The Thermal Cycloaddition of Dispiro[2.2.2.2]deca-4,9-diene to Isolated Carbon-Carbon Multiple Bonds

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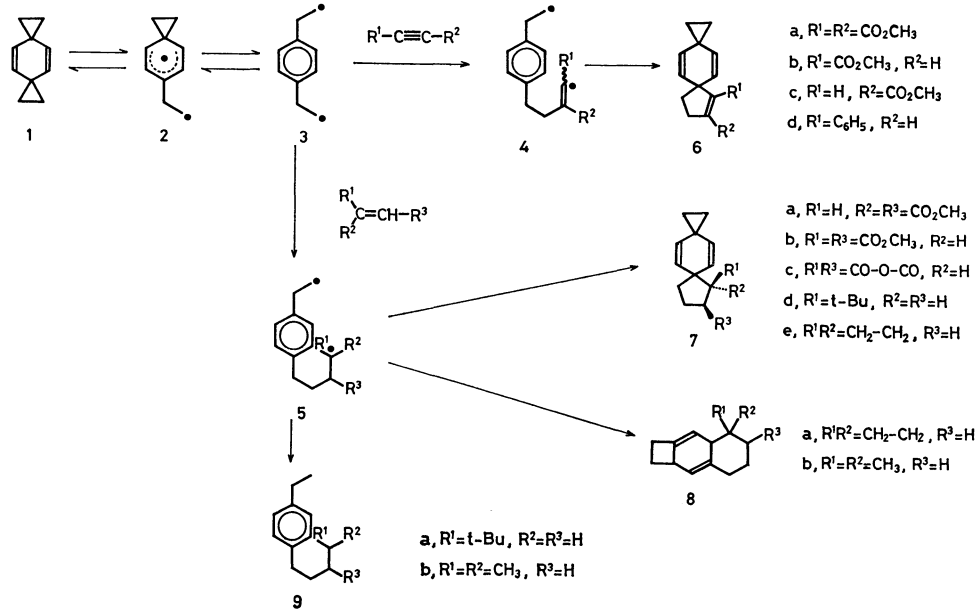
The cycloadditions of dispiro[2.2.2.2]deca-4,9-diene (**1**) to isolated carbon-carbon multiple bonds have proceeded in two different modes, giving dispiro[2.2.4.2]dodeca-4,11-diene and tricyclo[6.4.0.0^{3,6}]dodeca-2,7-diene derivatives. Mono- and 1,2-disubstituted olefins and acetylenes gave the former adducts, whereas 1,1-disubstituted olefins gave the latter, as the major products. Evidence for the intermediacy of biradicals is provided. The observed difference in the mode of the cycloaddition is explained in terms of the stereoelectronic and/or steric effects in the transition state for the cyclization of the intermediate. The addition of **1** to tetracyanoethylene (TCNE) in wet acetone has proceeded *via* a zwitterionic intermediate(s), giving a 1:1:1 adduct of **1**, TCNE, and water.

We have previously reported the thermal cycloaddition reactions of dispiro[2.2.2.2]deca-4,9-diene (**1**) with some conjugated unsaturated compounds[1] which demonstrated the one-step production of [8]paracycloph-4-enes,[1] [4.2]paracyclophanes,[2] and 3-oxa[8]paracycloph-4-enes.[3] As a further inverstigation of the chemistry of **1**, we have now studied the reactions of **1** with compounds possessing an isolated carbon-carbon multiple bond. In the present paper, two novel types of the cycloadditions of **1**, giving dispiro-[2.2.4.2]dodeca-4,11-diene and tricyclo[6.4.0.0^{3,6}]-dodeca-2,7-diene derivatives (**7** and **8**) will be described, and the evidence supporting the intermediacy of biradicals will be presented. We will also report the reaction of **1** with tetracyanoethylene (TCNE), which seems to proceed *via* dipolar intermediate(s).

Results

Addition Reactions Giving Dispiro[2.2.4.2]dodeca-4,11-diene Derivatives (7). As was reported briefly in the previous report,[1] **1** adds to dimethyl maleate (**10**) and dimethyl acetylenedicarboxylate (**11**) to give dispiro[2.2.4.2]dodecane derivatives, **7a** (42%) and **6a** (62%) respectively, under conditions (*ca.* 155 °C) giving rise to the homolytic scission of the cyclopropane ring in **1**. We have now further investigated the cycloaddition reactions of **1** to other unsaturated compounds possessing an isolated carbon-cabon multiple bond in order to examine the generality and the stereochemistry of the reactions.

The reactions were carried out as has previously been reported in *t*-butyl alcohol at 150 °C under a nitrogen atmosphere.[2] The reaction mixture of **1** with dimethyl fumarate (**12**) consisted of one major and five minor products and was quite similar in composition to that resulting from the reaction with **10**. Thus, the major product, isolated in an 11% yield, was found to be **7a**, identical with that produced in the reaction with **10**. On the other hand, the reaction with maleic anhydride (**13**) gave a single cycloadduct (**7c**) in a 29% yield. The successive treatment of **7c** with methanol and then with diazomethane afforded the dimethyl ester (**7b**) which was apparently different from **7a**, but which was identical with one of the minor products found in the product mixtures from both **10** and **12** in a proportion of six-hundredths of **7a**. The triethylamine-catalyzed epimerization at 155



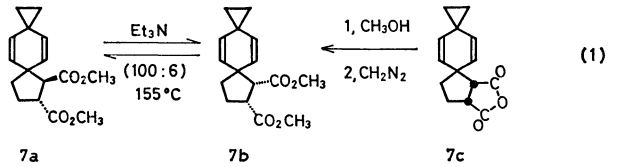
Scheme 1.

Table 1. Reaction products of **1** and unsaturated compounds[a)]

Reaction partner	[1]	[Reaction partner]	Solvent	Product (Yields/%)
10	0.025	0.10	*t*-butyl alcohol	**7a** (49)[b)], **7b** (3)[b)]
12	0.0031	0.013	*t*-butyl alcohol	**7a** (52)[b)], **7b** (4)[b)]
13	0.0062	0.025	hexane	**7c** (47)[b)]
14	0.20	0.40	*t*-butyl alcohol	**7d** (2.4), **9a** (2.2)
15	0.10	0.46	*t*-butyl alcohol	**7e** (8)[b)], **8a** (13)[b)], **21** (4)[b)], **22** (12)[b)], **29** (8)[b,e)]
18	0.20	1.0	*t*-butyl alcohol	**8b** (5), **9b** (1.6), **25** (15), **26** (2.3)
11	0.20	0.40	*t*-butyl alcohol	**6a** (62)
16	0.20	0.40	*t*-butyl alcohol	**6b** (21), **6c** (2.3), **27** (2.7)[c)]
17	0.20	0.40	*t*-butyl alcohol	**6d** (13), **28** (2.3)[d)]

a) The reactions were carried out at 155—160 °C for 9—13 h under nitrogen or argon. b) The yields were determined by GLC analysis. c) Methyl 3,4-dihydro-7-ethyl-1-naphthalenecarboxylate. d) [4.2]Paracycloph-1-ene. e) *p*-Diethylbenzene.

°C gave an equilibrium mixture composed of **7a** and **7b** in a 100:6 ratio starting from either compound. No epimerization, however, was observed in the absence of triethylamine.



(1)

7a 7b 7c

These results show unequivocally that the substituents in **7b** and **7c** have a *cis* geometry with respect to the five-membered ring, whereas those in **7a** have a *trans* geometry.[4)] Therefore, it may be concluded that the cycloadditions of **1** with **10** and with **12** are nonstereospecific and give mixtures of **7a** and **7b** in the same proportion as that in the equilibrium mixture.

In these reactions, it was noticed that the yields of the cycloadducts were remarkably dependent on the reactant concentrations and reached their maxima at 0.01—0.02 M (1 M=1 mol dm^{-3}) for **12**, at 0.1 M for **10** (**7a** in *ca.* 50% yields from both **10** and **12**), and at 0.03 M for **13** (**7c** in a 45% yield) when the reactions were carried out with the **1**/olefin molar ratio of 1/4. At concentrations lower or higher than the above optimums, the reactions resulted in lower yields. At a higher concentration, the addition of a second olefin molecule to the biradical intermediate, **5**, might become competitive with the ring closure of **5** to the product; hence the decreased yields might result. At a lower concentration, the interception of the biradical, **3**, (the interception of the biradical, **2**, would not be important; *vide infra*) by the solvent and/or the impurities prior to the addition of the olefin might reduce the product yield. According to Szwarc,[5)] **12** is nearly five times as reactive as **10** toward alkyl radicals. The optimum concentration for **12** was, indeed nearly one-fifth of that for **10**.

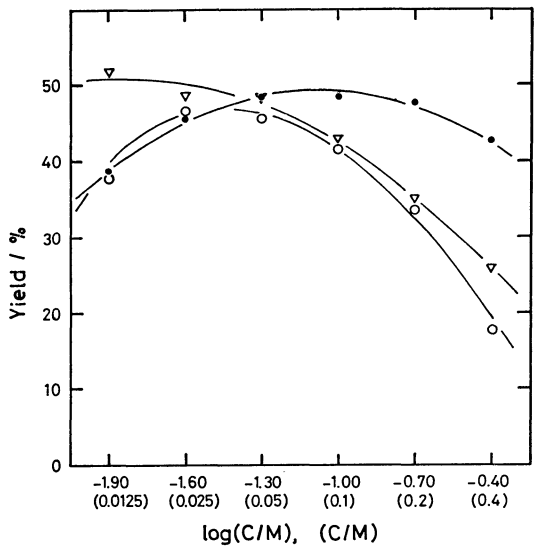
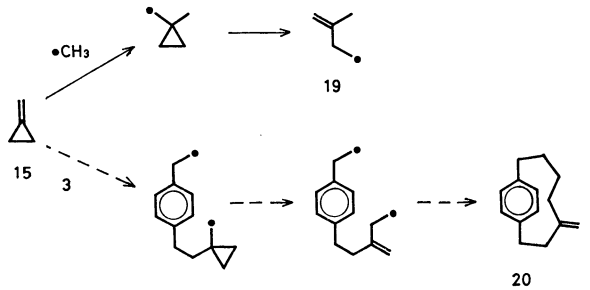


Fig. 1. Yields of the cycloadduct, **7a** or **7c**, *vs.* concentrations of the reactant, **10**, **12**, or **13**. The reactions were carried out maintaining the **1**/olefin molar ratio at a quarter.
●: Yields of **7a** from **1** and **10**, ▽: yields of **7a** from **1** and **12**, ○: yields of **7c** from **1** and **13**.

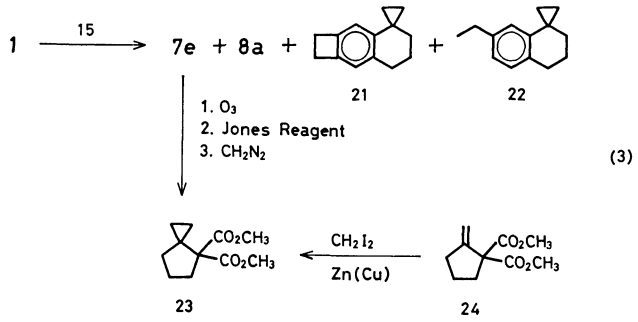
As is shown in Table 1, 3,3-dimethyl-1-butene (**14**) and methylenecyclopropane (**15**) underwent an analogous cycloaddition to give the dispiro products, **7d** and **7e**, though in lower yields. In addition to **11**, the acetylenic compounds, methyl propiolate (**16**) and ethynylbenzene (**17**),[2)] also gave the dispiro adducts, **6b** and **6c**, and **6d**, respectively.

Addition Reactions Giving Tricyclo[6.4.0.0^{3,6}]dodeca-2,7-diene Derivatives (8). Two olefins, **15** and 2-methylpropene (**18**), gave tricyclic compounds as the major product. Kawamura *et al.* have reported the addition of methyl radical to **15** at the inner carbon atom and the subsequent rearrangement to the 3-methyl-3-butenyl radical (**19**).[6)] If the addition of **1** to **15** proceeds analogously, the formation of 3-methylene-[7]paracyclophane (**20**) may be expected, as is de-



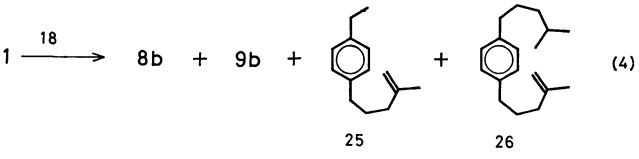
(2)

picted in Eq. 2. The reaction of **1** with **15**, however, gave a mixture of adducts which were isolated and assigned the structures represented by **7e**, **8a**, **21**, and **22**, but no cyclophane. The ozonolyiss of **7e** in methanol at −70——80 °C followed by an oxidative workup and subsequent treatment with diazomethane afforded the dimethyl dicarboxylate (**23**), in a 23% yield, this product was identical in all respects with the ester synthesized *via* an independent route, from **24** to **23**.

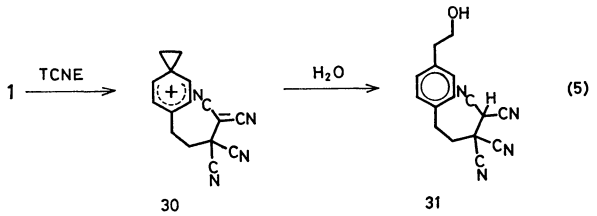


The product, **8a**, which showed two signals of olefinic protons at δ 4.88 and 5.29 in the NMR spectrum, could not be isolated in an analytically pure state because of its gradual conversion into **21** and a polymeric material during the purification. In the mass spectrum of **21**, the molecular ion peak appeared at *m/e* 184, indicating a loss of two hydrogens from a 1 : 1 adduct. The UV spectrum of **21** exhibited a characteristic fine structure which was very similar to those observed in the spectra of symmetrically substituted tetraalkylbenzenes,[7] but this structure was shifted considerably to a longer wave length (by 7 nm compared to 1,2,3,4,5,6,7,8-octahydroanthracene) and the NMR spectrum showed two singlets at δ 6.21 and 6.55, abnormally high field for aromatic proton. These observations are best accommodated by the structure identified as **21**, in which the spiro cyclopropane ring can give rise to the bathochromic shift in the UV spectrum and the high-field shifts of the aromatic proton signals in the NMR spectrum to the extents observed; hence, **8a**, a precursor of **21**, was assigned the 1,4-cyclohexadiene structure.[8] Compound **22**, as expected, also exhibited characteristic shifts in the UV and NMR spectra similar to those in the spectra of **21**.

The reaction of **1** with **18** afforded the tricyclic product, **8b**, in a 5% yield. The major product was *p*-(4-methyl-4-pentenyl)ethylbenzene (**25**) (15%), which was probably formed through the rapid intramolecular disproportionation. No dispiro adduct, however, was detected in the reaction mixture.



Reaction with TCNE. As has been reported previously, **1** reacts with tetracyanoquinodimethane to give [3.3]paracyclophanetetracarbonitrile *via* a zwitterionic intermediate.[1] TCNE is well known to add to electron-rich olefins,[9] and **1** is known to be an olefin possessing an unusually low ionization potential.[10] Therefore, it is of interest to investigate how **1** behaves toward TCNE. The reaction of **1** with TCNE proceeded rapidly in various solvents, such as acetonitrile, nitromethane, acetone, ethyl acetate, tetrahydrofuran, dichloromethane, and ether, accompanied by an apparent transient coloration of the mixtures in some of the solvents, and was completed in a few minutes at room temperature. In wet acetone, a 1:1:1 adduct of **1**, TCNE, and water, **31**, was obtained in a quantitative yield. In all other solvents, whether anhydrous or wet, however, the reactions gave only amorphous materials.



Discussion

Evidences for the Biradical Pathway for the Formation of Dispiro and Tricyclic Adducts. The cycloaddition of **1** to the olefins giving the dispiro[2.2.4.2]dodecane and tricyclo[6.4.0.0^{3,6}]dodecane derivatives, **6**, **7**, and **8**, can be reasonably explained by the pathway outlined in Scheme 1. Various observations support the above mechanism: 1) the occurrence of the reaction only above the temperature at which the homolytic cleavage of the cyclopropane ring in **1** commences; 2) the formation of the by-products characteristic to radical reactions, *i.e.*, a 1 : 2 adduct, **26**, hydrogen abstraction products, **9**,[11] and disproportionation products, **25** and **26**; 3) the inhibiting effect of the hydrogen donors, such as thiophenol, 2-propanol, and 2,2,4-trimethylpentane,[12] and 4) the nonstereospecificity of the reaction. The reactions of **1** with **10** and with **11** in methanol, as expected, did not show any notable differences in the product compositions.

Although the two biradicals, **2** and **3**, could react with the unsaturated compounds to produce the adducts, the major part, if not all, of the products would derive from **3**. The structure of **2** represents that **2** corresponds to the transition state (or the short-lived intermediate) for the 1,2-aryl shift in **3**.[13] Therefore, **2**, after its formation, would very rapidly rearrange to **3**[14] and have hardly any chance to react with the unsaturated compounds. The reaction of **1** with the styrene derivatives afforded only [4.2]paracyclophanes.[2] Neither dispiro[2.2.4.2]dodeca-4,11-diene nor tricyclo[6.4.0.0^{3,6}]dodeca-2,7-diene derivatives were detected. These results, in accord with the above reasoning, strongly support the ideas that the biradical reacting with the unsaturated compounds is **3** and that the cyclization of the resulting biradicals occurs in **5** (**32**).[15]

Two Modes of Ring Closure. The dispiro compound, **1**, underwent the cycloadditions in two different modes, depending on the unsaturated compounds.

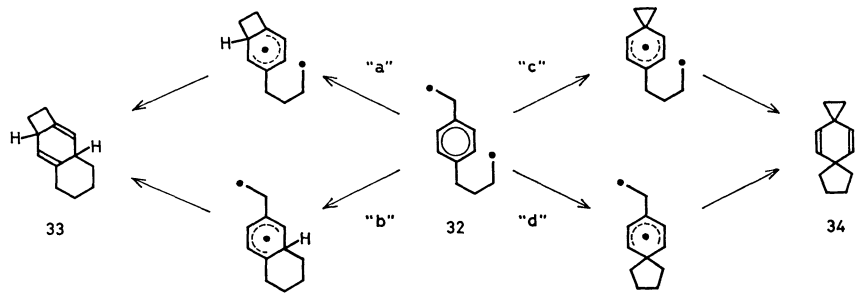
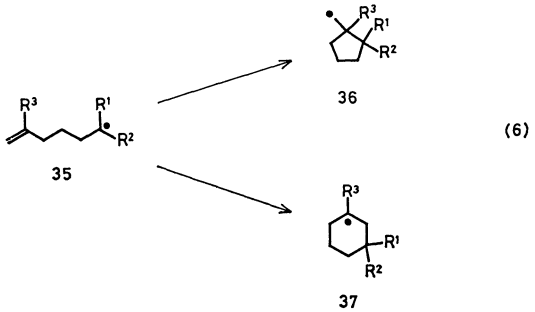


Fig. 2. Four possible cyclization routes for **32** to **33** and **34**. The substituents are omitted for clarity.

There could be four cyclization routes for the biradical intermediate, **32**, leading to two kinds of products, **33** and **34**, as is shown in Fig. 2. The (a) route, however, may be ruled out, since few, if any, instances of such a mode of cyclization of 2-arylethyl radicals have been established, whereas the other three cyclization modes are well documented.[13] In the reactions of the 1,2-disubstituted olefins and the acetylenes, **32** cyclized by the (c) and/or (d) pathways, which would be favored over the (b) pathway because of stereoelectronic[16] and/or steric[17a] effects. These cyclization pathways, (c) and (d), imply intramolecular trappings of the intermediates postulated for 1,2- and 1,4-aryl shifts in radical rearrangements, though the two possible pathways are not differentiated at present.

In the reaction with the 1,1-disubstituted olefins, however, the cyclization to the spiro compounds would be hindered by the repulsive interaction between the central six-membered ring and the two substituents, as is depicted in Fig. 3; hence, a less sterically hindered cyclization to the tricyclic products would result. The above explanation is supported by the finding that methylenecyclopropane, which seems to have less bulky substituents than 2-methylpropene,[18] afforded a mixture of the dispiro and tricyclic adducts. A similar substituent effect on the reaction mode has been known for the ring closure of 5-hexenyl radicals; that is, the less substituted **35** tend to rearrange to cyclopentylmethyl radicals, **36**, but increasing substitution results in an increasing **37**/**36** ratio.[16,17]



(6)

The cycloadditions leading to the dispiro products are formally insertions of the olefins into the cyclopropane ring. Although some analogous reactions producing five-membered rings from olefins and cyclopropane rings have been reported,[19] they are bimolecular or metal-catalyzed reactions. The present reactions are initiated by the unimolecular scission of the cyclopropane ring into the biradical, **3**, to which the unsaturated compounds then add. There is no precedent, to the best of our knowledge, for such an intermolecular cycloaddition of a biradical formed by the homolytic cleavage of a cyclopropane ring to a carbon-carbon multiple bond giving a five-membered ring, probably because 1,3-biradicals are generally too short-lived to be intercepted by unsaturated compounds.[20] In the present reactions, the biradical species reacting with the unsaturated compounds would be the 1,8-biradical, **3**, rather than the incipient 1,3-biradical, **2**; therefore, it would be sufficiently long-lived to add to the multiple bonds.[13]

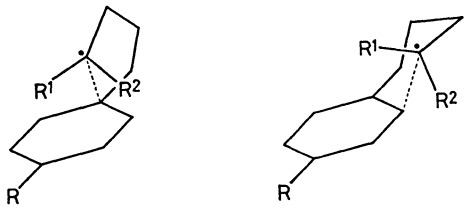
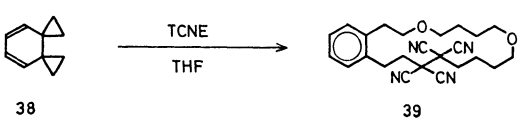


Fig. 3. Probable transition states for the two types of cyclization.

Reaction with TCNE. The rapid reaction of **1** with TCNE is clearly differentiated from the reactions initiated by the unimolecular ring scission in **1**. The formation of the water-incorporated product, **31**, is also incompatible with a radical mechanism and indicates the generation of the zwitterion, **30**. The ring-opening addition of TCNE to **1** rather than the usual addition to unsaturated bonds, and the low reactivity of **1** toward methylenemalononitrile, which adds no less rapidly than TCNE to such electron-rich olefins as vinyl ethers *via* zwitterions,[9b] coupled with the low ionization potential of **1**, suggest the electron transfer from **1** to TCNE prior to the formation of **30**.[9c]

The peculiar observations that **31** was produced only in wet acetone and that the reactions in many other kinds of solvents resulted in amorphous products are rather puzzling. De Meijere *et al.* have reported the reaction of TCNE with dispiro[2.0.2.4]deca-7,9-diene, **38**, a structural isomer of **1**, in tetrahydrofuran giving **39**,[21] but no related product was detected in the reaction of **1** with TCNE in tetrahydrofuran.



(7)

Experimental

General. The melting points are corrected. The NMR spectra were obtained with JEOL PS-100 and Hitachi R-24 spectrometers at 100 and 60 MHz respectively; the chemical shifts are given in ppm from $Si(CH_3)_4$. The IR spectra were taken on a Hitachi Model 215 grating spectrometer and are given in cm^{-1}. The mass spectra were recorded on a Hitachi Model RMU-6E spectrometer at an ionizing voltage of 80 eV, with the exception of that of **23**, which was recorded on a JEOL Model JMS-D300 spectrometer at an ionizing voltage of 70 eV; the ions of each spectrum were normalized to the spectrum's most intense ion, set equal to 100. The UV spectra were taken on a Cary Model 17 spectrophotometer and are given in nm. The GLC work was done on a Hitachi Type 063 gas chromatograph with a thermal conductivity detector, using helium as the carrier gas. The following glass columns were used: A, 20% Apiezon Grease L on Celite 545, 3 mm×1 m; B, 15% Apiezon Grease L on Celite 545, 3 mm×2 m; C, 20% PEG succinate on Celite 545, 4 mm×4 m; D, 15% Apiezon Grease L on Celite 545, 6 mm×1.5 m; E, 20% PEG 20M on Celite 545, 4 mm×1.8 m; F, 15% Apiezon Grease L on Celite 545, 3 mm×1 m; G, 5% Silicone Gum SE-30 on Chromosorb W, 3 mm×0.7 m; H, 20% Silicone DC-550 on Celite 545, 4 mm×1.5 m; I, 5% PEG phthalate on Celite 545, 4 mm×3 m; J, 20% Apiezon Grease L on Celite 545, 4 mm×2 m. The yields were calculated on the basis of the **1** used in the reaction.

Materials. The preparation of dispiro[2.2.2.2]deca-4,9-diene was carried out as has been described previously.[1] Methyl propiolate (**16**),[22] methylenecyclopropane (**15**),[23] 5-iodo-1-pentyne,[24] 3,3-dimethyl-1-butene,[25] TCNE,[26] and Zn–Cu couple[27] were prepared according to the procedures described in the literature. The other reagents were obtained from commercial sources and were purified by fractional distillation or by recrystallization except for 2-methylpropene (**18**), which was purchased from the Tokyo Kasei Co. and used without further purification.

*Reaction of **1** with Dimethyl Fumarate (**12**).* A solution of 132 mg of **1** (1.00 mmol) and 288 mg of **12** (2.00 mmol) in 50 ml of *t*-butyl alcohol was heated at 155 °C for 13.8 h under nitrogen. The solvent was then removed *in vacuo* and the residue was chromatographed on silica gel and eluted with chloroform. The first fraction contained 26 mg of **12**. From the second fraction, which weighed 100 mg, 66 mg of a crystalline mixture were separated by crystallization from petroleum ether. The removal of **12** by sublimation and the recrystallization of the residue from petroleum ether afforded **7a**; mp 68.2—68.7 °C (29 mg, 11%). The third fraction gave 231 mg of an intractable, viscous oil. The adduct obtained above showed no depression of its melting point in a mixed-melting-point measurement with that obtained from **1** and **10**.

*Reaction of **1** with Maleic Anhydride (**13**).* A solution of 132 mg of **1** (1.00 mmol) and 196 mg of **13** (2.00 mmol) in 50 ml of *t*-butyl alcohol was heated as above. After the solvent had been removed, the residue was distilled. The first fraction (bp 140 °C at 15 mmHg) (1 mmHg=133.322 Pa) was 24 mg of **13**. The second fraction (bp 170 °C at 0.02 mmHg) was 169 mg of a pale yellow liquid, from which 66 mg of crystalline **7c** were obtained (29%) by recrystallization from diethyl ether and preparative GLC separation (Column A, 200 °C). A mixture consisting of two components (15 mg) was separated by the preparative GLC, but the structures could not be determined. The residue of the distillation weighed 169 mg. **7c**, mp 79.0—80.5 °C; NMR (CCl_4, 100 MHz): 0.85 (m, 4H), 1.75 (m, 2H), 2.25 (m, 2H), 3.08 (d, J=9.5 Hz, 1H), 3.52 (m, 1H), 5.0—5.6 (m, 4H); mass: *m/e* 230 (M^+, 4), 130 (78), 129 (55), 118 (49), 117 (100), 115 (40), 91 (40); IR (KBr): 1862, 1773, 1222, 917. Found: C, 72.92; H, 6.25%. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13%.

Dimethyl cis-*Dispiro[2.2.4.2]dodeca-4,11-diene-7,8-dicarboxylate (**7b**).* A solution of 22 mg of **7c** (0.096 mmol) in 1.5 ml of methanol was heated at 100 °C for 10 h. After the solvent had been removed *in vacuo*, a solution of diazomethane in ether was added until the yellow color persisted. The subsequent distillation of the reaction mixture yielded 25 mg of **7b** (95%) (bp 150 °C at 0.02 mmHg), a colorless oil which differed from **7a** in GLC retention time and its spectral properties. **7b**, NMR (CCl_4, 100 MHz): 0.77 (s, 4H), 1.4—2.6 (complex m, 4H), 2.86 (d, J=8 Hz, 2H), 3.1 (m, 1H), 3,55 (s, 3H), 3.58 (s, 3H), 4.96 (d of m, J=10 Hz, 2H), 5.40 (m, 2H); mass: *m/e* 276 (M^+, 1), 216 (39), 158 (17), 157 (100), 156 (27), 129 (37), 117 (27); IR (liquid film): 1740, 1728. Found: C, 69.20; H, 7.26%. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30%.

*Epimerization between **7a** and **7b**.* A solution of **7b** in *t*-butyl alcohol (0.27 M) was heated at 155 °C for 22 h, but no epimerization was detected on GLC analysis (Column B, 200 °C). Similarly, a solution of **7a** in *t*-butyl alcohol (0.27 M) was stable at the above temperature. They, however, epimerized when they were heated at 155 °C in a 0.5 M methanolic solution of triethylamine. The ratio of **7b** to **7a** was found to be 0.06:1 after 10 h heating, regardless of the stereochemistry of the starting material; this ratio remained unchanged after 20 h heating. Reaction of **1** with **12** in methanol (155 °C, 12 h) gave the product mixture, in which the ratio of **7b** to **7a** was 0.05.

*Effect of the Reactant Concentration on the Yield of the Adducts, **7a** and **7c**.* To an aliquot (0.5 ml) of a solution of **1** in *t*-butyl alcohol in an accurately known concentration (*ca.* 0.1 M), were added 0.20 mmol of **10** or **12** and the following amount of the solvent; 0, 0.5, 1.5, 3.5, or 7.5 ml. These mixtures were heated in sealed ampoules at 151—153 °C for 14 h under nitrogen. After the reaction, the solvent was removed and the yields of the adducts were determined on GLC (Column B, 200 °C), using benzophenone as the internal standard. Similarly, hexane solutions of **1** and **13** were heated at 158 °C for 12 h under nitrogen and the product yields were determined. In the reactions of **1** with both **10** and **12**, the product ratio, **7b**/**7a**, was 0.06, regardless of the amount of the solvent added.

*Effect of Hydrogen Donors on the Reaction of **1** with **10**.* Five 200-μl aliquots were withdrawn from a solution of 35.5 mg of **1** (0.27 mmol) and 57.6 mg of **10** (0.40 mmol) in 1.00 ml of ether. From each aliquot, the solvent was removed and the following materials were added to the residue: (1) 2.00 ml of *t*-butyl alcohol, (2) 2.00 ml of *t*-butyl alcohol and 11 mg of thiophenol, (3) 2.00 ml of *t*-butyl alcohol and 55 mg of thiophenol, (4) 2.00 ml of 2-propanol, and (5) 2.00 ml of 2,2,4-trimethylpentane. These solutions were heated at 152—155 °C for 11 h under nitrogen, and then the relative yields of **7a** were determined on GLC, using benzophenone as the internal standard (Column B, 200 °C). The yield of **7a** in Run 1 was set equal to 100%. (1) 100%, (2) 38%, (3) 6.3%, (4) trace amount, and (5) 89%.

*Reaction of **1** with 3,3-Dimethyl-1-butene (**14**).* A solution of 132 mg of **1** (1.00 mmol) and 168 mg of **14** (2.00 mmol) in 5.0 ml of *t*-butyl alcohol was heated at 158 °C for 11.5 h under nitrogen. After the removal of the solvent, the residue was subjected to silica gel column chromato-

graphy and subsequently to preparative GLC (Column C, 170 °C), which yielded 4.7 mg of **9a** (2.2%), 5.3 mg of **7d** (2.5%), and 1.9 mg of an unidentified liquid. **7d**, NMR (CCl_4, 60 MHz): 0.65 (s, 4H), 0.86 (s, 9H), 1.2—1.8 (m, 7H), 4.75 (d, J=10 Hz, 2H), 5.26 (d, J=10 Hz, 1H), 5.54 (d, J=10 Hz, 1H). **9a**, NMR (CCl_4, 60 MHz): 0.80 (s, 9H), 1.0—1.8 (m containing t at 1.18, J=7 Hz, 9H), 2.45 (q, J=7 Hz, 4H), 6.83 (s, 4H).

*Reaction of **1** with Methyl Propiolate (**16**).* A solution of 132 mg of **1** (1.00 mmol) and 173 mg of **16** (2.06 mmol) in 5.00 ml of *t*-butyl alcohol was heated at 158 °C for 11.5 h under argon. After the reaction, 0.47 mmol of **16** remained. On GLC analysis (Column F, 170 °C), one major and six minor peaks were observed. The solvent was then removed, and the residue was chromatographed on silica gel. Elution with dichloromethane and then with a mixture of dichloromethane and ether (4:1) gave 53 and 164 mg of the product mixtures respectively. The preparative GLC (Column F, 170 °C) of the former mixture afforded 8.5 mg of **6b**, 4.9 mg of **6c** (2.3%), 5.9 mg of **27** (2.7%), and 1.6 mg of an unidentified product. That of the latter mixture gave 36.3 mg of **6b** (total 44.8 mg, 21%) and 5.9 mg of an unidentified product. An analytical sample of **6b** was obtained by recrystallization from petroleum ether, and those of others by preparative GLC (**6c**, with Column F and subsequently with Column I; **27**, with Column H and subsequently with Column I). Further elution with ether and with ethanol only produced an intractable, amorphous yellow solid. **6b**, mp 65.9—66.5 °C; NMR (CCl_4, 100 MHz): 0.76 (s, 4H), 1.97 (t, J=7.5 Hz, 2H), 2.46 (t of d, J=7.5 and 2.5 Hz, 2H), 3.61 (s, 3H), 4.96 (d, J=10 Hz, 2H), 5.34 (d, J=10 Hz, 2H), 6.67 (t, J=2.5 Hz, 1H); mass, *m/e* 216 (M^+, 8), 198 (25), 157 (21), 156 (24), 141 (27), 129 (100), 128 (36); IR (KBr): 1704, 1628. Found: C, 77.85; H, 7.48%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%. **6c**, NMR (CCl_4, 100 MHz): 0.76 (s, 4H), 1.93 (t, J=7.5 Hz, 2H), 2.59 (t of d, J=7.5 and 2.0 Hz, 2H), 3.68 (s, 3H), 4.96 (d, J=10 Hz, 2H), 5.38 (d, J=10 Hz, 2H), 6.29 (t, J=2 Hz, 1H); mass: *m/e* 217 (10), 216 (M^+, 75), 157 (100), 156 (24), 141 (42), 129 (93), 128 (42), 115 (29); IR (liquid film): 1713, 1626. **27**, NMR (CCl_4, 100 MHz): 1.24 (t, J=7.5 Hz, 3H), 2.40 (m, 2H), 2.5—2.9 (complex m, 4H), 3.79 (s, 3H), 6.89 (s, 2H), 7.03 (t, J=4.5 Hz, 1H), 7.58 (s, 1H).

*Reaction of **1** with Methylenecyclopropane (**15**).* A solution of 396 mg of **1** (3 mmol) and 400 mg of **15** (7.4 mmol) in 21 ml of *t*-butyl alcohol was heated at 152—155 °C for 8 h under nitrogen. The reaction mixture was found by GLC analysis to consist of four major and four minor products, besides *p*-diethylbenzene. Distillation (bath temp, 170 °C at 2 mmHg) and subsequent separation by preparative GLC (Column D, 180 °C) yielded 27.2 mg of **7e** (4.9%), 26.0 mg of **8a** (4.7%), 31.6 mg of **21** (5.7%), and 72.3 mg of **22** (13%). Analytical samples of **7e**, **21**, and **22** were obtained through further purification by GLC (**7e** and **21**, with Column E at 180 °C; **22**, with Column H at 200 °C). The NMR spectrum of **8a** was recorded, but other spectral and analytical data could not be obtained because of the decomposition, which gave **21** and a polymeric material. **7e**, NMR (CCl_4, 100 MHz): 0.34 (AA′ BB′ m, 4H), 0.68 (s, 4H), 1.6—1.9 (m, 6H), 4.91 (d, J=11 Hz, 2H), 5.37 (d, J=11 Hz, 2H); mass: *m/e* 186 (M^+, 4), 158 (35), 157 (40), 143 (25), 130 (100), 129 (80), 128 (34), 115 (34), 91 (30). Found: C, 90.33; H, 9.71%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%. **8a**, NMR (CCl_4, 100 MHz); −0.1—0.7 (complex m, 4H), 0.8—1.2 (two m, 2H), 1.2—3.0 (complex m, 9H), 3.16 (m, 1H), 4.88 (m, 1H), 5.29 (m, 1H). **21**, NMR (CCl_4, 100 MHz): 0.76 (AA′ BB′ m, 4H), 1.48—1.72 (m, 2H), 1.72—2.00 (m, 2H), 2.81 (t, J=6.5 Hz, 2H), 3.04 (s, 4H), 6.20 (s, 1H), 6.54 (s, 1H); mass: *m/e* 185 (17), 184 (M^+, 100), 183 (46), 169 (55), 156 (38), 155 (70), 141 (41); IR (liquid film): 3075, 1478, 890, 857; UV (hexane), max: 277 (ε=2610), 282 (3360), 287 (3400), 292 (3450). Found: C, 91.13; H, 8.79%. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75%. **22**, NMR (CCl_4, 100 MHz): 0.81 (AA′ BB′ m, 4H), 1.18 (t, J=7.7 Hz, 3H), 1.55—1.75 (m, 2H), 1.75—2.05 (m, 2H), 2.51 (q, J=7.7 Hz, 2H), 2.82 (t, J=6 Hz, 2H), 6.34 (s, 1H), 6.77 (AB q, J=8 Hz, 2H); mass: *m/e* 186 (M^+, 43), 158 (40), 157 (100), 129 (56), 128 (19), 115 (17), IR (liquid film): 3075, 1493, 1450, 810; UV (hexane), max: 268^{sh} (ε=670), 274 (1030). 283 (330). Found: C, 90.32; H, 9.78%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%.

*Yields of the Adducts of **1** and **15**.* To 6.6 mg of **1** and 40 μl of a 50 vol % hexane solution of **15** was added a specified volume of *t*-butyl alcohol bubbled with argon, after which the mixture was heated at 155 °C for 9 h under argon. The yields of the adducts were determined by GLC (Column B, 180 °C), using benzophenone as the internal standard. In Run 2, the yield of *p*-diethylbenzene and the amount of **1** remaining were also determined to be 7.7 and 7.2% respectively, using tetralin as the internal standard.

Run	[1] M	[15] M	Yields of adducts/% 7e	8a	21	22
1	0.032	0.12	3	7	7	2
2	0.10	0.46	8	13	12	4
3	0.25	1.0	7	8	13	5

*Ozonolysis of **7e**.* Compound **7e** (8.0 mg) was dissolved in 5.0 ml of anhydrous methanol, after which ozone/oxygen was bubbled through the solution held at −70—−80 °C for 30 min. After bubbling nitrogen to displace the excess ozone, the methanol was removed *in vacuo* (2 mmHg). The residue was dissolved in 10 ml of acetone, cooled in an ice bath, and treated with 0.5 ml of a 2.67 M Jones reagent. After 20 min, 1.0 ml of methanol was slowly added to destroy the excess oxidizing reagent and the solvent was removed. The residue was dissolved in 5.0 ml of ether, treated with anhydrous magnesium sulfate, and decanted, and the precipitate was washed with another 5.0 ml of ether. The combined ethereal solutions were extracted with two 2-ml portions of aq potassium hydrogencarbonate (2.5 M). The combined extracts were acidified with dil sulfuric acid, saturated with sodium sulfate, and extracted with two 5-ml portions of ether. To the combined ethereal solutions dried with anhydrous magnesium sulfate, was added diazomethane in ether under ice cooling until the yellow color persisted. After standing for 15 min, the excess diazomethane was removed by bubbling nitrogen, and then the ether was evaporated. The isolation of the products by preparative GLC (Column G, 90—130 °C) yielded 2.2 mg of dimethyl 1,1-cyclopropanedicarboxylate, 2.1 mg of **23**, and 0.5 mg of an unidentified material. The Compound **23** thus obtained was identical to that synthesized *via* an independent route (*vide infra*) in all respects.

*Dimethyl 2-Methylene-1,1-cyclopentanedicarboxylate (**24**).* To 40 ml of anhydrous methanol was added 1.6 g of sodium (0.07 mol), and then 8.8 g of dimethyl malonate (0.066 mol) was slowly added to the stirred solution. After heating under reflux for 10 min, 9.7 g of 5-iodo-1-pentyne (0.05 mol) was added slowly and heating was continued for 4 h. Most of the methanol was removed under reduced pressure, the residue was dissolved in 200 ml of water, and the solution was extracted with ether three times. The ethereal extracts

were dried with anhydrous magnesium sulfate and distilled through a spinning-band column *in vacuo* to give 3.1 g of **24** (bp 34 °C at 0.02 mmHg), 2.2 g of dimethyl 4-pentyne-1,1-dicarboxylate (bp 46 °C at 0.02 mmHg), and 1.6 g of a mixture of the two compounds. **24**, NMR (CCl_4, 60 MHz): 1.65 (apparent quintet, J=7 Hz, 2H), 2.05—2.55 (complex m, 4H), 3.60 (s, 6H), 5.20 (m, 2H); IR (liquid film): 1665.

*Dimethyl Spiro[2.4]heptane-4,4-dicarboxylate (**23**).* A mixture of 645 mg of **24** (3.25 mmol), 2.7 g of diiodomethane (10 mmol), and 2.0 g of Zn(Cu) couple (30 mmol) in 17 ml of absolute ether was vigorously stirred under reflux. (A small amount of iodine was added at the start.) Two additional 2.7-g portions of diiodomethane were added after 21 and 45 h. After 78 h of reaction (then, the ratio of the product to the starting material was nearly 1, on the basis of GLC analysis), the ethereal solution was decanted, washed with saturated aq ammonium chloride four times, saturated aq potassium carbonate, and saturated aq sodium chloride, and dried with anhydrous magnesiun sulfate. After the removal of the solvent, distillation gave 611 mg of a liquid (bath temp, 140 °C at 3 mmHg), which was subjected to preparative GLC, affording 200 mg of the starting material (32%), 64 mg of an unidentified product, and 200 mg of **23** (30%). **23**, NMR (CCl_4, 100 MHz): 0.40—0.70 (AA′ BB′ m, 4H), 1.58—1.88 (m, 4H), 2.35 (s, 2H), 3.63 (s, 6H); mass: *m/e* 212 (M^+, 2), 153 (48), 152 (100), 121 (22), 120 (39), 93 (80); IR (liquid film): 3080, 1735, 1150. Found: C, 62.25; H, 7.70%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

*Reaction of **1** with 2-Methylpropene (**18**).* Into a solution of 133 mg of **1** (1.01 mmol) in 5.0 ml of *t*-butyl alcohol was bubbled **18** at 20 °C until the absorption of the gas became slow. (*Ca.* 5 mmol of **18** was dissolved, judging from the change in weight.) The mixture was heated at 156 °C for 12 h under argon. Then the solvent was removed, and the residue was divided by column chromatography on silica gel with petroleum ether into five fractions, which weighed 24, 12, 5, 31, and 92 mg respectively. They were subjected to preparative GLC (Column B, 170 °C). Thus, 9.5 mg of **8b** (5%) and a small amount of **9b** were obtained from the first fraction, a small amount of **9b** (total 3.0 mg, 1.6%) from the second, 2.7 mg of **25** and 5.8 mg of **26** (2.3%) from the fourth, and 25 mg of **25** (total 27.7 mg, 15%) from the fifth. Analytical samples of these compounds were obtained through further purification by GLC (Column B). **8b**, NMR (CCl_4, 100 MHz): 0.65 (s, 3H), 0.93 (s, 3H), 1.2—2.9 (complex m, 11H), 3.13 (m, 1H), 5.17 (m, 1H), 5.37 (broad s, 1H); mass: *m/e* 188 (M^+, 1), 145 (100), 118 (43), 117 (66), 91 (25); IR (liquid film): 1704, 1643; UV (hexane), max: 212^{sh} (ε=12000). Found: C, 89.41; H, 10.58%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%. **9b**, NMR (CCl_4, 60 MHz): 0.82 (d, J=6 Hz, 6H), 1.0—1.8 (complex m containing t, J=7.5 Hz at 1.15, 8H), 2.42 (apparent quintet, J=7.5 Hz, 4H), 6.86 (s, 4H); mass: *m/e* 190 (M^+, 22), 120 (19), 119 (100), 105 (10), 91 (15). **25**, NMR (CCl_4, 100 MHz): 1.23 (t, J=7.7 Hz, 3H), 1.6—1.9 (m containing s at 1.71, 5H), 2.00 (t, J=7.5 Hz, 2H), 2.57 (q, J=7.7 Hz, 4H), 4.67 (s, 2H), 7.00 (s, 4H); mass: *m/e* 188 (M^+, 2), 133 (12), 132 (100), 119 (17), 117 (49), 91 (17); IR (liquid film): 1646; UV (hexane), max: 255^{sh} (ε=180), 260 (310), 266 (420), 268 (400), 274 (480). Found: C, 89.34; H, 10.70%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%. **26**, NMR (CCl_4, 100 MHz): 0.88 (d, J=7 Hz, 6H), 1.0—1.4 (m, 2H), 1.4—1.9 (complex m containing s at 1.70, 8H), 2.00 (t, J=8 Hz, 2H), 2.52 (m, 4H), 4.64 (s, 2H), 6.92 (s, 4H); mass: *m/e* 244 (M^+, 3), 189 (17), 188 (99), 175 (18), 118 (20), 117 (100), 91 (19); IR (liquid film): 1646; UV (hexane), max: 255^{sh} (ε=245), 260 (370), 266 (490), 268 (400), 275 (540).

*Reaction of **1** with TCNE.* TCNE (33 mg, 0.26 mmol) and **1** (33 mg, 0.25 mmol) were each dissolved in 1 ml of simply distilled acetone, and nitrogen was bubbled through each solution for 5 min. When the two solutions were then mixed, a pale violet color appeared, but it then faded within a few min. After standing for 5 d, the reaction mixture was worked up. The crystallization of the product from chloroform yielded 69 mg of **31** (≈100%); mp 104.5—106.5 °C. Successive recystallization from ether and from a 5:1 mixture of ether and acetone gave an analytical sample melting at 107.8—109.0 °C. **31**, NMR (acetone-d_6, 100 MHz): 2.6—3.3 (complex m, 7H), 3.69 (t, J=7 Hz, 2H), 5.97 (broad s, 1H), 7.08—7.32 (m, 4H); mass: *m/e* 251 (M^+—HCN, 9), 221 (18), 135 (33), 105 (79), 104 (100), 103 (11), 91 (11); IR (KBr): 3550, 2120. Found: C, 69.25; H, 4.96; N, 20.06%. Calcd for $C_{14}H_{14}ON_4$: C, 69.05; H, 5.07; N, 20.13%. When the reaction of **1** with TCNE was repeated without bubbling nitrogen and for a shorter reaction time (15 min), **31** melting at 107.7—109.0 °C was obtained in an 85% yield after crystallization from ether. If the acetone distilled through a fractionation column and stored over a Linde 4A Molecular Sieve was used as the solvent, the product was an intractable yellow liquid.

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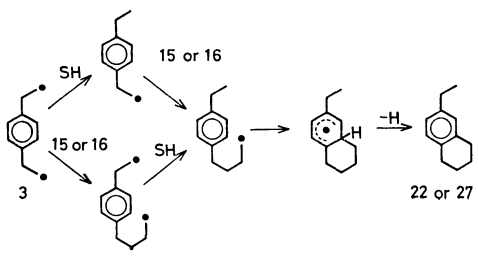
11) The formation of the 7-ethyltetralin derivatives, **22** and **38**, along with that of the hydrogen abstraction product, **9**, can be explained as follows (the substituents are omitted for the sake of clarity):



12) It is noteworthy that the extent of the inhibition by 2,2,4-trimethylpentane (*ca.* a 10% decrease in the yield of **7a** when it is used as the solvent) was nearly as large as that to be expected from the data of Szwarc *et al.*[6] assuming that the addition of **3** to **10** is in competition with the hydrogen abstraction.

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