of **1a**). The both products were shown to be a 1 : 1 adduct of **1a** and **3** (EA and mass), but neither was found to be the 2 + 2 cycloadduct as above. The yellow crystals (mp 159-160°C) exhibited the following spectral characteristics: ir (Nujol) 2250(w), 2220(m), 1640(s) cm^{-1} and others; nmr ($CDCl_3$, 100°C)[7] δ 7.52 (s, 10 H), 5.70 (ddd, J = 16, 10, and 7 Hz, 1 H), 5.30 (br d, J = 10 Hz, 1 H), 5.20 (br d, J = 16 Hz, 1 H), 3.68 (br q, J = 8 Hz, 1 H), 2.86 (dd, J = 13 and 8 Hz, 1 H), 2.50 (dd, J = 13 and 9 Hz, 1 H); uv (ethanol) λ_{max} (log ε) at 274 (4.31) and 335^{sh} nm (3.38). Thus the structure **6a** is deduced for the yellow crystals. The structure was further supported by an observation that acid-catalyzed hydrolysis of **6a** yielded benophenone

(48%) and crystalline enamine 8 (mp 182-184°C, 90%).

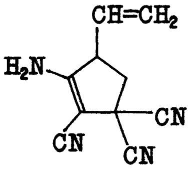
The colorless crystals (mp 171-172°C) obtained in a minor amount are tentatively assigned as 7 from EA, mass, ir, nmr, and uv. Yields of 6a and 7 based on the consumed amount of 1a were 81% and 11%, respectively.



6a

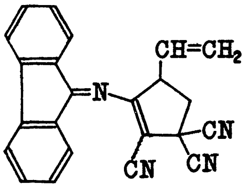


7

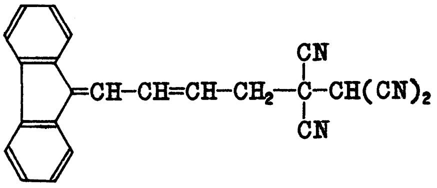


8

Similarly, the reaction of 1c with 3 produced 6c (yellow, mp 177-179°C, 39%) and a new compound 9c (greenish yellow, mp 181-182°C with dec, 48%). Acid-hydrolysis of 6c gave fluorenone (92%) and the enamine 8 (66%), while permanganate oxidation of 9c yielded fluorenone (80%) and oxalic acid hydrate (50%).



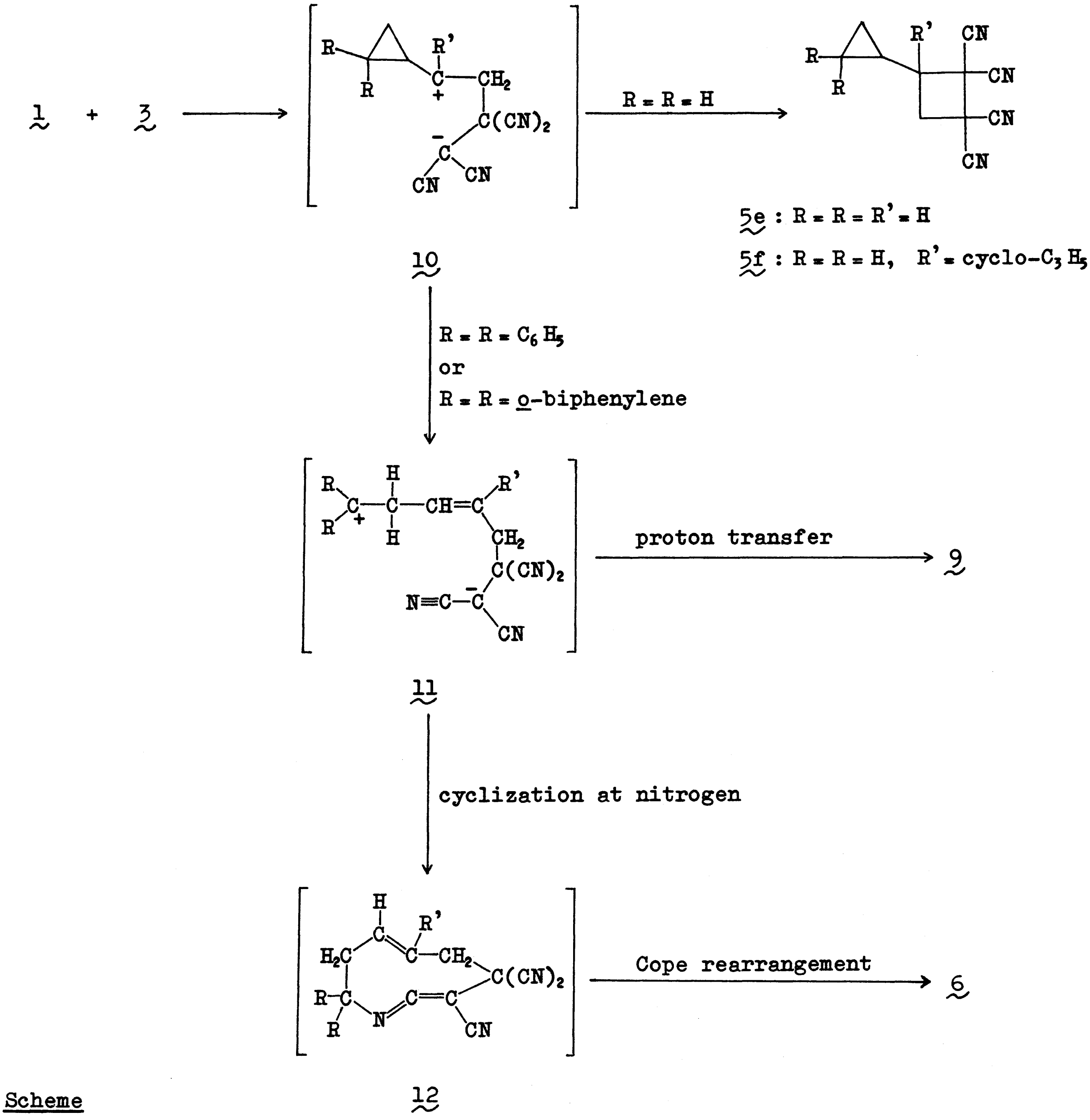
6c



9c

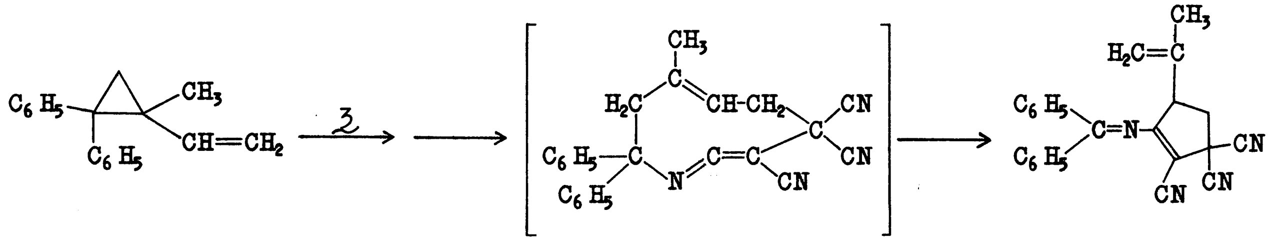
Discussion. The result that the Diels-Alder reaction gave no adduct other than the normal diene adduct is in accord with an expectation that the reaction proceeds in a concerted fashion. On the other hand, the reaction between 1 and 3 should take a stepwise process because the formation of unexpected adducts (6, 7, and/or 9) can be accomplished only after a cleavage of the three-membered ring. Thus, this donor-acceptor type cycloaddition should most reasonably be explained by the reaction scheme shown below. A zwitterion 10, derived from 1 and 3, will take two competing routes, a ring closure to 5 and a cyclopropylcarbinyl-allylcarbinyl rearrangement to the second zwitterion 11. This competition seems to be ruled by a substituent on the three-membered ring. When the ring carries no substituent, the cyclization process overwhelms the rearrangement; the barrier for the rearrangement must be sufficiently higher than that for the ring closure.[1]

The barrier is, however, lowered significantly by the aryl substitution on the three-membered ring.[8] Thus, in the reaction of **1a** or **1c** with **3**, the zwitterion **10** rearranges to **11** exclusively. The nitrogen atom of the cyano group in **11** then attacks the cationic center to give **12**, which undertakes a Cope rearrangement to afford **6**.[9] This is a major path in the reaction of **1a** with **3**, but a proton abstraction by the carbanion to yield **9** becomes a preferred path in the intermediate **11** derived from **1c** and **3**.[10] Steric hindrance will be a reason for the absence of **9** in the reaction of **1a** with **3**.



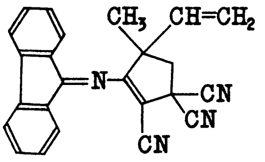
Scheme

The Cope rearrangement process in the scheme is supported by an observation that the reaction of **1b** with **3** resulted in the formation of **6b** (yellow, mp 152-152.5°C, 80%). The vinyl side chain in **1b** is no longer present in **6b**, but a 2-propenyl group is attached to the cyclopentene ring, which is most clearly demonstrated in its nmr: characteristic signals due to the 2-propenyl group are observed at δ 4.95 (s, 1 H), 4.75 (s, 1 H), and 1.73 (s, 3 H).

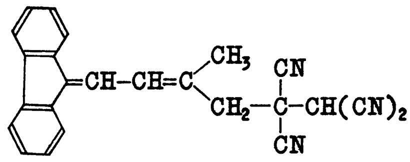


1b **6b**

Similarly, **1d** produced **6d** (yellow, mp 206-207°C, 38%) and **9d** (yellow, mp 180-181°C, 18%). These methyl labeling experiments strongly support the proposed mechanism described above.



6d



9d

It can thus be concluded that the present donor-acceptor type cycloaddition involves the zwitterionic intermediate, and hence the two step mechanism is adequate for this type of cycloaddition. A properly substituted vinylcyclopropane, therefore, could be used as a unique substrate to investigate the polar cycloaddition[11] as well as radical cycloadditions.

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REFERENCES AND NOTES

(1) (a) N. Shimizu and S. Nishida, *Chem. Commun.*, 389 (1972); (b) N. Shimizu and S. Nishida, *J. Amer. Chem. Soc.*, **96**, 6451 (1974); (c) N. Shimizu, M. Ishikawa, K. Ishikura, and S. Nishida, *ibid.*, **96**, 6456 (1974).

(2) The olefin **1a** was prepared by the photolysis of diphenyldiazomethane in 1,3-butadiene-ether mixture, bp 107-108° (0.4 mmHg), 78%.

(3) For reactions of vinyl ether and related compounds with **3**, the two step process has been proposed: (a) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2210 (1962); (b) P. D. Bartlett, *Quart. Rev.*, London, **24**, 473 (1970); (c) R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5054, 5055 (1973); (d) G. Steiner and R. Huisgen, *ibid.*, **95**, 5056 (1973).

(4) Although the stereochemistry was not firmly established, **4a** and **4e** might be the endo isomer (nmr). Since the first crop of the adduct from **1a** and **2** showed a considerably wide melting range, mp 164-180°C, the epimer might also be produced in a small amount. The dimer of **2** was produced in a varing amount in all runs.

(5) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

(6) S. Nishida, I. Moritani, and T. Teraji, *J. Org. Chem.*, **38**, 1878 (1973).

(7) Nmr abbreviations are: s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, q = quartet, br = a peak whose half-width is 2.5-4.0 Hz with splitting into triplet or multiplet with J = ca. 1 Hz.

(8) In the addition of CSI to vinylcyclopropane, Pasto and Chen reported that the reaction of *trans*-2-(prop-2'-enyl)phenylcyclopropane gave exclusively the cyclopropane cleaved adduct, whereas 2-cyclopropylpropene resulted in the formation of a β-lactam, a 2 + 2 cycloadduct with retention of the cyclopropane, at a low temperature (D. J. Pasto and A. F. T. Chen, *Tetrahedron Lett.*, 713 (1973)).

(9) The first cycloadduct **12** was not detected. An examination on a molecular model indicates that the cyclization of **11** at the nitrogen will be feasible in both *E*-**11** or *Z*-**11**.

(10) A molecular model shows that the intramolecular proton abstraction may be possible only in *Z*-**11**.

(11) In the CSI addition to olefins, the Wagner-Meerwein rearrangement has also been utilized to prove that the reaction proceeds in a stepwise fashion (J. R. Malpass and N. J. Tweddle, *J. C. S. Chem. Commun.*, 1244 (1972)).

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