# Stereospecific [2π+2π+2π] Cycloaddition Reaction of Norbornadiene[1)]

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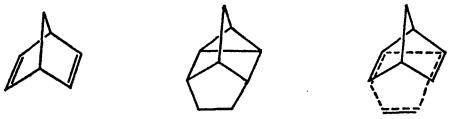
[2π+2π+2π] cycloaddition reaction of *cis*- or *trans*-disubstituted olefinic dienophiles (**4a–4e**) to bicyclo-[2.2.1]hepta-2,5-diene (**1**, norbornadiene) was found to be stereospecific. The cycloadducts obtained, 4,5-disubstituted tetracyclo[4.2.1.0.$^{2,9}$0$^{3,7}$]nonane (**5,6**) conserved the original stereochemistry in the dienophiles, strongly suggesting the presence of *homo*-conjugation in **1**. A striking contrast between cycloaddition reaction of quadricyclane (a valence bond isomer of **1**) and that of norbornadiene was understood by application of the principle of orbital symmetry conservation to these cycloadditions.

[2π+2π+2π] cycloaddition reaction of norbornadiene (**1**) with dienophiles are known as *homo*-Diels-Alder reaction in several cases,[2)] giving tetracyclo-[4.2.1.0.$^{2,9}$0$^{3,7}$]nonanes (**2**). The unique and very interesting mode of these cycloadditions of **1** may be interpreted by means of a six-membered transition state (**3**).



**1** **2** **3**

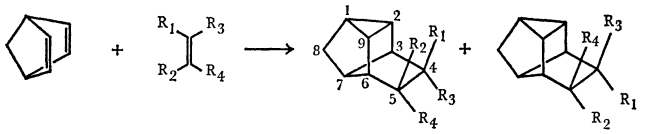
It was suggested by Hoffmann *et al.*[3)] that there exists a (through-space) conjugation between the two double bonds in the ground electronic state of **1**, and several physico-chemical investigations (photoelectron spectroscopy,[4)] photoionization spectroscopy[5)]) or quantum chemical studies[3,4b)] afforded good evidences for the suggestion.

If the unusually effective *homo*-conjugation in **1** also strongly contributes to the assumed transition state (**3**), the cycloadducts must conserve the original stereochemistry of the starting dienophiles. No investigation appeared so far, which showed that the *homo*-Diels-Alder reactions are concerted ones, except for crotononitrile which is reported to conserve the substituents' configuration, *cis* or *trans*, in the cycloadducts.[2f)] If these reactions are concerted, the difference in the symmetry of the highest occupied molecular orbital (HOMO) between norbornadiene (SA) and quadricyclane (AS) could be attributed to the striking difference in regiospecificity of the cycloaddition reactions between these two valence bond isomers.[8)]

Now we wish to report stereochemistry in *homo*-Diels-Alder cycloadditions of **1** with several *cis*- and *trans*-disubstituted olefinic dienophiles (**3a**—**3e**). These cycloaddition reactions were concluded to be completely stereospecific, based on results of chemical and spectroscopic studies of the adducts, therefore, it seems to be concerted, suggesting that the *homo*-conjugation in **1** is very important to control its cycloaddition reactions.

## Results and Discussion

Dimethyl fumarate (**4b**) was treated with excess amount of norbornadiene (**1**) in a sealed tube at 180 °C for 50 hr, in the presence of hydroquinone (2% to **4b**) as an inhibitor to radical polymerizations. Distillation under the reduced pressure gave an oily product (bp 120—125°/5 mmHg) in 78% yield. Determination of the product's structure was made chemically (*vide infra*) and spectroscopically. The mass spectrum of the product showed molecular peak ($M^+$, 236 *m/e*) and expected fragment peaks ($M^+-HCO_2CH_3$, 176 *m/e* and $M^+-HCO_2CH_3-CO_2CH_3$, 117 *m/e*). Infrared spectrum of **5b** exhibited an absorption at 800 cm$^{-1}$, characteristic to nortricyclane skeleton,[7)] and nuclear magnetic resonance spectrum showed absorptions of two protons α to methoxycarbonyls (δ 3.42, 3.22), two protons β to methoxycarbonyls (δ 2.40, 2.32), $C_7$–H proton[8)] (δ 2.04, 1H), and cyclopropane ring protons (δ 0.9—1.3, 3H), which also strongly supported the structure **5b**.



**1** **4** **5** **6**

a) $R_1R_2$=-COOOC-; $R_3$=$R_4$=H
b) $R_1$=$R_4$=$CO_2CH_3$; $R_2$=$R_3$=H
c) $R_1$=$R_2$=$CO_2CH_3$; $R_3$=$R_4$=H
d) $R_1$=$R_4$=CN; $R_2$=$R_3$=H
e) $R_1$=$R_2$=CN; $R_3$=$R_4$=H

4,5-*trans*-Dicyanotetracyclo[4.2.1.0.$^{2,9}$0$^{3,7}$]nonane (**5d**) was obtained in 69% yield, when fumaronitrile (**4d**) was treated at 120 °C with norbornadiene in a similar manner to that described above. The structure **5d** was again supported by mass spectrum (Table 1), IR spectrum (2240 and 800 cm$^{-1}$), and NMR spectrum (Table 2), the latter strongly resembled to that of *trans*-dicarboxylate, **5b**, in every detail (chemical shifts and coupling patterns) except for the chemical shifts of $H_{4x}$ and $H_{5n}$.

Two *homo*-Diels-Alder stereoisomers, *endo-cis*- (**5**) and *exo-cis*-4,5-disubstituted, were obtained from each of maleic anhydide (**4a**), dimethyl maleate (**4c**), and maleonitrile (**4e**) additions to **1**. The NMR spectrum of each cycloadduct (**5a**, **6a**, **5c**, **6c**) exhibited characteristic absorptions of symmetrical two α protons ($H_{4,5}$) and two β protons ($H_{3,6}$) to the substituents, $CO_2X$, together with absorptions of isolated bridgehead proton ($H_7$) and three cyclopropane ring protons, again strongly supporting the products' structure of tetracyclo-

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Table 1. Mass spectra of the *homo*-Diels-Alder adducts[a)]

| Adduct | *m/e* |
|---|---|
| **6a** | p+2 192(1.8), p+1 191(14.4), p 190(100), 162(31), 118(294), 117(283), 115(47), 58(114), 51(100) |
| **5b** | p+2 238(7.3), p+1 237(15.2), p 236(100), 176(415), 145(285), 126(415), 117(769), 116 (423), 115(377), 91(392) |
| **5c** | p+2 238(5), p+1 237(26), p 236(100), 205 (69), 204(52), 177(46), 176(114), 145(106), 118(69), 117(543), 116(106), 115(91), 91(57) |
| **6c** | p+2 238(2.5), p+1 237(16), p 236(100), 205 (73), 204(44), 177(110), 145(120), 126(68), 118(41), 117(288), 116(63), 115(54) |
| **5d** | p+2 172(0.7), p+1 171(11.5), p 170(100), 169(94), 144(122), 130(89), 104(82), 92(91), 91(96) |

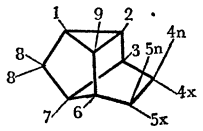
a) Relative intensities are in parentheses.

[4.2.1.0.$^{2,9}$0$^{3,7}$]nonane skeleton. Based on all of spectral data, NMR (*vide infra*), IR, and/or mass spectra, and chemical conversion cited below, it was concluded that cycloadducts, **5a—5d**, **6a—6d** differ only in substituents or in stereochemistry at $C_4$ and $C_5$.

Product distribution in dienophiles' addition to **1** were carefully determined by means of gas liquid phase chromatography (glpc) and the results are shown in Table 3. In each case of addition of a *trans*-disubstituted olefin (**4b** and **4d**) to **1**, no or little corresponding *cis*-4,5-disubstituted isomer was produced within the precision of glpc detection (0.3%) (runs 3 and 7). It was also shown by glpc analysis of crude products that, in the cases of additions of the *cis*-disubstituted olefins (**4c** and **4f**), corresponding *trans* isomers were not detected for **4c** (run 4) or produced only in a trifling amount (5%, run 8) for **4e**. From the present results, therefore, it was concluded that the cycloadducts conserved the original stereochemistry, *cis* or *trans*, of the dienophiles.

Table 3 shows that the stereospecificity mentioned

Table 2. Chemical shifts and coupling constants of the protons of the *homo*-Diels-Alder products




| | **5a**[a,d)] (*endo*) | **6a**[a)] (*exo*) | **5b**[a)] (*trans*) | **5c**[b)] (*endo*) | **6c**[b)] (*exo*) | **5d**[a)] (*trans*) |
|---|---|---|---|---|---|---|
| $H_{1,2,9}$ | 1.1—1.4 | 1.1—1.4 | 0.9—1.3 | 1.1—1.3 | 0.9—1.2 | 1.1—1.5 |
| $H_{3,6}$ | 2.58 | 2.57 | 2.40<br>2.32 | 2.40 | 2.30 | 2.48 |
| $H_{4n}$ | | 2.58 | | | 3.15(s) | |
| $H_{4x}$ | 3.50(dd) | | 3.42(dd) | 3.20(dd) | | 3.21(dd) |
| $H_{5n}$ | | 3.25(s) | 3.22(d) | | 3.15(s) | 3.07(d) |
| $H_{5x}$ | 3.50(dd) | | | 3.20(dd) | | |
| $H_7$ | 2.20 | 1.81 | 2.04 | 2.02 | 1.73 | 2.19 |
| $H_8$ | 1.65 | 1.67 | 1.54 | 1.50 | 1.60 | 1.76 |
| $CO_2CH_3$ | | | 3.72(s)<br>3.70(s) | 3.68(s) | 3.64(s) | |
| $J_{3,4x}$ | 3 | | 4 | 2 | | 4 |
| $J_{6,5n}$ | | 0 | 0 | | 0 | 0 |
| $J_{4n,5x}$ | | | 5 | | | 5 |

a) $\delta$ value in $CDCl_3$. b) $\delta$ value in $CCl_4$. c) Hertz. d) R. C. Cookson *et al.*, Ref. 2d.

Table 3. Product distribution in additions of olefinic dienophiles to **1**.

| Run | Addenda | Temp. (°C) | Hydroquinone | *homo*-Diels-Alder adduct | | |
|---|---|---|---|---|---|---|
| | | | | *cis-endo* | *cis-exo* | *trans* |
| 1 | **4a** | 130 | 2% | 79 | 21 | — |
| 2 | | 200 | 2% | 66 | 34 | — |
| 3 | **4b** | 180 | 2% | <0.2[a)] | <0.2[a)] | >99.6 |
| 4 | **4c** | 150 | 2% | 73 | 27 | < 0.3[a)] |
| 5 | | 200 | 2% | 41 | 24 | 35 |
| 6 | | 200 | 4% | 41 | 24 | 35 |
| 7 | **4d** | 120 | 2% | <0.3[a)] | <0.3[a)] | >99.4 |
| 8 | **4e** | 100[b)] | 2% | *ca.* 80 | *ca.* 15 | 5 |
| 9 | | 120 | 2% | 73 | 16 | 11 |

a) Not detected. b) The conversion was less than 2%.

above holds under the conditions of the controlled reaction temperatures for cases of *cis*-disubstituted dienophiles' additions to **1**. Thus, 35% and 11% of the *trans* isomers isomerized were produced in additions at higher temperature; from *cis* olefin **4c** at 200 °C (run 5) and **4e** at 120 °C (run 9), respectively.

Since maleonitrile (**4e**) was unstable (to isomerize to fumaronitrile, **4d**) at the higher temperatures than 130 °C, the addition reaction of **4e** with **1** was followed at 120 °C up to *ca.* 2% conversion. Glpc analysis of the crude mixture gave a product ratio : **5e** : **6e** : **5d**=73 : 16 : 11. Products **5e** and **6e** could be purified through a preparative glpc, whose IR spectra exhibited absorptions at 2230 and 800 $cm^{-1}$, demonstrating the presence of nortricyclane skeleton and the cyano substituents.

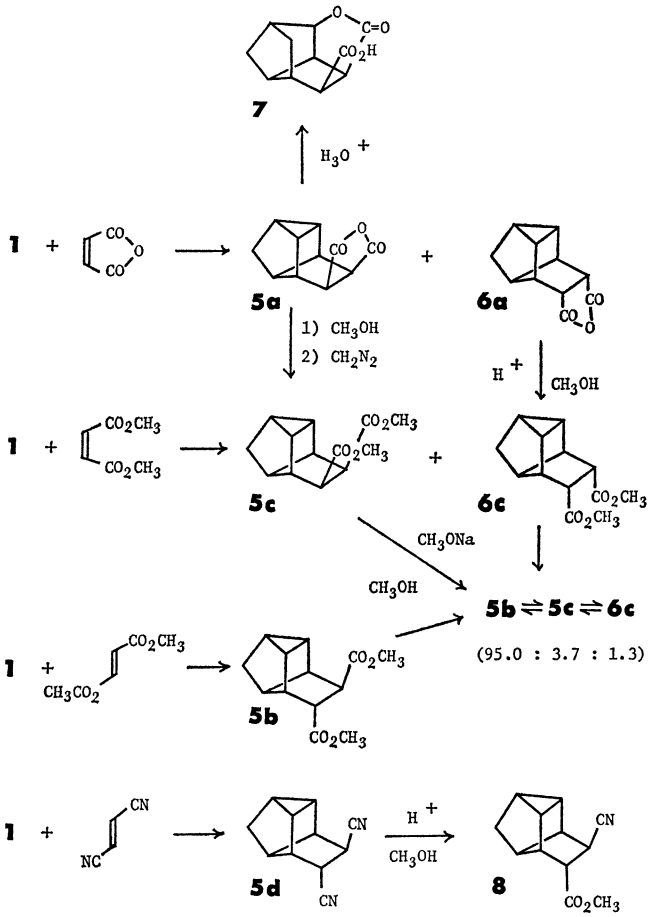
*Chemical Conversion of the Cycloadducts.* Two stereoisomers, tetracyclo[4.2.1.0.$^{2,9}$0$^{3,7}$]nonane-*endo-cis*-4,5-dicarboxylic anhydride (**5a**) and *exo-cis*-dicarboxylic anhydride (**6a**), were obtained in the ratio of 66 : 34,*** when maleic anhydride was treated with excess amount of norbornadiene at 200 °C (Table 3).

The *endo* anhydride (**5a**) was converted to the corresponding half ester on treatment with methanol, followed by estirification with diazomethane giving *endo-cis*-4,5-diester (**5c**) exclusively. Acid catalyzed esterification of the *exo* anhydride (**6a**) in HCl methanol led to the *exo-cis*-4,5-dicarboxylate (**6c**). Dicarboxylates thus obtained, **5c** and **6c**, were identical with those obtained in the reaction of dimethyl maleate (**4c**) with **1**, respectively in every detail (NMR and IR spectra, glpc retention times, see Experimental Section).

It is noteworthy that an equilibrium was attained between the three isomeric dicarboxylates (**5b** : **5c** : **6c**=95.0 : 3.7 : 1.3), when any pure sample of the three was treated with sodium methoxide in methanol at 30 °C for 10 hr.

The conversion of the *trans* dinitrile (**5d**) to the *trans* dicarboxylate (**5b**) was attempted by refluxing a solution of **5d** in HCl acidic methanol for *ca.* 8 hr. However, 4-*endo*-cyano-5-*exo*-methoxycarbonyltetracyclo[4.2.1.0.$^{2,9}$0$^{3,7}$]nonane (**8**) was isolated instead of **5b**. NMR spectroscopic evidence (next paragraph), nevertheless, strongly supported that the *trans* dinitrile (**5d**) had the same skeletal structure as the *trans* dicarboxylate (**5b**), and therefore, it was concluded that the cycloadducts (**5a**—**5d**, **6a**, and **6c**) differ only in substituents (with the same stereochemistry) or in stereochemistry (with the same substituent). Structural correlations are shown in Scheme 1.

*Stereochemistry and NMR Spectra of the Cycloadducts.* Careful examinations of chemical shifts data in Table 2 reveal a very characteristic trend : the $\delta$ values of the *endo* protons at $C_4$ ($C_5$) were somewhat smaller (0.05—0.25 ppm) than those of the *exo* protons at $C_4$ ($C_5$). For example, in *trans* diester **5b** (*trans* dinitrile **5d**), the chemical shift of $H_{5n}$ was $\delta$ 3.22 ($\delta$ 3.07) and that of $H_{4x}$ was $\delta$ 3.42 ($\delta$ 3.21). A similar trend




Scheme 1.

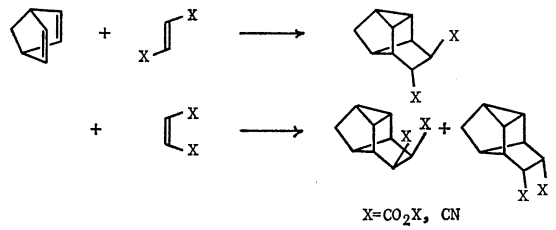
is well known in norbornanes[9] or norbornenes,[10] where the resonances of *exo* protons were observed at somewhat lower field than those of *endo* protons. These were mainly explained as the result of C–C shielding effect.[11]

The chemical shift, $\delta$ 3.50 ($\delta$ 3.20), of $\alpha$ protons of **5a** (**5c**) was larger than that of $\alpha$ protons, $\delta$ 3.25 ($\delta$ 3.15), of **6a** (**6c**). This strongly indicated that **5a** (**5c**) and **6a** (**6c**) have *exo* protons and *endo* protons, respectively, in good agreement with the structures assigned on the basis of chemical conversions.

NMR decoupling experiments of the *trans*-dicarboxylate (**5b**) (*trans*-dinitrile, **5d**) were carried out, which made it possible to calculate $J_{3,4x}$, $J_{6,5n}$, or $J_{4,5x}$ (Table 2). Apparently there observed a large coupling of the *exo* proton ($H_{4x}$) with the bridgehead proton ($J_{3,4x}$=4 Hz), whereas coupling between the *endo* proton ($H_{5n}$) and the corresponding proton ($C_6$-H) was not appreciable. Therefore, the appreciable coupling constants, $J$=3 Hz and $J$=2 Hz, of the resonances of $\alpha$ protons of **5a** and **5c**, respectively, again strongly supported that these $\alpha$ protons are *exo*, in good agreements with the assigned structures.

*Regiospecificity and Stereospecificity of* homo-*Diels-Alder Reaction.* Based on the assigned structures of the cycloadducts, it was concluded that the *homo*-Diels-Alder reaction is stereospecific as shown in Scheme 2. The regiospecificity and stereospecificity observed implies that the reaction is concerted and allowed, giving

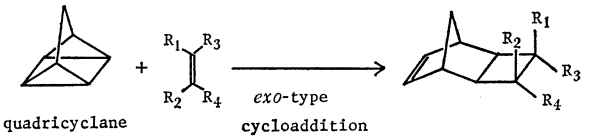
*** Cookson *et al.*[2d] isolated only the *endo-cis* isomer (**5a**), the structure of which was determined by the fact that **5a** could be converted to lactone **7** (Scheme 1).




Scheme 2.

a strong evidence for the *homo*-conjugation in **1** on a reactivity ground.

The present results make a striking contrast to the [2σ+2σ+2π] cycloaddition reaction of quadricyclane reported by the authors,[6] where another type of regiospecificity (*exo*-type addition) together with stereospecificity were observed.




These regiospecificities and stereospecificities in Scheme 3 required a presence of an effective interaction between the two cyclopropane ring bonds in a transition state. Consideration of the usual orbital correlation diagram[12] (Fig. 1) suggests that the *homo-endo*-type cycloaddition to norbornadiene is allowed, whereas the *exo*-type addition, shown in Scheme 3, is forbidden. Thus, the present experimental results are in good agreement with the orbital symmetry consideration.

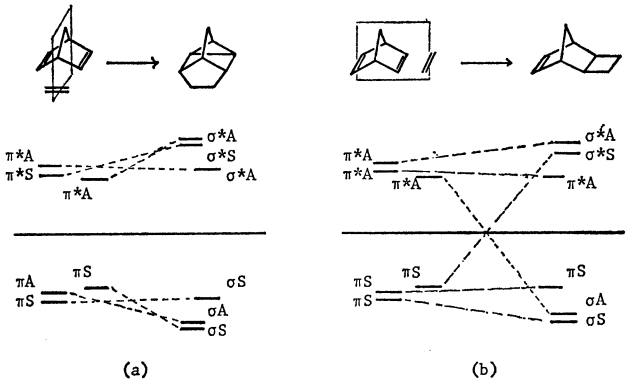
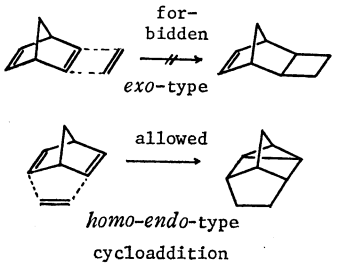



Fig. 1. Orbital correlation diagram.
(a) *homo-endo*-type cycloaddition; (b) *exo*-type cycloaddition.




Scheme 3.

On the other hand, for quadricyclane, *exo*-type cycloaddition is allowed and *homo-endo*-type cycloaddition is forbidden. Again experimental results[6] are in good agreement with the prediction from the orbital symmetry consideration.

It is concluded, therefore, that the striking difference in regiospecificity of the cycloaddition reaction between quadricyclane and norbornadiene is attributable to the differed orbital symmetry of these two valence bond isomers.

## Experimental

Measurements of nuclear magnetic resonance spectra were performed on Varian T-60, JEOL 60-H, or JEOL 100-H spectrometer. Infrared spectra were obtained with a Hitachi model 215 infrared spectrometer. Elemental analyses were performed by Microanalysis Laboratory in Faculty of Pharmaceutical Sciences, Kyushu University or by Microanalysis Center of Kyoto University. Measurements of mass spectra were performed by Analysis Laboratory of Faculty of Pharmaceutical Sciences, Kyushu University or of Department of Synthetic Chemistry, Kyoto University.

For the determination of the product distribution, glpc analyses were carried out with Shimadzu model GC 4B-IT on two different liquid phases: Silicone DC 550 and polyethylene glycol 20 M. Retention times are shown below.

*Reaction of* ***1*** *with Dimethyl Fumarate (****4b****).* A mixture of 1.00 g (6.9 mmol) of dimethyl fumarate (**4b**) and 10 ml (*ca.* 97 mmol) of norbornadiene (**1**) and 10 mg of hydroquinone was sealed in a Pyrex tube (30 ml volume). The sealed tube was heated at 180 °C in a bath for 50 hr. After the evaporation of excess of norbornadiene *in vacuo*, the residue was distilled at the reduced pressure: (**5b**); bp 120—130 °C/5 mmHg; 1.27 g (78%); IR (neat) 3080, 2950, 1735 ($\nu_{C=O}$), 1435, 1180—1200, 1038, 1015, 800, 786 $cm^{-1}$; Found C, 65.94; H, 6.94%. Calcd for $C_{13}H_{16}O_4$ C, 66.08; H, 6.83%.

*Reaction of* ***1*** *with Dimethyl Maleate (****4c****).* A mixture of 1.0 g (6.9 mmol) of dimethyl maleate (**4c**) and 10 ml (97 mmol) of **1** and 10 mg of hydroquinone was sealed in a Pyrex tube and heated at 200 °C for 24 hr. After the distillation off the excess of **1** *in vacuo*, the residue was distilled at the reduced pressure: bp 120—140 °C/5 mmHg; **5c** : **6c** : **5b**=41 : 24 : 35. **5c** : IR (neat) 3060, 2960, 2875, 1740 ($\nu_{C=O}$), 1438, 1200, 818, 794 $cm^{-1}$; glpc retention time, 18.2 min on 2 m polyethylene glycol (190 °C, $H_2$, 1.7 atm); Anal. Calcd for $C_{13}H_{16}O_4$ C, 66.08; H, 6.83%. Found; C, 65.45; H, 6.90%. **6c**: IR (neat) 3060, 2960, 2870, 1740 ($\nu_{C=O}$), 1438, 1120, 1195, 818, 792 $cm^{-1}$; glpc retention time 16.1 min on 2 m polyethylene glycol (190 °C, $H_2$, 1.7 atm); Found C, 65.75; H, 6.60%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

*Reaction of* ***1*** *with Maleic Anhydride (****4a****).* A mixture of 0.50 g (5.1 mmol) of maleic anhydride (**4a**) 1.0 g (*ca.* 11 mmol) of **1**, and 30 mg of hydroquinone was heated in a sealed Pyrex tube at 130 °C for 5 hr. Glpc analysis of the crude mixture on a 2.5 m column of polyethylene glycol at 230 °C ($H_2$, 3.0 atm) revealed that two products were formed: **5a**, 79% (retention time, 8.8 min) and **6a**, 21% (6.7 min). The product ratio at 200 °C was also shown in Table 2. Purifications of **5a** and **6a** were carried out through preparative glpc. **5a** : IR (KBr) 2980, 1860, 1780, 1220, 1080, 906, 895, 830, 800 $cm^{-1}$; **6a** : IR (KBr) 2960, 1860, 1780, 1212, 980, 908, 896, 830, 800 $cm^{-1}$. The NMR chemical shifts of the *endo* anhydride (**5a**) were identical with the values reported by Cookson *et al.*[2d]

*Reaction of* ***1*** *with Fumaronitrile (****4d****).* A mixture of 1.00 g (12.8 mmol) of fumaronitrile (**4d**), 10 ml of norbornadiene, and 10 mg of hydroquinone was heated in a sealed tube at 120 °C for 50 hr. After the excess of **1** was distilled off at the reduced pressure, the residue was distilled at 10 mmHg : **5d**; 1.5 g (69%); bp 165 °C/10 mmHg; mp 77—77.5 °C (from methylene chloride or methanol); IR (neat) 3070, 2950, 2240 ($\nu_{C=N}$), 1305, 1210, 800 $cm^{-1}$; glpc retention time, 1.75 min (polyethylene glycol, 1 m, 190 °C, $H_2$, 1 atm); Found C, 77.83; H, 5.81%. Calcd for $C_{11}H_{10}N_2$ C, 77.62; H, 5.92%.

*Reaction of* ***1*** *with Maleonitrile (****4e****).* A mixture of 0.75 g (9.6 mmol) of maleonitrile (**4e**), 4 ml (43 mmol) of **1**, and 10 mg of hydroquinone was heated in a sealed tube at 100 °C for 17 hr. Glpc analysis on polyethylene glycol (1 m, 190 °C, $H_2$, 1 atm) showed two peaks (3.1 and 4.0 min) and a ratio of 15 : 85. IR spectrum of each product exhibited characteristic absorptions at 2240 and 800 $cm^{-1}$.

*Chemical Conversion.* ***5a*** *to* ***5c***: After 100 mg of **5a** was dissolved in 5.0 ml of methanol at 50 °C, excess methanol was distilled off *in vacuo*. Then 10 ml of ether was added and the solution was treated with etheral solution of diazomethane. After the evaporation of ether, the residue was analyzed by glpc, IR and NMR spectra.

***6a*** *to* ***6c***: A mixture of 100 mg of **6a**, 5 ml of methanol, two drops of concentrated HCl was heated at 60 °C for 3.0 hr. The methanol solution was condensed to one third and then poured into ice cooled water, to which was added an aqueous solution of sodium bicarbonate to neutralize hydrochloric acid. The aqueous solution was extracted with 25 ml of ether twice, and the glpc analysis of the etheral solution revealed that the product was the *endo-cis*-diester (**6c**).

***5d*** *to* ***8***: A mixture of 50 mg (0.29 mmol) of **5d**, a drop of concentrated hydrochloric acid, and 10 ml of dry methanol in a 25 ml flask was stoppered and heated at 80 °C for 8 hr. After the solution was neutralized with an aqueous solution of sodium bicarbonate, the product was extracted with chloroform. Evaporation of chloroform gave an oily product, and the product was identified as **8** by means of glpc analysis and the identical infrared spectrum with an authentic compound. **8** : retention time, 9.5 min on polyethylene glycol 20 M (2 m, 190 °C, $H_2$, 1 atm); IR (neat) 3070, 2948, 2240, 1740, 1438, 818, 799 $cm^{-1}$.

## References

1) A part of this work was presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, Preprint p. 1122 (1972). After this oral presentation, it was reported by Kobuki *et al.* that the *homo*-Diels-Alder reaction of **1** with crotonitrile took place stereospecifically (Ref. 2f).

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