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Reaction of 1,1-Diphenyl-2-vinylcyclopropane with Tetracyanoethylene, Diene, Diborane, and Dibromocarbene. Formation of Unusual Adducts after Rearrangements Supporting a Two-Step Process[1,2]

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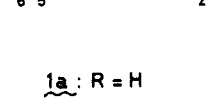
Abstract: 1,1-Diphenyl-2-vinylcyclopropane (**1a**) reacts with tetracyanoethylene yielding *N*-diphenylmethylene-2,3,3-tricyano-5-vinylcyclopent-1-enylamine (**2a**) as a major adduct. The related ethylene **1c** produces fluorenylideneamine **2c** and the chain adduct **4a.** The expected cycloadducts did not form in both cases. In contrast, the Diels-Alder reaction of **1a** with tetrachlorocyclopentadienone ethylene acetal gives the normal cycloadduct **6c.** Hydroboration-oxidation and dibromocarbene addition also yield expected products, 2-(2,2-diphenylcyclopropyl)ethanol (**7**) and a pair of bicyclopropyls (**8a** and **8b**), respectively. It can thus be concluded that the concerted processes preserve the 2,2-diphenylcyclopropyl group. The reactions of vinylcyclopropanes with TCNE are, therefore, not a concerted but a stepwise reaction, in which extensive rearrangements take place. A probable path to **2** and **4** is proposed.

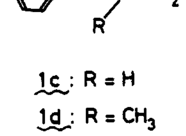
It has been recently demonstrated that the utilization of vinylcyclopropane derivatives as a substrate in the investigation of radical cycloadditions to a carbon-carbon double bond permits us to discuss the intermediacy of a diradical species in such reactions.[3] It is hoped presently that similar demonstrations can also be made in cycloaddition reactions involving a dipolar intermediate.[4,5] Thus the reactions of 1,1-diphenyl-2-vinylcyclopropane (**1a**) and the related ethylenes (**1b–d**) with tetracyanoethylene (TCNE) were examined and the results are compared with those of Diels-Alder, hydroboration-oxidation, and singlet carbene addition reactions. Both stepwise[5a,1] and concerted processes[6] have been discussed for the related TCNE cycloadditions.

Results

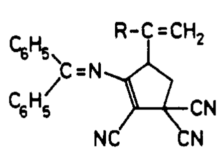
Reaction of 1a–d with Tetracyanoethylene. The reaction of **1a** with TCNE proceeded slowly at room temperature yielding an adduct of unexpected structure.[7] Thus, after a 1:1 mixture



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

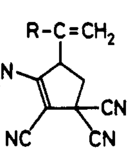


1c : R = H
1d : R = CH_3



2a : R = H

2b : $R = CH_3$



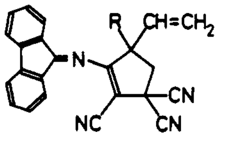
3a : R = H

3b : $R = CH_3$

in 1,2-dichloroethane was left standing for 2 months, a 1:1 adduct assigned to *N*-diphenylmethylene-2,3,3-tricyano-5-vinylcyclopent-1-enylamine (**2a,** 82%) was obtained. The reaction was not completed even at this stage and some **1a** and TCNE were recovered. No isomerization of **1a** was observed. Acid hydrolysis of **2a** under mild conditions yielded benzophenone (48%) and 2,3,3-tricyano-5-vinylcyclopent-1-enamine (**3a,** 93%). UV and IR spectra of **3a** were in accord with those of β-cyanoenamines.[8]

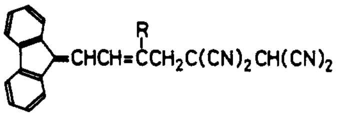
1,1-Diphenyl-2-methyl-2-vinylcyclopropane (**1b**) produced *N*-diphenylmethylene-2,3,3-tricyano-5-prop-2′-enylcyclopent-1-enylamine (**2b,** 75%). The side chain in **1b** was a vinyl whereas that in **2b** was a 2-propenyl. Acid hydrolysis of **2b** gave benzophenone (75%) and the enamine **3b** (64%).

The reaction of spiro[2-vinylcyclopropane-1,9′-fluorene] (**1c**) with TCNE gave two 1:1 adducts, *N*-fluorenylidene-2,3,3-tricyano-5-vinylcyclopent-1-enylamine (**2c,** 39%) and 5,5,6,6-tetracyanohex-2-enylidenefluorene (**4a,** 41%). Acid hydrolysis of **2c** gave fluorenone (92%) and the enamine **3a** (66%). The structure of the second adduct **4a** was elucidated by spectral examinations and it was supported by the observation that permanganate oxidation yielded fluorenone (83%) and oxalic acid hydrate (65%). Similarly, 2-propenyl derivative **1d** gave the adducts **2d** (38%) and **4b** (18%).



2c : R = H

2d : $R = CH_3$



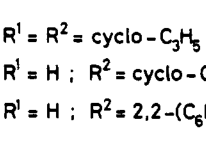
4a : R = H

4b : $R = CH_3$

Effect of Solvent Polarity. The reaction of **1a** with TCNE proceeded more rapidly in polar solvents. Thus, after 4 days at 65 °C, the yield of **2a** was only 9% in 1,2-dichloroethane (recovery of **1a** 78%) while it was 86% in nitromethane (recovery of **1a** 6%).

Reactions Preserving the 2,2-Diphenylcyclopropyl Group. 1,1-Dicyclopropylethylene, vinylcyclopropane, and **1a** reacted smoothly with tetrachlorocyclopentadienone ethylene acetal (**5**) to give the diene adducts (**6**).[9] Thus, **1a** produced **6c** (97.5%) preserving the 2,2-diphenylcyclopropyl group, presumably at the endo position.[10]

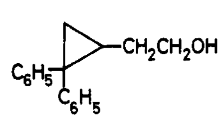
Hydroboration-oxidation[11] of **1a** and dibromocarbene (generated from phenyltribromomethylmercury)[12] addition to **1a** yielded expected adducts, **7** and **8** (a mixture of geometrical isomers), respectively.



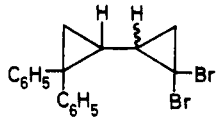
6a : $R^1 = R^2 =$ cyclo-C_3H_5

6b : $R^1 = H$; $R^2 =$ cyclo-C_3H_5

6c : $R^1 = H$; $R^2 = 2,2\text{-}(C_6H_5)_2$-cyclo-$C_3H_5$



7



8 (a and b)

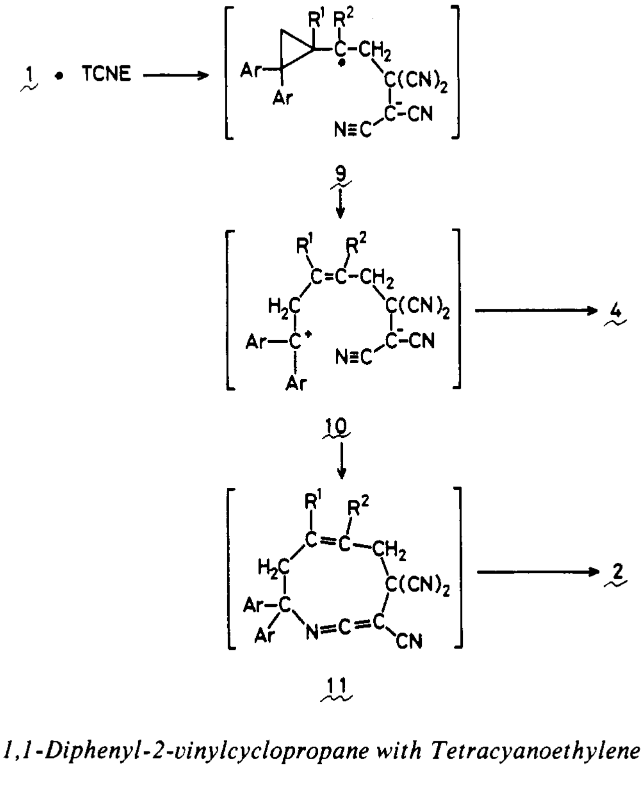
Discussion

Reaction of Vinylcyclopropane with Tetracyanoethylene. Cyclopropylethylenes are those olefins possessing a low ionization potential[13] and they undergo a thermal [2 + 2] cycloaddition with TCNE under mild conditions.[5c,d,g,i,m] In contrast to the radical cycloadditions,[3] the mode of the reaction is totally a [2 + 2] cycloaddition leaving the cyclopropane ring intact. Although this is reasonable if the cycloaddition in question is a concerted process, the investigations on the related reactions[5a,l] suggest a possibility that the reaction is stepwise via a zwitterionic intermediate but the rate of the rearrangement of cyclopropylcarbinyl cation to allylcarbinyl cation is slow compared to the ring closure at the intermediate. If the latter is the case, a rearranged adduct would be produced when the rearranging process is sufficiently accelerated. Indeed, an introduction of two aromatic groups at the 2 position of the vinylcyclopropane changed the course of the reaction completely and the results are compatible with the stepwise mechanism.

Reaction Scheme. The formation of **2** and **4** can be best explained in the following manner. Addition of TCNE to the double bond of **1a** produces a zwitterion **9**,[14] which has a cyclopropylcarbinyl cation portion. The two phenyl groups will play no significant part in the stabilization of this intermediate, but the rearranged zwitterion **10** will be greatly stabilized by them. Thus the zwitterion **10** forms and cyclizes at the nitrogen of the cyano group to give a nine-membered heterocycle **11**,[15] where a Cope-type rearrangement[16] took place yielding amine **2**. When the substituent is an *o*-biphenylene group, a proton transfer occurs to produce a chain adduct **4**.

Because of the intervention of the Cope rearrangement, the vinyl side chain in the product **2a** is not identical with that in

Scheme I



the starting olefin **1a.** This is proved by methyl tagging experiments. The olefin **1b,** which holds a vinyl and a methyl group, gave **2b,** in which a 2-propenyl group is present instead of the vinyl group. A similar conversion was made in the reaction of **1d.** These transformations are compatible with the proposed scheme.

Concerted Reactions. The Diels–Alder reaction of vinylcyclopropanes was achieved successfully in the reaction with an electron-deficient diene **5,** but was unsuccessful with 9,10-dimethylanthracene. However, practically no effect of the solvent polarity on the reaction rates gives support for the concerted nature of the reaction. Hence the present [2 + 4] cycloadditions will be the usual Diels–Alder reaction of inverse electron demand.[17] Hydroboration-oxidation[18,19] and dibromocarbene transfer[12] also proceeded normally. Based on these observations, it may be concluded that the preservation of the 2,2-diphenylcyclopropyl group in the concerted reactions will be a logical consequence so far as the kinetically controlled conditions are concerned.

Stereochemistry and Rearrangement. A technique which is most frequently employed in the mechanistic studies of cycloaddition reactions is a stereochemical examination of the reaction in question.[20] This is based on the fact that the rate of rotation around a single bond has a sufficient rapidity to compete with that of ring closure of the intermediate. However, it is known that stepwise cycloadditions, particularly dipolar cycloadditions, may not always lose the stereochemical individuality of the starting substrate.[20,21] As demonstrated previously,[3] the formation of a rearranged adduct is another reasonable indication that the reaction is stepwise. However, stepwise reactions also do not always result in the formation of a rearranged adduct when the rate of the rearrangement is not sufficiently high.[3] Thus, in the application of these techniques, insufficiently high rate of the key process competing with ring closure is problematic. Therefore, *it will be of considerable value if an unquestionably fast competing process can be realized.* In this respect, it should be noted that, unlike the limited manner of increasing the rate of rotation, there may be efficient means of accelerating the rearranging process. An introduction of a suitable substituent in the substrate may be one of the possibilities. The present results discussed so far are in good agreement with this assumption.

The cyclopropylcarbinyl–allylcarbinyl rearrangement is in fact an equilibrium process.[22] The substituent at the ring, as in **1a,** should shift the equilibrium far to the rearranged adduct unless the termination of the reaction in the second intermediate, such as **10,** is hindered. If the termination at the first-formed intermediate, such as **9,** is hindered, the rearranged adduct would also be produced. The reaction of α-fenchene with *N*-chlorosulfonyl isocyanate (CSI) may be such an example.[23] However, this would not apply to the present case, because even 1,1-dicyclopropylethylene, which should produce a more hindered cationic portion at the first intermediate than **1a,** forms a [2 + 2] cycloadduct with great ease in the reaction with TCNE.[5d,g] It can thus be concluded that the rearranged adduct is produced because of the fast rate of the rearrangement.

In their investigation on CSI cycloadditions, Pasto and Chen[24] argued that the different behavior between 1-cyclopropylstyrene and 2-(*trans*-2-phenylcyclopropyl)propene is due to the different stabilization (*phenyl* vs. *methyl*) provided at the cationic portion in the first intermediate. This is certainly one of the factors as demonstrated in radical additions,[3] but the exclusive formation of the rearranged adduct in the present case is most probably due to the stabilization of the rearranged species. In this respect, it should be noted that 2-cyclopropylpropene, which lacks phenyl stabilization, reacts with CSI to give an unrearranged adduct at a relatively low temperature.[25] Thus, both cycloadditions (TCNE and CSI) are probably stepwise dipolar reactions and the rearrangement occurs only when appropriate stabilizing groups are substituted at the 2 position of the three-membered ring. The reactions of ring-unsubstituted cyclopropylethylenes with TCNE are stereospecific (at least to an extent of 90%).[5d,g] The ring closure at the first intermediate is presumably faster than both rotation and rearrangement in such reactions.

Radical Cycloadditions and Dipolar Cycloadditions. The formation of [2 + 2] cycloadducts in the reaction of ring-unsubstituted cyclopropylethylenes with TCNE is shown to be true even at 147 °C, at which temperature the rearranged adduct predominates in radical cycloadditions.[3] This result suggests that the rearrangement in the radical intermediate is faster than that in a cationic species.[26,27] It suggests that the dipolar and the diradical processes in cycloaddition reactions may be distinguished by the utilization of adequate vinylcyclopropanes as a substrate. The rapid rearrangement seems to be a feature of the cyclopropylcarbinyl radical[28] and hence the present type of investigations, including both ring-substituted and ring-unsubstituted vinylcyclopropanes, will be of considerable importance in the mechanistic studies of cycloaddition reactions.

Experimental Section

IR spectra were recorded on a Hitachi 215 grating infrared spectrophotometer and UV spectra on a Hitachi EPS-2 recording spectrophotometer. NMR spectra were recorded on a JEOL PS-100 high-resolution spectrometer using Me_4Si as an internal standard. The abbreviations given in the NMR data are s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Both preparative and analytical GLC were carried out on a Yanagimoto G-8 gas chromatograph using columns packed with either 20% polyethylene glycol succinate on Chromosorb W (PEGS), or 20% polyethylene glycol on Celite 545 (PEG). All boiling and melting points are uncorrected.

Vinylcyclopropanes. 1,1-Diphenyl-2-vinylcyclopropane (**1a**) was prepared and purified as follows. A mixture of 14 g of diphenyldiazomethane and 150 mL of butadiene in 500 mL of dry ether was irradiated through a Pyrex filter with a 450-W medium-pressure mercury lamp at −20 °C for 3 h. Solvent and excess diene were removed by distillation on a steam bath and the residual oil was passed through a silica gel column. The eluted oil was fractionated giving 12 g (78%) of **1a:** bp 105–107 °C (0.4 mm); IR (neat) 3090, 3040, 1635, 1500, 1445, 1135, 1070, 1030, 1010, 985, 900, 750, 695 cm^{-1}; UV max (95% ethanol) 224 nm (log ϵ 4.22), 260 (2.87), 267 (2.83), 275 (2.60); NMR (CCl_4) δ 7.05 (m, 10), 4.62–5.12 (m, 3), 2.18 (m, 1), 1.42 (d, 2, J = 7 Hz). Anal. Calcd for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.6; H, 7.3.

1,1-Diphenyl-2-methyl-2-vinycyclopropane (**1b**) was prepared similarly from diphenyldiazomethane and 2-methylbuta-1,3-diene. The crude product (83%) was chromatographed over alumina eluting with petroleum ether (bp 40–55 °C). The first fraction gave pure **1b,** bp 108–109 °C (0.3 mm): IR (neat) 3100, 3075, 3040, 3000, 2960, 2940, 2875, 1630, 1600, 1495, 1080, 1030, 1015, 995, 895, 770, 740, 700, 690 cm^{-1}; NMR (CCl_4) δ 7.02–7.45 (m, 10), 4.75–5.60 (m, 3), 1.50 (s, 2), 1.10 (s, 3). Anal. Calcd for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.7.

Similarly, spiro[2-vinylcyclopropane-1,9′-fluorene] (**1c**) was prepared from 9-diazofluorene and butadiene in 65% yield: mp 42–43 °C; IR (Nujol) 3050. 1630, 1220, 1090, 985, 900, 835, 795, 740, 720 cm^{-1}; UV max (95% ethanol) 261 nm (log ϵ 4.23), 271 (4.26), 293 (3.90), 304 (3.90); NMR (CCl_4) δ 7.65 (m, 2), 6.75–7.35 (m, 6), 5.92 (ddd, 1, J = 16, 10, and 7 Hz), 5.15 (dd, 1, J = 16 and 2 Hz), 5.08 (dd, 1, J = 10 and 2 Hz), 2.48 (q, 1, J = 7 Hz), 1.95 (dd, 1, J = 8 and 5 Hz), 1.79 (dd, 1, J = 7 and 5 Hz). Anal. Calcd for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.3; H, 6.4.

The isopropenyl derivative (**1d**) was prepared by the reaction of 9-diazofluorene and 2-methylbuta-1,3-diene. Separation of the isomers was performed by repeated column chromatography over alumina and pure **1d,** mp 67–69 °C, was isolated in 31% yield: IR (Nujol) 3075, 1645, 1605, 1450, 1245, 1085, 1020, 985, 920, 895, 755, 725 cm^{-1}; NMR (CCl_4) δ 7.59–7.84 (m, 2), 6.86–7.49 (m, 6), 5.62 (br s, 2), 2.49 (br t, 1, J = 7 Hz), 1.90 (d, 2, J = 7 Hz), 1.38 (s, 3). Anal. Calcd for $C_{18}H_{16}$: C, 93.1; H, 6.9. Found: C, 93.1; H, 6.8.

Reaction of 1,1-Diphenyl-2-vinylcyclopropane (1a) with TCNE. Equivalent amounts of **1a** (435 mg, 1.98 mmol) and TCNE (253 mg, 1.98 mmol) were dissolved in 100 mL of 1,2-dichloroethane and the solution was allowed to stand at room temperature for 2 months under argon atmosphere. A charge transfer band was observed at 410 nm in the fresh solution. Evaporation of the solvent left a yellow solid. Recrystallization from 1:1 benzene-petroleum ether (bp 60-70 °C) gave a mixture of yellow needles and colorless plates. Separation of the two kinds of crystals was made by small pincers. Recrystallization of the yellow needles from 2-propanol gave 257 mg of the adduct **2a:** mp 159-160 °C; IR (Nujol) 3090, 2250, 2220, 1640, 1595, 1575, 1445, 1315, 1280, 985, 945, 925, 910, 820, 780, 715, 705, 685 cm^{-1}; NMR ($CDCl_3$) δ 7.52 (s, 10), 5.70 (ddd, 1, J = 16, 10, and 7 Hz), 5.30 (d, 1, J = 10 Hz), 5.20 (d, 1, J = 16 Hz), 3.68 (q, 1, J = 8 Hz, each splits to t, J = 1 Hz), 2.86 (dd, 1, J = 13 and 8 Hz), 2.50 (dd, 1, J = 13 and 9 Hz); UV max (95% ethanol) 274 nm (log ϵ 4.38), 335 (sh, 3.38); mass spectrum (70 eV) *m/e* (rel intensity) 348 (48), 165 (100). Anal. Calcd for $C_{23}H_{16}N_4$: C, 79.3; H, 4.6; N, 16.1. Found: C, 79.4; H, 4.6; N, 15.9.

Recrystallization of the white solid from benzene gave colorless cyrstals, which were assigned to 1,1-diphenyl-2,2,3,3-tetracyano-4-vinylcyclopentane (50 mg, 11.4%) from the following spectral properties: mp 171-172 °C; IR (Nujol) 3050, 2250, 1635, 1600, 1445, 900, 885, 860, 790, 745, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.42 (m, 10), 6.04 (d of t, 1, J = 17 and 8 Hz), 5.56 (d, 1, J = 10 Hz), 5.52 (d, 1, J = 17 Hz), 3.48 (dd, 1, J = 14 and 8 Hz), 3.38 (d of t, 1, J = 10 and 8 Hz), 2.88 (dd, 1, J = 14 and 10 Hz); UV max (95% ethanol) 227 nm (log ϵ 3.90), 249 (2.86), 255 (2.93), 261 (2.90), 270 (2.70); mass spectrum (70 eV) *m/e* (rel intensity) 348 (1), 220 (81), 205 (51), 165 (24), 142 (49), 129 (100). Anal. Calcd for $C_{23}H_{16}N_4$: C, 79.3; H, 4.6; N, 16.1. Found: C, 79.3; H, 4.5; N, 16.1.

The filtrates were combined and evaporated. Recrystallization of the residue from benzene-petroleum ether (1:1) gave an additional 100 mg of **2a.** The mother liquid was evaporated and the residue was washed with *n*-hexane. The brown solid thus obtained (75 mg) was characterized as TCNE. Removing the solvent from the washings left an oil (157 mg), which was practically pure **1a** (GLC, IR, and NMR). The total yield of **2a** based on consumed **1a** was 81.8%.

In order to examine the effect of solvent polarity on the reaction rates, two solutions, (a) equivalent amounts (1.22 mmol) of TCNE and **1a** in 50 mL of 1,2-dichloroethane and (b) equivalent amounts (1.14 mmol) of TCNE and **1a** in 50 mL of nitromethane, were prepared, deoxygenated by bubbling nitrogen, and sealed in two separate glass tubes. The tubes were immersed in a bath at 65 °C. After 4 days, the mixtures were analyzed as follows: (a) Solvent (1,2-dichloroethane) was removed by a rotary evaporator and the residue was washed with pentane. TCNE was recovered from the residue by sublimation (64 mg, 41%). The residue was recrystallized from benzene-hexane (1:1) to give 40 mg (9%) of **2a.** From the pentane washings, 210 mg (78%) of **1a** was recovered after chromatography over alumina eluting with light petroleum ether. (b) Solvent (nitromethane) was evaporated and the residual solid was washed with pentane and recrystallized from benzene-hexane (1:1) to give 298 mg of **2a.** An additional 43 mg of **2a** was isolated from the filtrate. The starting **1a** was isolated from the pentane washings (17 mg, 6%). The yield of **2a** was 86%. If an assumption is made that the reaction is second order, the rate of the reaction in nitromethane relative to that in 1,2-dichloroethane was estimated to be ca. 60 from both the amounts of the recovered **1a** and the yields of **2a.**

Reaction of 1,1-Diphenyl-2-methyl-2-vinylcyclopropane (1b) with TCNE. A mixture of **1b** (475 mg, 2.03 mmol) and TCNE (260 mg) in 25 mL of 1,2-dichloroethane was heated at 60 °C for 6 days under argon atmosphere. Solvent was removed by a rotary evaporator. The residue was dissolved in benzene-hexane (5:1) and the solution was cooled in a refrigerator. The separated crystals were collected and recrystallized from 2-propanol giving yellow needles (450 mg), which were found to be the adduct **2b:** mp 152-152.5 °C; IR (Nujol) 3075, 2250, 2220, 1635, 1595, 1445, 1315, 1280, 1140, 1000, 960, 945, 910, 800, 785, 720, 700, 685 cm^{-1}; NMR ($CDCl_3$) δ 7.48 (s, 10), 4.95 (s, 1), 4.75 (s, 1), 3.28 (dd, 1, J = 9 and 7 Hz), 2.78 (dd, 1, J = 13 and 7 Hz), 2.51 (dd, 1, J = 13 and 9 Hz), 1.73 (s, 3). Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.5; H, 5.0; N, 15.5. Found: C, 79.5; H, 4.9; N, 15.5.

The filtrate was concentrated and another 105 mg of **2b** was isolated from the residue. The filtrate was evaporated and the residue was washed with chloroform. The brown solid, TCNE (15 mg), was recovered. The choroform solution gave only black tar (130 mg). The yield of the adduct **2b** was 75.5%.

Reaction of Spiro[2-vinylcyclopropane-1,9′-fluorene] (1c) with TCNE. A mixture of **1c** (916 mg, 4.20 mmol) and TCNE (570 mg, 4.45 mmol) in 100 mL of 1,2-dichloroethane was heated at 55 °C for 8 days under argon atmosphere. The initial deep purple color turned into a dark greenish-red at the end of the reaction. The solution was concentrated on a rotary evaporator and cooled in a refrigerator. Greenish-yellow crystals (645 mg), mp 181-182 °C dec, were collected: IR (Nujol) 3070, 1605, 1450, 965, 955, 885, 775, 720 cm^{-1}; NMR (acetone-d_6) δ 8.20-7.24 (m, 10), 6.40 (d of t, 1, J = 15 and 7 Hz), 6.08 (s, 1, disappeared in the presence of D_2O), 3.68 (d, 2, J = 7 Hz). Double irradiation at δ 3.68 altered the signal at δ 6.40 into a sharp doublet with J = 15 Hz. These data support the assigned structure, **4a.** Anal. Calcd for $C_{23}H_{14}N_4$: C, 79.8; H, 4.1; N, 16.2. Found: C, 80.0; H, 4.1; N, 16.2.

The filtrate was evaporated and the residue was recrystallized from benzene giving another adduct **2c** as yellow needles (565 mg): mp 177-179 °C; IR (Nujol) 3075, 2220, 1670, 1605, 1580, 1550, 1300, 1210, 1155, 1100, 980, 935, 785, 725 cm^{-1}; NMR (acetone-d_6) δ 7.84-7.20 (m, 8), 6.03 (ddd, 1, J = 16, 10, and 7 Hz), 5.35 (d, 1, J = 16 Hz), 5.18 (d, 1, J = 10 Hz), 4.45 (q, 1, J = 7 Hz), 3.53 (dd, 1, J = 13 and 7 Hz), 3.14 (dd, 1, J = 13 and 7 Hz). Anal. Calcd for $C_{23}H_{14}N_4$: C, 79.8; H, 4.1; N, 16.2. Found: C, 79.8; H, 4.1; N, 16.1.

From the combined filtrate, additional **4a** (60 mg) was isolated together with black tar (195 mg). The yields of the adducts **2c** and **4a** were 39.0 and 48.6%, respectively.

Reaction of Spiro[2-isopropenylcyclopropane-1,9′-fluorene] (1d) with TCNE. A mixture of equimolar amounts of **1d** (473 mg, 2.04 mmol) and TCNE (261 mg, 2.03 mmol) in 50 mL of 1,2-dichloroethane was heated at 60 °C for 4 days under argon atmosphere. The solution was concentrated on a rotary evaporator under reduced pressure and cooled in a refrigerator. Yellow, fibrous crystals were collected. Recrystallization from benzene gave 80 mg of **4b** as yellow crystals: mp 180-181 °C dec; IR (Nujol) 3070, 1625, 1355, 1235, 1155, 885, 860, 780, 775, 740, 720 cm^{-1}; NMR (acetone-d_6) δ 8.23-7.20 (m, 10), 6.09 (s, 1, disappeared in the presence of D_2O), 3.78 (s, 2), 2.39 (s, 3). Anal. Calcd for $C_{24}H_{16}N_4$: C, 80.0; H, 4.5; N, 15.6. Found: C, 80.0; H, 4.5; N, 15.4.

The filtrate was evaporated and the residue was recrystallized twice from 2-propanol giving 280 mg of yellow crystals identified as **2d:** mp 206-207 °C; IR (Nujol) 3100, 2220, 1680, 1585, 1305, 1295, 1100, 930, 785, 730 cm^{-1}; NMR (acetone-d_6) δ 7.93-7.20 (m, 8), 6.18 (dd, 1, J = 18 and 11 Hz), 5.43 (d, 1, J = 18 Hz), 5.25 (d, 1, J = 11 Hz), 3.43 (d, 1, J = 14 Hz), 3.20 (d, 1, J = 14 Hz), 1.63 (s, 3). Anal. Calcd for $C_{24}H_{16}N_4$: C, 80.0; H, 4.5; N, 15.6. Found: C, 80.1; H, 4.4; N, 15.6.

From the combined filtrate, additional **4b** (55 mg) was isolated together with a black tar (296 mg). The yields of **2d** and **4b** were 38.2 and 18.4%, respectively.

Acid Hydrolysis of the Adduct 2. Into a solution of **2a** (100 mg) in 10 mL of 2-propanol was added 5 drops of concentrated hydrochloric acid and the solution was allowed to stand overnight at room temperature. The solution was neutralized by adding sodium carbonate solution. Organic material was extracted with benzene, washed with water, and dried over sodium sulfate. Solvent was removed by a rotary evaporator and the residue was washed with hexane. The remaining solid was recrystallized from benzene to give 49 mg of **3a** as colorless crystals: mp 182-184 °C dec; IR (Nujol) 3440, 3355, 3280, 3245, 2250, 2200, 1660, 1275, 1010, 990, 935, 810 cm^{-1}; NMR (acetone-d_6) δ 6.95 (br s, 2, disappeared in the presence of D_2), 5.94 (d of t, 1, J = 18 and 7 Hz), 5.40 (dd, 1, J = 18 and 2 Hz), 5.36 (dd, 1, J = 8 and 2 Hz), 3.82 (q, 1, J = 7 Hz), 3.12 (dd, 1, J = 14 and 7 Hz), 2.70 (dd, 1, J = 14 and 7 Hz); UV max (95% ethanol) 261 nm (log ϵ 4.17); mass spectrum (70 eV) *m/e* (rel intensity) 184 (94), 158 (87), 144 (100), 130 (53), 106 (98). Anal. Calcd for $C_{10}H_8N_4$: C, 65.2; H, 4.4; N, 30.4. Found: C, 65.3; H, 4.3; N, 30.1.

3a-ND$_2$ was obtained by dissolving **3a** in acetonitrile containing D_2O followed by evaporation to dryness: IR (Nujol) 2575, 2420, 2400, 2250, 2200, 1630, 1010, 990, 935 cm^{-1}. Dissolving this sample in aqueous acetonitrile regenerated **3a.**

Hexane solution was evaporated and the residue was recrystallized from methanol giving 25 mg of benzophenone 2,4-DNP, mp 236-237 °C (lit.[29] 232 °C).

Similarly, **2b** (80 mg) gave **3b** (25 mg, 64%) and benzophenone (30 mg, 75%), and **2c** (100 mg) gave **3a** (35 mg, 66%) and fluorenone (48 mg, 92%, 2,4-DNP mp 286–290 °C (lit.[30] 289–290 °C). Spectroscopic and analytical data of **3b** were as follows: mp 135–137 °C; IR (Nujol) 3445, 3355, 3180, 3145, 2205, 1665, 1615, 1600, 905 cm^{-1}; NMR (acetone-d_6) δ 6.79 (br s, 2, disappeared in the presence of D_2O), 5.05 (q, 2, J = 1 Hz), 3.89 (t, 1, J = 8 Hz), 3.09 (dd, 1, J = 14 and 8 Hz), 2.68 (dd, 1, J = 14 and 8 Hz), 1.75 (t, 3, J = 1 Hz). Anal. Calcd for $C_{11}H_{10}N_4$: C, 66.7; H, 5.1; N, 28.3. Found: C, 66.6; H, 5.0; N, 28.1.

Permanganate Oxidation of the Adduct 4a. Pulverized **4a** (36 mg) was suspended in 30 mL of 2% aqueous solution of potassium permanganate and 1 mL of 5% sodium hydroxide solution was added to it. The mixture was stirred for 1 h at room temperature and extracted with benzene. After the extracts were dried over anhydrous sodium sulfate, benzene was evaporated and the residue was recrystallized from ethanol giving 15 mg (80%) of fluorenone. The aqueous layer was acidified with hydrochloric acid and extracted with ether. Removal of the solvent left a white solid (7 mg), mp 98–100 °C, which was characterized as oxalic acid hydrate.

Reaction of 1,1-Diphenyl-2-vinylcyclopropane (1a) with 2,3,4,5-Tetrachlorocyclopentadienone Ethylene Acetal (5). A mixture of **1a** (277 mg, 1.26 mmol), the acetal **5**[31] (338 mg, 1.29 mmol), and a small amount of p-hydroquinone in 10 mL of benzene was heated at 110–120 °C for 24 h in a glass ampule. Solvent evaporation gave a residue, which was recrystallized from hexane giving 29 mg of colorless crystals characterized as the dimer of the acetal **5**, mp 279–280 °C (lit.[31] 279 °C). The filtrate was concentrated and the resulting residue was chromatographed over alumina. Elution with petroleum ether (bp 40–70 °C) gave a colorless oil (18 mg), which was practically pure **1a** (GLC, IR, and NMR). Elution with ether–petroleum ether (5:95) gave a colorless solid (545 mg), mp 164–180 °C. Recrystallization from benzene gave 340 mg of the cycloadduct **6c**: mp 197–198 °C; IR (Nujol) 3100, 3075, 1600, 1505, 1490, 1450, 1280, 1250, 1230, 1215, 1045, 1030, 955, 785, 770, 755, 700, 695 cm^{-1}; NMR (CCl_4) δ 7.30–7.08 (m, 10), 4.07 (s, 4), 2.54 (ddd, 1, J = 9, 6, and 4 Hz), 1.84 (dd, 1, J = 12 and 9 Hz), 1.72 (m, 1), 1.26 (dd, 1, J = 12 and 4 Hz), 1.24–1.02 (m, 2). Anal. Calcd for $C_{24}H_{20}Cl_4O_2$: C, 59.8; H, 4.2; Cl, 29.4. Found: C, 59.9; H, 4.2; Cl, 29.3.

The observed vicinal coupling constants ($J_{2,3}$), 9 and 4 Hz, can be assigned to those between exo-exo and exo-endo protons in the bicyclo[2.2.1]heptyl system indicating that **6c** will be the endo isomer.[32]

Workup of the mother liquid gave additional **6c** (150 mg). Thus, the yield of **6c** based on consumed **1a** was 97.5%.

Reaction of 1,1-Dicyclopropylethylene with 5. (1) Neat Reaction. A mixture of **5** (5.00 g, 19.1 mmol) and 1,1-dicyclopropylethylene (2.00 g, 18.5 mmol) was heated at 110–115 °C for 8 h. The resulting solid mixture was crushed and washed with ether. Insoluble dimer of **5** was collected in this way (4.14 g, 83%, mp 278–279 °C). From the filtrate, crude **6a**, mp 92–94 °C, was isolated, which was recrystallized from benzene giving pure **6a** (0.99 g, 14%, or 82% after subtracting the amount of the dimer): mp 97.5–98 °C; IR (Nujol) 3110, 3090, 3010, 1610, 1280, 1250, 1225, 1210, 1120, 1100, 1040, 990, 955, 905, 835, 805, 790, 780, 720 cm^{-1}; NMR (CCl_4) δ 4.22 (dd, 4, J = 12 and 5 Hz), 1.96 (d, 1, J = 12 Hz), 1.68–1.84 (m, 1), 1.24 (d, 1, J = 12 Hz), −0.1 to 0.80 (m, 9). Anal Calcd for $C_{15}H_{16}Cl_4O_2$: C, 48.7; H, 4.4; Cl, 38.3. Found: C, 48.8; H, 4.1; Cl, 37.5.

(2) In Toluene and in Nitromethane. The same reaction as above was carried out in toluene and in nitromethane at 155–160 °C. A trace amount of p-hydroquinone was added to the mixture to reduce polymerization. The amounts of the dimer were 63 and 70% in toluene and in nitromethane, respectively. The yield of **6a** was 28% in toluene and 23% in nitromethane, which corresponded to 76 and 77% after correcting for the formation of the dimer.

(3) Effect of the Solvent Polarity on the Reaction Rate. Two solutions, 51 mg of 1,1-dicyclopropylethylene and 125 mg of **5** in 1 mL of toluene and 51 mg of the olefin and 125 mg of **5** in 1 mL of nitromethane, were prepared and their 100-μL portions were sealed in small glass tubes. The reaction was performed by soaking them in a bath at 160 ± 5 °C. The solutions were directly analyzed by GLC (PEG at 240 °C) for the formation of the adduct **6a** at appropriate intervals. After 30 min, the reaction was found to be 38% complete in both solvents. After 1 h, it was 52% in nitromethane and 53% in toluene.

Reaction of Vinylcyclopropane with 5. A solution of 0.379 g (5.57 mmol) of vinylcyclopropane, 1.23 g (4.17 mmol) of **5**, and a trace amount of p-hydroquinone in toluene was heated in a glass ampule at 155–160 °C for 10 h. After excess olefin was evaporated, benzene was added to the residue and the dimer of **5** was collected (233 mg, 19%). The mother liquid was passed through a short alumina column to remove the colored materials and distilled under reduced pressure. A fraction boiling at 130–135 °C (0.07 mm) was found to be **6b**, 1.19 g (77%): IR (neat) 3100, 3020, 2920, 1600, 1280, 1255, 1230, 1120, 1055, 1035, 960, 920, 865, 830, 800, 790, 760 cm^{-1}; NMR (CCl_4) δ 4.16 (s, 4), 2.40 (dd, 1, J = 11 and 9 Hz), 1.84–2.16 (m, 1), 1.46 (dd, 1, J = 11 and 3 Hz), 0.0–0.8 (m, 5). Anal. Calcd for $C_{12}H_{12}Cl_4O_2$: C, 43.7; H, 3.7; Cl, 43.0. Found: C, 43.8; H, 3.7; Cl, 43.0.

Hydroboration–Oxidation of 1a. To a THF solution of **1a** (2.2 g, 10.0 mmol), externally generated diborane (1.0 g of $NaBH_4$ and 5.1 g of boron trifluoride etherate) was introduced.[11] After being oxidized with hydrogen peroxide, the resulting liquid was vacuum distilled. A fraction boiled at 137–142 °C (0.02 mm) was found to be **7**, 1.99 g (83%): NMR (CCl_4) δ 7.0–7.2 (m, 10), 3.50 (t, 2, J = 6 Hz), 2.48 (s, 1, disappeared in the presence of D_2O), 1.3–1.8 (m, 2). Anal. Calcd for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.6; H, 7.6. 3,5-Dinitrobenzoate, mp 116.3–117.5 °C.

Reaction of 1a with Phenyltribromomethylmercury. A benzene (25 mL) solution of **1a** (1.5 g, 6.8 mmol) and phenyltribromomethylmercury (3.61 g, 6.8 mmol)[33] was heated under reflux for 2 h. After phenylmercuric bromide was removed by filtration, the solution was concentrated on a rotary evaporator. The residue was purified by repeated column chromatography on silica gel eluting with petroleum ether. There were obtained two crystalline adducts, **8a** and **8b**, which were assigned to isomeric bicyclopropyls.[34] For **8a**: mp 97.2–97.8 °C; 396 mg (15%); IR (KBr) 3090, 3070, 3030, 1600, 1495, 1445, 1435, 1415, 1105, 1075, 1055, 1040, 1030, 1020, 1010, 1000, 945, 920, 770, 750, 705, 695 cm^{-1}; NMR (CCl_4) δ 7.6–6.9 (m, 10), 1.8–1.2 (m, 5), 1.00 (d of t, 1, J = 10 and 8 Hz). Anal. Calcd for $C_{18}H_{16}Br_2$: C, 55.1; H, 4.1; Br, 40.8. Found: C, 55.2; H, 4.3; Br, 40.6. For **8b**: mp 91.5–91.8 °C; 1.01 g (38%); IR (KBr) 3060, 3025, 1600, 1580, 1495, 1445, 1425, 1320, 1220, 1185, 1135, 1110, 1090, 1065, 1050, 1035, 1030, 1010, 985, 970, 935, 900, 820, 785, 765, 700, 695, 670 cm^{-1}; NMR (CCl_4) δ 7.4–6.9 (m, 10), 1.85–1.3 (m, 5), 1.0–0.6 (m, 1). Anal. Calcd for $C_{18}H_{16}Br$: C, 55.1; H, 4.1; Br, 40.8. Found: C, 55.1; H, 4.1; Br, 40.8.

References and Notes

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of **5** was produced in a various amounts in all cases, subtractions were made for the yields of the diene adducts given hereafter.
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Trends in Disproportionation Equilibria and Kinetics of Radical Anions Derived from 1,2-Diphenylcyclobutene, -cyclopentene, and -cyclohexene

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Abstract: Sodium salts of radical anions and dianions of 1,2-diphenylcyclobutene, -cyclopentene, and -cyclohexene were characterized through their spectra. The equilibrium and kinetics of disproportionation (eq 1) were studied. The results showed that $K_{\rm dispr}$ increases from 0.15 for the butene system to 110 for the pentene and to 3000 for the hexene. Rate constants k_1's are only slightly affected by the size of the ring, being 2.4×10^7, 3.8×10^7, and $\sim 9 \times 10^7$ $M^{-1}\,s^{-1}$ for the four-, five-, and six-membered rings, respectively, whereas the rate constants of the reverse reactions, k_{-1}, strongly decrease along this series from 1.6×10^8 to 3.5×10^5 and again to 3×10^4 $M^{-1}\,s^{-1}$. Disproportionation of sodium salts of *trans*- and *cis*-stilbenides was thoroughly discussed. It was shown that $K_{\rm dispr,T^{-\cdot},Na^+}$ (0.03) is 10 000 times smaller than that of the cis isomer (250) implying that the strain operating in *cis*-stilbene and its radical anion is alleviated in the dianion. Literature pertaining to the shape and thermodynamics of the pertinent species was fully reviewed. ^{1}H and ^{13}C NMR spectra and mass spectra of the investigated diphenylcycloalkenes were studied and discussed.

Studies of disproportionation of aromatic radical anions reported previously[1-4] have now been extended to radical anions derived from 1,2-diphenylcyclobutene (B), 1,2-diphenylcyclopentene (P), and 1,2-diphenylcyclohexene (H) with the intention of investigating how the strain of the ring affects the equilibria and rates of their disproportionation. We restricted this investigation to systems involving sodium salts of the respective radical anions dissolved in tetrahydrofuran. Under our conditions all the studied radical anions are paired with Na^+ cations and the dianions are present in the form of disodium associates (cyclo-Alk^{2-},$2Na^+$).

The distinction between the cis and trans radical anions of stilbenes was demonstrated by the work of Ward et al.,[5] and even more conclusively by the spectral studies of Wang et al.[6] Ward et al.[5] showed also that the sodium salts of the stilbene dianions exist in THF in two forms, one referred to as "cis",