Acc. Chem. Res. 1984, 17, 56-61

warning fire-detection system.[44] Poly(phenylacetylene) absorbs lights of long wavelength to exhibit a photoconductive property.[45]

Membranes for oxygen enrichment have recently been the subject of intensive research.[46] Poly(dimethylsiloxane) is famous for its highest permeability coefficient [P; cm^3(STP)·cm/(cm^2·s·cmHg)] to oxygen among those of the polymers so far examined (P_{O_2} = 6.0 × 10^{-8}; P_{O_2}/P_{N_2} = 1.9). We found that some of the present polymers exhibited fairly high permeabilities[47,48] (see Figure 2). Quite interestingly, poly[1-(trimethylsilyl)-1-propyne], which was prepared with halides of niobium (Nb) and tantalum (Ta) as catalysts, showed a value about 10 times larger than that of poly(dimethylsiloxane) (P_{O_2} = (61 × 10^{-8})–(83 × 10^{-8}); P_{O_2}/P_{N_2} = 1.7).[48] The high gas permeability of poly(dimethylsiloxane) has been attributed mainly to the large free volume resulting from the flexible backbone. Findings with the present polymers must be explained in other terms since the polymers are considerably rigid.

Concluding Remarks

In this account the effectiveness of Mo- and W-based catalysts for the polymerization of substituted acetylenes has been examined. We claim that the present polymerization is, following olefin metathesis and metathesis polymerization, the third important reaction mediated by W and Mo carbenes.

Recently it has been found that disubstituted acetylenes are polymerized by organo-Nb(III) and -Ta(III)[49] and by halides of Nb(V) and Ta(V).[48,50] It is worth noting that the latter catalysts afford poly(1-phenyl-1-propyne)[50] and poly[1-(trimethylsilyl)-1-propyne][48] whose molecular weights reach about one million. It is reported that acetylenes are polymerized by lanthanide-containing catalysts as well.[51] Thus the study on the polymerization of acetylenes will further advance, promoted by the exploitation of novel catalysts.

Only a few studies have been performed on the application of polymers from substituted acetylenes. We expect that useful functions will be developed.

We are grateful to Professor John K. Stille at Colorado State University who urged us to write this Account.

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Thermal Ring-Opening Cycloadditions of Cyclopropyl Derivatives with Activated Olefins

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Cyclopropane is conspicuous among alicyclic compounds by its similarity to olefins in its physical and chemical properties.[1] Thus, three-membered carbocycles are known to effectively conjugate with unsaturated groups, are susceptible to attack by electrophiles, and are capable of undergoing nucleophilic ring opening when the ring is activated with strongly electron-withdrawing groups.[1,2] In addition, the lability of cyclopropanes to homolytic ring cleavages[1] and the high ability of cyclopropyl groups to stabilize adjacent electron-deficient centers[3] have been well-documented. These multifaceted features confer various interesting aspects on the chemistry of cyclopropyl derivatives. Among such reactions that are characteristic to cyclopropyl derivatives, ring-opening cycloadditions with unsaturated compounds are of particular interest, since odd-membered ring compounds can be prepared from two fragments in a single operation.

In the structural and geometrical isomerizations of cyclopropanes, trimethylene biradicals are commonly

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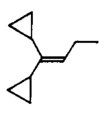
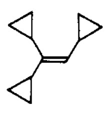
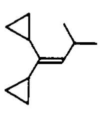
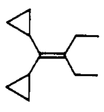
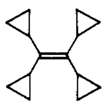
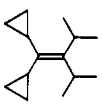
postulated as intermediates.[4] It is hence natural that considerable effort has been devoted to accomplish the interception of intermediate 1,3-diyls with unsaturated functions (diylophiles). However, successes reported so far have largely been limited to such reactions occurring intramolecularly;[5] the intermolecular trapping of the 1,3-diyls with diylophiles is generally not possible. The failure probably arises from the fact that the reclosure of trimethylene biradicals is so rapid that intermolecular processes cannot kinetically compete with it.[6] In the limited examples of the intermolecular cycloadditions of cyclopropyl derivatives, it has been demonstrated that only such cyclopropanes that are constructed in a highly strained molecular framework, such as bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane, are capable of being incorporated in the cycloaddition.[7] In the reactions of these compounds, the electron-demanding unsaturated function in the reagent molecule attacks the back lobe of the bent central σ-bond in a radical fashion to generate 1,5-biradicals, which produce the expected [2 + 3] cycloadduct. The relatively ready production of the 1,5-biradicals in these cases is probably due to the specifically highly strained nature of the central σ-bond. Hence, cycloadditions via 1,5-biradicals will not be generally applicable for simpler cyclopropyl derivatives.

The intermolecular trappings of trimethylenemethane biradicals,[4b,8] which can be generated fairly easily from methylenecyclopropanes, with unsaturated functions have generally been unsuccessful likewise.[9,10] Eventually, it may thus be concluded that the trapping of 1,3-diyls generated from relatively simple three-membered carbocycles is not a good means to achieve the cycloaddition, and hence certain specific devices may be required to effect the reaction. Some of the features of cyclopropyl derivatives summarized above are put to practical use as exemplified in the following examples.

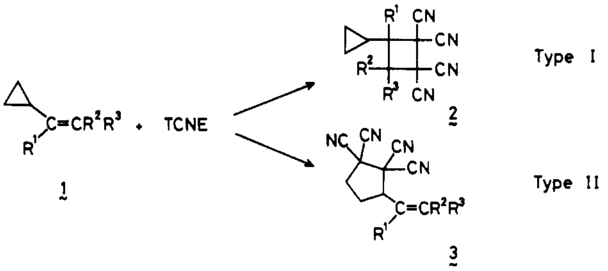
Donor–Acceptor Type Cycloadditions

In analogy to the $[_{\pi}2 + _{\pi}2]$ cycloaddition of electron-rich alkenes with electron-deficient olefins,[11] it is anticipated that the cycloadditions between donor–acceptor pairs of cyclopropanes and unsaturated compounds will be feasible. A number of such reactions have indeed been found so far. They include the cycloadditions of cyclopropyl-,[12] 1,1-diphenyl-,[13] and 1,1-dialkoxy-substituted[14] cyclopropanes with ethenetetracarbonitrile (TCNE). With regard to the cycloadditions between inverse donor–acceptor pairs, the reaction of cyclopropanes substituted by electronegative groups with enamines are representative.[15] In these reactions, 1,5-zwitterions are generally postulated as intermediates.

Table I
Relative Reactivities of Cyclopropylethylenes with TCNE (Dichloromethane, 25 °C)

Trisubstituted Ethylene			
Rel. Rate	430	74	1.0
(Type I : ethyl > cyclopropyl > isopropyl)			
Tetrasubstituted Ethylene			
Rel. Rate	0.43	8.7	1.0
(Type II : cyclopropyl > isopropyl > ethyl)			

We have studied the reactions of several cyclopropyl-substituted ethylenes, **1**, with TCNE.[16] The reaction usually took place at the π-bond in the substrate[16a,17] and a four-membered cycloadduct, **2**, was produced (type I). When the ethylene was substituted with four relatively bulky groups, however, a different reaction occurred and a vinylcyclopentane derivative, **3**, was formed (type II).[16b] Both types of cycloadditions proceeded equally well at room temperature.



On the basis of the results obtained in the extensive studies on these reactions,[16,18] we proposed that the type I reaction is an ordinary $[_{\pi}2 + _{\pi}2]$ cycloaddition via

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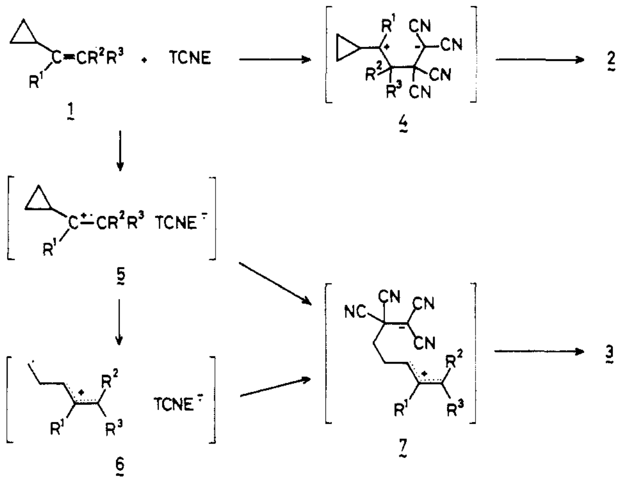
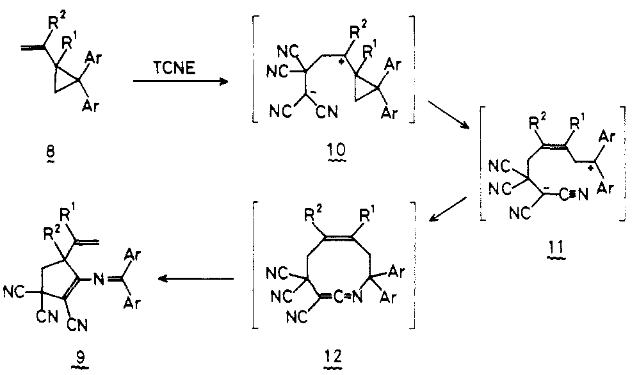
Scheme I



Scheme II



1,4-zwitterions, 4, whereas the type II reaction, in which only a cyclopropane σ-bond is incorporated, is initiated by an electron transfer from the cyclopropylethylenes to TCNE. The formation of 3 can be rationalized in terms of the reactions of the resultant radical ion pairs. This proposal appears to be supported by the explicit difference observed in the structure–reactivity sequences for the two types (Table I).[18]

On the basis of the relative reactivity of three substrates examined in each type, it can be concluded that, in the type I reactions, steric hindrance for the access of TCNE at the π-bond in the cyclopropylethylene is a controlling factor, whereas electronic effects (electron-donating ability expected: cyclopropyl > isopropyl > ethyl) appear to play a role in type II reactions. With regard to the electronic effects exerted by cyclopropyl groups, it was observed that the substitution of olefinic hydrogens with cyclopropyl groups remarkably lowers the ionization potential (IP) of the corresponding ethylenes.[19] Thus, the IP_a of tetracyclopropylethylene was found to be exceedingly low (7.25 eV)[18] for an alkene. Furthermore, a statement made by Scott et al.[20] should be cited here to indicate the feasibility of the electron transfer in the type II process. They pointed out that the electron transfer is presumed to be thermodynamically favored when the difference between the IP of the donor and the electron affinity (EA) of the acceptor is less than about 4–5 eV, which appears to be the case in the present pairs of reactants readily undergoing the type II reactions.[21]

The feasibility of the electron transfer in related reactions has been substantiated by Arnold and Humphreys[22] and Scott et al.[20] Thus, it may be reasonable to assume that the initial step of the type II reaction is the electron transfer, and the incipient cation radical 5 undergoes a relatively slow ring opening to 6. The resultant second cation radical, 6, combines with a nearby TCNE anion radical to form 7, which ultimately cyclizes to 3 (Scheme I). There is also the possibility that the TCNE anion radical directly attacks the cyclopropyl methylene carbon in 5 to produce 7.

Recently, Steinberg et al.[23] have proposed, primarily on the basis of the stereochemical consequences of the cycloaddition, that the cycloaddition of cyclopropanone monothioacetal with TCNE might be a concerted $[_{\pi}2_s + {}_{\sigma}2_a]$ process. Concerted mechanisms have also been proposed for the reactions of methylenecyclopropanes with electron-deficient unsaturated compounds.[24]

Alkenylcyclopropanes and Related Compounds

One may anticipate that the double-bond character of the cyclopropyl ring will enable alkenylcyclopropanes to behave as homo-1,3-dienes in cycloaddition reactions. Thus, if the alkenylcyclopropanes were incorporated in the Diels–Alder type reactions, seven-membered rings could be constructed in a one-step process. Realization of such reactions, however, has generally met with difficulties and appears to be possible only in the limited cases.

The reactions of alkenylcyclopropanes with powerful dienophiles, such as TCNE and *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD), generally give a four-membered $[_{\pi}2 + {}_{\pi}2]$ cycloadduct as a kinetic product.[16a,17,25] The stepwise, polar nature of the reaction is verified either by the solvent polarity effect on the reaction rates or by the observation that cation-stabilizing groups on the cyclopropane ring greatly facilitate the formation of the ring-opened, rearranged products. For example, we[26] found that the introduction of two aryl groups at one of the methylene groups of the ring in vinylcyclopropane brought about total alteration of the reaction course. Thus, the reaction of parent vinylcyclopropane with TCNE gave the type I product, whereas the reaction of 1,1-diaryl-2-vinylcyclopropane, 8, with TCNE yielded an unexpected product, 9. The formation of 9 could be rationalized in terms of the cationic rearrangement in the intervening zwitterion, 10 → 11, fol-

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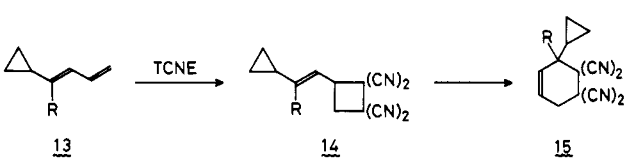
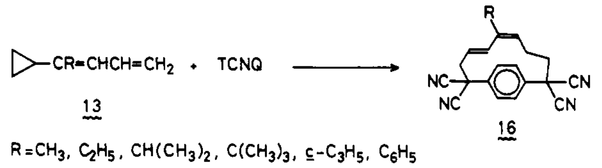
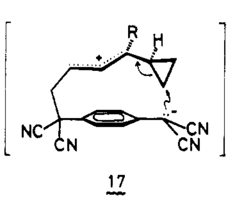
lowed by the Cope type rearrangement of the first formed cycloadduct, 12 (Scheme II).

Cationic rearrangements in zwitterionic intermediates have also been observed in the reactions of cyclopropylethylenes, fused in a polycyclic framework, with some electron-deficient unsaturated compounds.[27] The propensity of alkenylcyclopropanes for undergoing polar cycloadditions undoubtedly arises from the high cation-stabilizing ability of cyclopropyl groups.[3] Some of these $[_{\pi}2 + {}_{\pi}2]$ cycloadducts regenerate the zwitterion at elevated temperature and ultimately yield the cyclopropane-cleaved products.[28]

Sarel and Langbeheim[29] and Paquette et al.[27a] have reported that the reactions of 1,2-dialkenylcyclopropanes with electrophilic unsaturated compounds give nine-membered cyclic dienes. The two π-bonds and the cyclopropane σ-bond in the reactants are incorporated. However, in the reactions of 1-cyclopropyl-1,3-butadiene derivatives, **13**, we[30] found that TCNE reacted mainly with the terminal double bond of the dienes to give $[_{\pi}2 + {}_{\pi}2]$ cycloadducts, **14**, which in turn undergo ring enlargement to produce formally the $[_{\pi}4 + {}_{\pi}2]$ adducts, **15**. No further isomerization accompanied by the cyclopropane cleavage was observed even at a somewhat elevated temperature. In contrast, however, **13** smoothly reacted with 3,6-bis(dicyanomethylene)-1,4-cyclohexadiene (TCNQ) with involvement of the cyclopropane opening to afford [9]paracyclophadienes, **16**.[31] The product **16**, possessed 3-trans–5-cis geometry irrespective of the stereochemistry in the starting **13**. In analogy with the reactions forming **14**, as well as the type I reactions, we proposed that the first step of the reaction would be a polar attack of TCNQ at the terminal double bond to give **17**. The cyclization of **17** to **16** may be accomplished by an intramolecular attack of the cyano-bearing carbanion at the methylene carbon of the cyclopropyl group activated with the allylic cation moiety, as depicted in **17**. The specific formation of the cis–trans isomer in the cycloadditions will be the consequence of the preferred conformation of the chain in **17**.[31] The stereoelectronic requirement for the backside attack in the cyclopropane opening[2] may be fulfilled with this conformer. The cycloaddition of TCNQ producing cyclophane derivatives is not known, to the best of our knowledge, except for the reactions with cyclopropylethylenes.



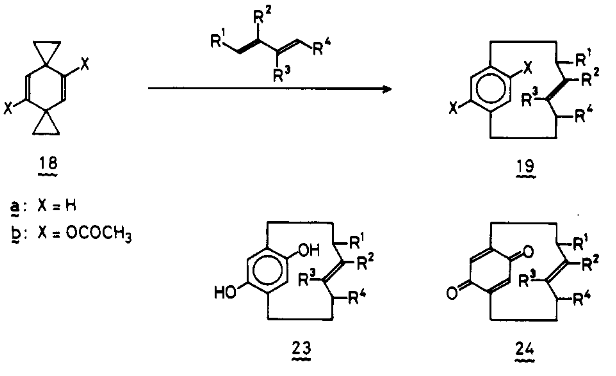




It is well-known that quadricyclane, a bicyclopropyl constructed in a polycyclic framework, reacts with a number of dienophiles in a concerted $[_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2]$ fashion.[32] Concerted mechanisms have also been suggested for the $[_{\pi}2 + {}_{\pi}2 + {}_{\pi}2]$ cycloaddition of bicyclo[2.1.0]pent-2-ene[33] and for the $[_{\pi}2 + {}_{\pi}4 + {}_{\sigma}2]$ cycloaddition of homofulvenes[34] with dienophiles. In contrast, simple cyclopropylethylenes, as well as bicyclopropyls, rarely show tendencies to behave as homologues of dienes toward dienophiles. It appears, therefore, that these compounds do so only when the functions are fused in a polycyclic carbon framework and take an arrangement well-adapted to carry out the concerted reactions.

1,2-Dicyclopropylethylenes and Related Compounds

When heated in the presence of various unsaturated compounds, dispiro[2.2.2.2]deca-4,9-diene, **18a**, undergoes efficient ring-opening cycloadditions.[35] Thus, the thermal reactions of **18a** with 1,3-dienes, styrenes, and monoenes afforded [8]paracycloph-4-enes, **19**, [4.2]paracyclophanes, **20**, and a mixture of **21** and **22**, respectively. The reactions of 4,9-diacetoxy derivative **18b** with 1,3-dienes proceeded analogously and provided a convenient route for the preparation of C_8-bridged hydroquinones **23** and *p*-benzoquinones, **24**. These



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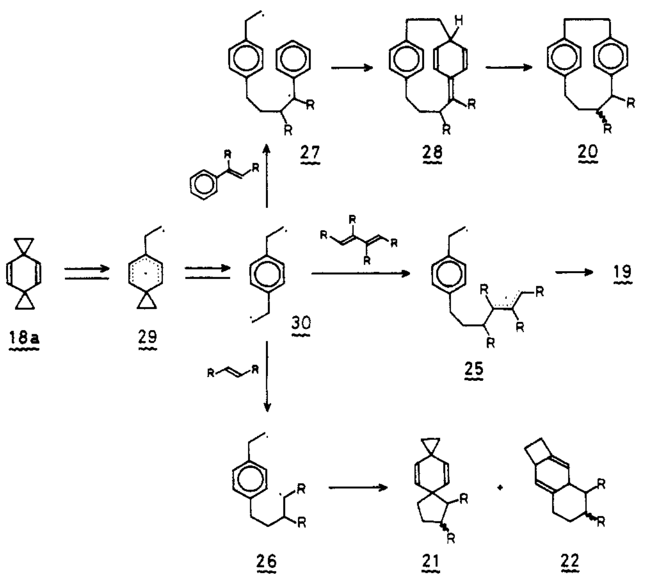
Scheme III



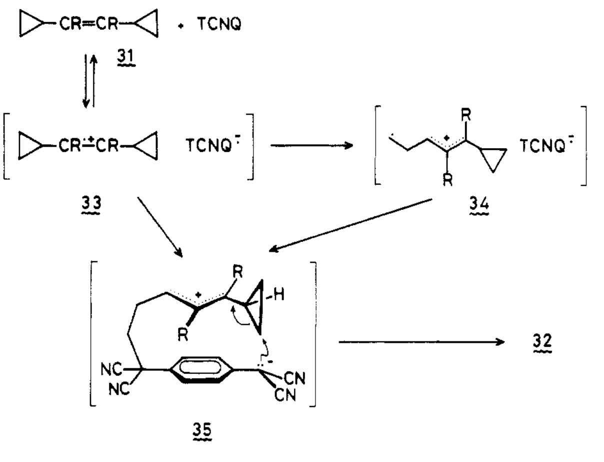
C_8-bridged compounds exhibited interesting spectroscopic and chemical properties.[36]

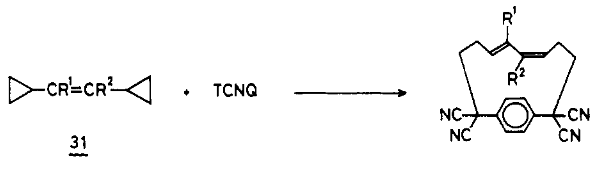
The reactions of **18** with olefinic substrates are explained by the pathways outlined in Scheme III. In the reaction with conjugated dienes, **25** undergoes cyclization to **19**, whereas **26**, produced in the reaction with monoenes, can not cyclize to a highly strained [6]paracyclophane and hence is forced to collapse to **21** and **22**. The formation of [4.2]paracyclophanes may be rationalized as shown in the scheme (**27** → **28** → **20**).

The successful intermolecular captures of the biradical intermediates[37] in these reactions, in particular the formation of **21**, are seemingly in contradiction to the fact that 1,3-diyls can hardly be trapped with diylophiles intermolecularly. However, rationalization may be found in the fact that the reacting species would most probably be not the 1,3-biradical **29** but a 1,8-biradical, **30**.[35] The cyclopropane rings in **18a** would rupture in a stepwise manner to produce **29**, but it would undergo ready rearrangement to **30**, because the spiro[2.5]octadienyl structure in **29** corresponds to that of a transient species postulated in the 1,2 aryl shift of arylethyl radicals.[38] Considerations of energy barriers for the ring opening of spiro[2.5]octadienyl radical[39] and for the reverse process[40] suggest that the 1,8-biradical **30**, once formed, sustains a somewhat long lifetime before recyclizing to **29** and hence is captured with unsaturated compounds. In addition, it should be pointed out that the process from **18a** to **29** to **30** is reversible, as was unequivocally demonstrated by CIDNP studies on **18a**.[41] Thus, the unsaturated functions will have numerous opportunities to seek out the reactive **30**, which is repeatedly produced.[10]

As described previously, reactions of alkenylcyclopropanes with TCNE are classified into two types. The type II reaction, which is characteristic of the reactions of heavily substituted ethylenes, appears to be initiated with the electron transfer. With these results in mind, we treated certain tetrasubstituted 1,2-dicyclopropylethylenes, **31**, with TCNQ.[31b,42] After relatively prolonged heating at 85–90 °C, 1:1 cycloadducts were isolated in fairly good yields. The adducts were assigned as [10]paracyclophadienes, **32**, possessing the double bonds of cis–trans configuration.

Scheme IV

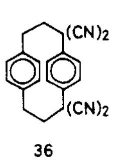




a: $R^1 = R^2 = c\text{-}C_3H_5$
b: $R^1 = R^2 = C_6H_5$
c: $R^1 = CH_3$, $R^2 = c\text{-}C_3H_5$

With regard to the mechanism for the formation of **32**, we proposed that the first step would be an electron transfer from **31** to TCNQ, as in the type II reaction. The combination of radical ion pairs, either **33** or **34**, will yield **35**, which cyclizes in a manner similar to that of **17** (Scheme IV). In **35**, the allyl cation unit will selectively be in the transoid–transoid configuration for steric reasons. The stereoelectronic requirement for backside attack[2] may then be fulfilled only in the s-cis conformer as depicted in **35**, and the cis–trans isomer might be selectively produced.[31b]

In the reactions of di- and trisubstituted 1,2-dicyclopropylethylenes, TCNQ may preferentially attack the π-bond and the resultant intermediates would have no proper way to yield isolable products. In contrast, **18a**, which is essentially the disubstituted substrate, reacted with TCNQ in a manner similar to that of **31**; [3.3]paracyclophane, **36**, was obtained.[35c,43] Steric hindrance may not be severe, but the attack of TCNQ



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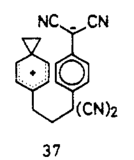

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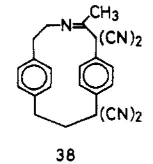

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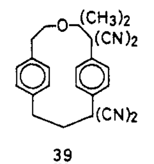

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[37] Several observations,[35] including the CIDNP effects (Tsuji, T.; Nishida, S. *Chem. Lett.* **1973**, 1335), support the intermediacy of biradical species.

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at the π-bond would be kinetically less favorable than the electron transfer in this particular substrate, which has an exceptionally low IP (IP_v = 7.5 eV).[19b] The combination of the resultant ion pairs yields **37**, which culminates in the production of **36**. The intermediacy of **37** was verified by conducting the reaction in either acetonitrile or acetone. The products obtained in the reactions in these solvents were **38** and **39**, respectively. Apparently, the dipolar addition of **37** to the heteromultiple bond in the solvent molecules took place.[35c,43]

Dispiro[2.0.2.4]deca-4,6-diene[1d,44] undergoes cycloaddition with TCNE in dioxane to afford a benzocyclooctane derivative as the major adduct.[1d] Cleavages of the two cyclopropane rings take place. Since most other dienophiles produce the normal Diels–Alder adducts,[45] a mechanism similar to those discussed above has been proposed by de Meijere.[1d]

Concluding Remarks

In spite of the fact that the thermal cycloadditions of cyclopropanes with olefins can rarely be accomplished, **18** produced a variety of cycloadducts in its reactions with various unsaturated compounds. The ready rearrangement of the incipient 1,3-biradical **29** to the 1,8-biradical **30**, which may have a prolonged lifetime owing to the intervention of an aromatic ring between the two radical centers, as well as the repeated production of the biradical species under the reaction conditions, might be the reason for the successes.

Some heavily substituted cyclopropylethylenes, **1**, reacted with TCNE to afford vinylcyclopentane derivatives, **3**. Certain tetrasubstituted 1,2-dicyclopropylethylenes **31**, reacted with TCNQ to afford [10]paracyclophadienes, **32**, and the dispiro compound **18** produced [3.3]paracyclophane, **36**, in its reaction with TCNQ. The success of these cycloadditions is ascribed to the low IP of the substrate ethylenes, the high EA of TCNE or TCNQ, and, in some cases, the difficulties for the access of TCNE or TCNQ to the π-bond in the reactants. Thus, an initial electron transfer is assumed, and the reactions of the resultant radical ion pairs appear to be accompanied by the efficient cyclopropane cleavage in the subsequent steps. In the paracyclophane formations with TCNQ, the intramolecular nucleophilic opening of the cyclopropane ring at the final stage of the reaction appears to be essential.[31]

The thermal ring-opening cycloadditions of cyclopropyl derivatives have not yet been well-explored, but some promising developments have been achieved as illustrated in this Account.

It is a great pleasure to acknowledge the contributions of our very able collaborators: Drs. T. Teraji, N. Shimizu, M. Murakami, T. Shibata, Y. Hienuki, and F. Kataoka and M. Ishikawa, K. Ishikura, S. Ishizuka, and T. Fujioka. The studies described here have been supported by a Grant-in-Aid for Scientific Research administered by the Ministry of Education, Science and Culture, and by the funds provided by Kuraray Co. Ltd. and the Kurata Foundation, to whom we are grateful.

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Nonhomolytic Cleavage Pathways in the Photochemistry of Metal–Metal-Bonded Carbonyl Dimers

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The dominant photochemical process of many metal–metal-bonded carbonyl dimers is homolytic cleavage of the metal–metal bond to produce two 17-electron metal carbonyl fragments (eq 1).[1] The results of numerous photochemical, flash photolysis, and ESR spin-trapping experiments are consistent with this conclusion.[1]

$$L_nM{-}ML_n \xrightarrow{h\nu} L_nM + ML_n \tag{1}$$

For a considerable period of time it was thought that all of the photochemistry of metal–metal-bonded carbonyl complexes could be explained by invoking the primary photoprocess in eq 1. Recent results, however, suggest that other primary photoprocesses might also be important in accounting for the photochemistry of these complexes. It is noteworthy that the mechanistic evidence for primary photoprocesses other than homolytic cleavage is often less than definitive. From our examination of these reactions, we hope to draw some conclusions about the relative importance of nonhomolytic cleavage pathways in the photochemistry of metal–metal-bonded carbonyl dimers.

Electronic Excited States of Metal–Metal-Bonded Complexes

Of the molecules discussed in this account, detailed electronic spectral studies have been carried out only

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(1) The most recent review dealing with the photochemistry of metal carbonyl dimers can be found in Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

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