The endo Selectivities of Some Methyl-Substituted Dienophiles in Diels–Alder Reactions with Cyclopentadiene

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Abstract: The stereochemistry of Diels–Alder reactions of cyclopentadiene with CH_2=CHY, *cis*- and *trans*-CH_3CH=CHY, and CH_2=$C(CH_3)$Y, where Y denotes CN, $COCH_3$, CHO, COOH, and COOR, was investigated. The customary endo-addition rule has been found to be of minor importance in determining the endo/exo ratios of the products formed in reactions of these dienophiles. The relative endo selectivities of the methyl-substituted dienophiles decrease in the order *cis*-β-CH_3 > H > *trans*-β-CH_3 > α-CH_3, indicating that the methyl group itself possesses an appreciable endo-orienting ability. Thermodynamic data have shown that the stereochemical courses of the reactions are enthalpy-controlled processes with an even greater contribution of the methyl group as compared with the roles of the various polar unsaturated groups. A proposal is made that the rate-controlling process consists of the parallel but asymmetric approach of a dienophile to the diene. It has been shown that the conformational change of a dienophile can also be a factor influencing the endo orientation of the reaction.

The rule of endo addition[2] in the Diels–Alder reactions is a subject of interest to both organic and physical-organic chemists because of its synthetic usefulness in predicting products with particular stereochemical features. In fact, a great number of examples have manifested wide applicability of this rule.[3]

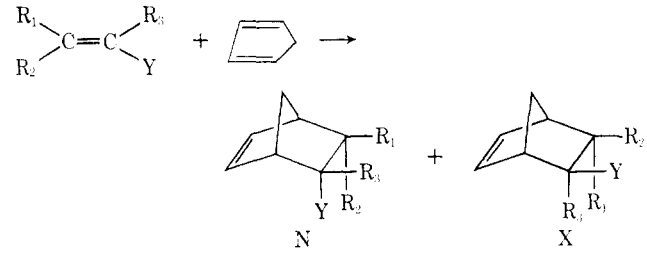
The endo rule is usually rationalized as a result of the principle of "maximum accumulation of unsaturation." The principle has not merely been a phenomenological expression of the endo rule, but has implicitly assumed some additional stabilization of the transition state due to intermolecular interaction between the reactants through the so-called π-orbital overlap. Thus, Woodward and Katz[4] explained the origin of the endo rule as due to secondary binding forces operative in the transition state.

Several authors[5] have given theoretical support to this interpretation with molecular orbital calculations. In particular, Hoffmann and Woodward[6] have attempted to correlate the rule with orbital symmetry characteristics of the 4 + 2 cycloaddition reaction.

Although the above treatments have certainly illuminated the role of mobile π electrons in governing the stereochemical course of the reaction, it has also been known that the original endo rule suffers some limitations depending on the structure of both dienes and dienophiles.[7,8] The deviations from the endo rule have so far been ascribed mainly to steric factors.[7] Alternatively, there is the possibility that the stereochemical courses of the Diels–Alder reaction may be governed by the intermolecular dispersion forces operating in the transition state.[9] The magnitude of these forces should be determinable after due consideration of the pertinent behavior of the reacting systems.

It has already been pointed out[7] that the most revealing indication of the delicate balance among the forces which either encourage or oppose endo orientation comes from the use of dienophiles with substituents on opposite sides of the double bonds, where groups are pitted against each other in their ability to control the stereochemistry of the products. Although a large body of studies has been undertaken from this point of view, there has been no systematic investigation.

In the present study we have undertaken to compare the stereoselectivities of some vinyl compounds with those of the corresponding α-methyl-substituted derivatives as well as a pair of geometrical isomers of β-methyl derivatives in their reactions with cyclopentadiene.



Y = CN, $COOCH_3$, $COCH_3$, CHO, COOH

R_1, R_2, R_3 = H, CH_3

It has been found that the customary rule of endo addition is of minor importance in predicting the stereoselectivities of these methyl-substituted dienophiles. Methyl substitution at the side opposite to the Y group was found to uniformly decrease the relative yields of the endo products, the exo adducts being major products in most α-methyl- and some *trans*-β-methyl-substituted olefins. These results suggest that the methyl group has a greater tendency toward endo orientation

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(2) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).
(3) See, for instance, A. Wasserman, "Diels-Alder Reactions," Elsevier, Amsterdam, 1965; J. Sauer, *Angew. Chem.*, **79**, 76 (1967).
(4) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).
(5) (a) N. Tyutyulkov and P. Markov, *Monatsh. Chem.*, **96**, 2030 (1965); (b) P. Markov and N. Tyutyulkov, *ibid.*, **97**, 1229 (1966); (c) W. C. Herndon and L. H. Hall, *Theoret. Chim. Acta*, 7, 4 (1967); (d) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968).
(6) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).
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(8) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).
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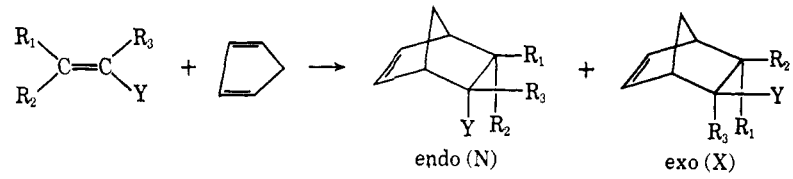
Table I. The endo Percentage and Activation Parameters in the Diels–Alder Reactions of Cyclopentadiene with Various Dieonophiles



endo (N) exo (X)

No.	R_1	R_2	R_3	Y	endo, %[a] 25.0°	50.0°	100.0°	$\Delta H_N^{\ddagger} - \Delta H_X^{\ddagger}$,[b] kcal/mol	$\Delta S_N^{\ddagger} - \Delta S_X^{\ddagger}$,[b] eu
1c	H	CH_3	H	CN	79.5	76.6	73.2	−1.01 ± 0.09	0.69 ± 0.27
1	H	H	H	CN	57.5	56.4	55.3	−0.28 ± 0.02	0.34 ± 0.06
1t	CH_3	H	H	CN	28.1	29.6	29.6	0.38 ± 0.08	0.57 ± 0.25
1α	H	H	CH_3	CN	12.0	13.4	16.2	1.03 ± 0.07	0.50 ± 0.21
2c	H	CH_3	H	$COCH_3$	74.7	73.6	71.0	−0.57 ± 0.02	−0.25 ± 0.07
2	H	H	H	$COCH_3$	79.4	77.1	75.0	−0.72 ± 0.09	−0.24 ± 0.26
2t	CH_3	H	H	$COCH_3$	64.6	63.3	61.3	−0.41 ± 0.01	0.18 ± 0.04
2α	H	H	CH_3	$COCH_3$	47.0	45.9	45.1	−0.22 ± 0.02	0.98 ± 0.06
3c	H	CH_3	H	COO-*sec*-Bu	79.6	76.5	73.8	−0.68 ± 0.01	−0.23 ± 0.02
3t	CH_3	H	H	COO-*sec*-Bu	49.3	49.3	49.5	0.02 ± 0.01	0.03 ± 0.02
3′	H	H	H	$COOCH_3$	74.3	73.2	70.5	−0.56 ± 0.04	−0.23 ± 0.12
3′t	CH_3	H	H	$COOCH_3$	50.9	51.1	50.8	−0.01 ± 0.02	−0.05 ± 0.06
3′α	H	H	CH_3	$COOCH_3$	30.1	30.0	31.8	0.25 ± 0.08	0.86 ± 0.25
4	H	H	H	CHO	74.4	72.3	70.5	−0.57 ± 0.06	−0.19 ± 0.18
4t	CH_3	H	H	CHO	63.1	61.6	59.2	−0.49 ± 0.01	0.56 ± 0.02
4α	H	H	CH_3	CHO	17.0	19.1	23.6	1.21 ± 0.04	−0.91 ± 0.12
5c	H	CH_3	H	COOH	83.7	82.0	79.5	−1.01 ± 0.03	0.13 ± 0.15
5	H	H	H	COOH	80.2	78.7	76.5	−0.65 ± 0.01	−0.59 ± 0.03
5t	CH_3	H	H	COOH	62.4	61.8	59.9	−0.33 ± 0.02	0.08 ± 0.08
5α	H	H	CH_3	COOH	29.2	31.4	34.7	0.74 ± 0.01	−0.74 ± 0.04

[a] Most of these entries are the averages of two independent runs. Deviations from the averages are no more than 0.3%. [b] The uncertainties indicate the probable errors.

than most of the electron-accepting polar groups Y, probably as a result of the stronger intermolecular attractive force of the methyl group.

Results and Discussion

To begin with, cyclopentadiene was allowed to react with acrylonitrile (**1**) in varying molar ratios. The amount of the endo adduct (N) formed relative to that of the exo isomer (X) (60% N at a 1:1 ratio of reactants) showed a clear tendency to decrease with the increasing molar ratio of cyclopentadiene to acrylonitrile used in the range where the ratio was less than 3 (57% N at a 3:1 ratio of reactants). This trend is in accord with the observation[8] that a polar solvent favors the formation of endo products. However, the relative yields of the product isomers are almost independent of the molar ratio of the reactants when the ratio exceeds a value of 3. Thus, in the following experiments, excess cyclopentadiene (usually five times the amount of dienophile in moles) was used in order to examine the factors controlling the stereoselectivity of reactions in a nonpolar reaction medium.

Next, it was confirmed for the same reaction as above that the isomer proportions are entirely independent of the yields. At yields of product which varied from 11 to 97%, the endo/exo ratio did not vary by more than ±0.2%. The results indicate that neither of the isomeric norbornenes suffers endo–exo isomerization during the course of the reaction and that neither isomer adduct was consumed by preferential reaction with excess cyclopentadiene.

Measurements of the relative yields of the product isomers were extended to various dienophiles at varying temperatures. The results are summarized in Table I. As kinetic control of the product mixtures has been proved to hold in reactions of this series of dienophiles under similar reaction conditions,[8] the product ratio endo/exo, N/X, is considered to be equal to the ratio of the specific rate coefficients k_N/k_X. Examination of the temperature dependence of the product ratios thus gives the values for the differences in the heat and entropy of activation between the two reaction courses. These differences in the activation parameters were evaluated usually from the plots of the values of log (N/X) against $1/T$. The results are listed in the final two columns of Table I.

$$2.303R \log (N/X) = (\Delta S_N^{\ddagger} - \Delta S_X^{\ddagger}) - (\Delta H_N^{\ddagger} - \Delta H_X^{\ddagger})/T$$

Shown in Figure 1 are the plots of the values of log (N/X) obtained for the various dienophiles at 25° *vs.* the values of $-(\Delta H_N^{\ddagger} - \Delta H_X^{\ddagger})$. It may be seen in Figure 1 that the two quantities are roughly in linear correlation with each other, irrespective of the type of the dienophiles studied. The correlation coefficient was found to be 0.97. The approximate linearity holding between log (N/X) and $-(\Delta H_N^{\ddagger} - \Delta H_X^{\ddagger})$ suggests that the relative endo selectivities of the reactants are governed primarily by the enthalpy term.

Inspection of the data summarized in Table I shows a general tendency that, except for the case of methyl vinyl ketone (**2**), the relative endo selectivities of any given series of methyl-substituted dienophiles decrease in the order of cis-β > H > trans-β > α. That is, substitution of the methyl group for a cis-β hydrogen uniformly increases endo selectivity of vinyl compounds, while substitution for a trans-β or -α hydrogen decreases it. It may be emphasized here that in this latter class of methyl-substituted dienophiles, the rule

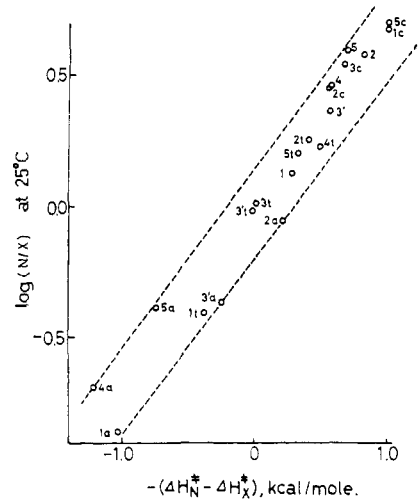


Figure 1. Plots of $\log(N/X)$ *vs.* $-(\Delta H_N^{\ddagger} - \Delta H_X^{\ddagger})$ for the Diels–Alder reactions of cyclopentadiene with various methyl-substituted dienophiles at 25°. Numbers are the same as those in Table I.

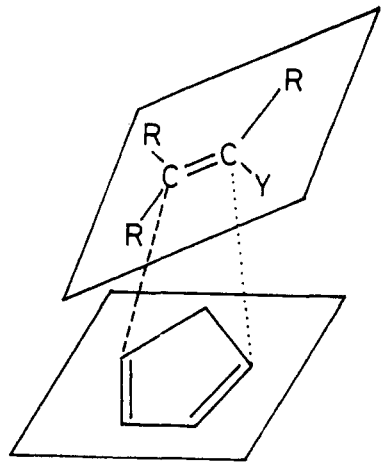


Figure 2. Asymmetric approach in the Diels–Alder reaction.

of endo addition is apparently violated, the exo products being favored in all the α- and some of the trans β-substituted olefins.

The above generalization that the types of methyl substitution have different effects on the endo selectivity deserves some comments. α substitution has a larger favorable effect than β substitution on exo orientation. In some previous reports,[5d,10] the approach of dienophiles to a diene molecule has been assumed to be asymmetrical, *i.e.*, their planes are not parallel in the region of the intermolecular attractive forces, as is depicted in Figure 2. This scheme implies that the β-carbon atom of the dienophile first interacts with diene, leaving the α-carbon atom further from the diene plane. If this picture were the true representation of the rate-controlling step of the concerted cycloaddition, the effect of methyl substitution, whether it favors the endo or exo addition, should be greater in the β substitution than in the α substitution, because of closer interaction of the β- rather than the α-methyl groups with dienes. Clearly, this is incompatible with

(10) J. A. Berson and A. Remanick, *J. Amer. Chem. Soc.*, **83**, 4947 (1961).

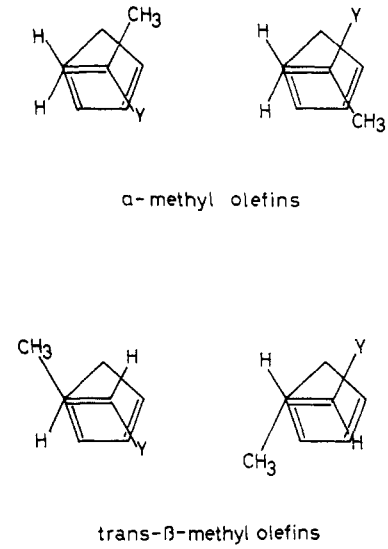


Figure 3. Schematic representation for the transition state of the Diels–Alder reactions of cyclopentadiene with α- and *trans*-β-methyl-substituted acrylic compounds.

our experimental results, thus implying the proposed transition state model as dubious.

Instead, we postulate a nearly parallel approach of the two reactants, in favor of the model for the rate-controlling process proposed by Woodward and Katz.[4] In this transition-state model, the β-carbon of dienophile is assumed to be in the very vicinity of one of the terminal sp^2 carbon atoms of the cyclopentadiene molecule. The α-carbon of dienophile is thus at a longer distance from the other terminal carbon atom of the diene, as is schematically illustrated in Figure 3. With the above model of the transition state, we may expect that the methyl group of α-methyl-substituted olefins will be situated above the cyclopentadiene ring, whereas the methyl group of a *trans*-β-methyl-substituted olefin will not be as close as to the diene molecule. The different substituent effects of the α- and β-methyl groups may thus be explained: the methyl group in the α position could interact fairly strongly with diene while that in the trans β position would be located at a position unfavorable for the proper interaction with diene.

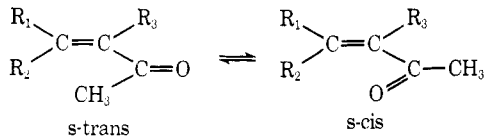
The apparently anomalous preference of the methyl substituent for the endo position may not be directly accounted for by theories based on π-orbital overlap alone.[5,11] It might appear that the failure of the endo rule could be ascribed to the steric repulsions between the methylene group of cyclopentadiene and the *trans*-β- or α-methyl group of dienophiles in the endo orientation, as was suggested in a previous summary[7] with limited data. However, an alternative explanation is also possible for the origin of this failure, if it is assumed that the methyl group leads to strong intermolecular attractive forces, overcoming the secondary attractive forces of carbonyl or nitrile groups toward diene molecules. The endo-orienting abilities of the various groups may then be regarded as decreasing in the order: CH_3 > COOH, COOR, $COCH_3$, CHO > CN > H.

The above assumption may find support in the theoretical demonstration[12] that σ interactions make

(11) W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, 3095 (1967).
(12) (a) W. C. Herndon and J. Feuer, *J. Amer. Chem. Soc.*, **90**, 5914

an important contribution to the stabilities of various molecular complexes and that they even outweigh π interactions in importance in the so-called π complexes of methylbenzenes, which have greater stabilities than the π complex of benzene itself.[12a] Nevertheless, it is our feeling that precise assessment of the relative contributions of the σ and π interactions to the stabilities of the molecular complexes still has to await more thorough analysis. Until then, the present interpretation of the effect of methyl groups in the Diels–Alder reactions is merely a challenging possibility.

One exceptional behavior for the above mentioned relative selectivity is seen in methyl *cis*-propenyl ketone (**2c**). The endo percentage of this dienophile is small compared with that of methyl vinyl ketone (**2**), despite its methyl substitution at the cis β position. Most probably, this anomaly reflects the change in conformation of methyl vinyl ketone on β-methyl substitution. According to the results of the conformational equilibrium studies, most of the α,β-unsaturated ketones exist in both s-cis and s-trans conformations in variable ratios, depending on the types of the groups, R_1, R_2, and R_3.[13]



We have thus measured the infrared spectra of the four unsaturated ketones **2c**, **2**, **2t**, and **2α**, which are compared in Figure 4. The discrepancy between methyl *cis*-propenyl ketone (**2c**) and the remaining three ketones is seen at the C=O stretching region. The absorptions at higher wave number may be attributed to the s-cis conformer, and those at lower wave number to the s-trans conformer. Consequently, the *cis*-propenyl ketone is predominantly in the s-cis conformation, while the other three ketones are stable in the s-trans conformation, in accord with the results[13] reported for similar unsaturated ketones. The prevalence of the s-cis conformation in the *cis*-propenyl ketone might reduce the endo-preferring effect of *cis*-β-methyl substitution, which would otherwise render the ketone more endo orienting. The above view is based on the hypothesis that an s-trans conformer has a greater endo selectivity than its corresponding s-cis conformer. This hypothesis is not at all unlikely but is consistent with the proposal that the methyl group has a greater endo-orienting ability than the C=O or C≡N group. In the s-trans conformer, the methyl group is located above the cyclopentadiene ring, while it is the C=O group that is located above the diene molecule in the s-cis conformer. The endo orientation would thus be more favorable in the case of the s-trans conformer, because of the more effective interaction through the methyl group.

In conclusion, the customary endo-addition rule is violated in the Diels–Alder reactions of a series of methyl-substituted dienophiles with cyclopentadiene.

(1968); (b) G. Briegleb, *Z. Phys. Chem. Abt. B*, **16**, 2449 (1932); (c) H. O. Hooper, *J. Chem. Phys.*, **41**, 599 (1964); (d) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron, Suppl.*, **No. 7**, 97 (1966); (e) M. J. Mantione and B. Pullman, *C. R. Acad. Sci.*, **262**, 1492 (1966); (f) R. Rein and M. Pollak, *J. Chem. Phys.*, **47**, 2039 (1967); (g) M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968).

(13) J. K. Groves and N. Jones, *Tetrahedron*, **25**, 223 (1969).

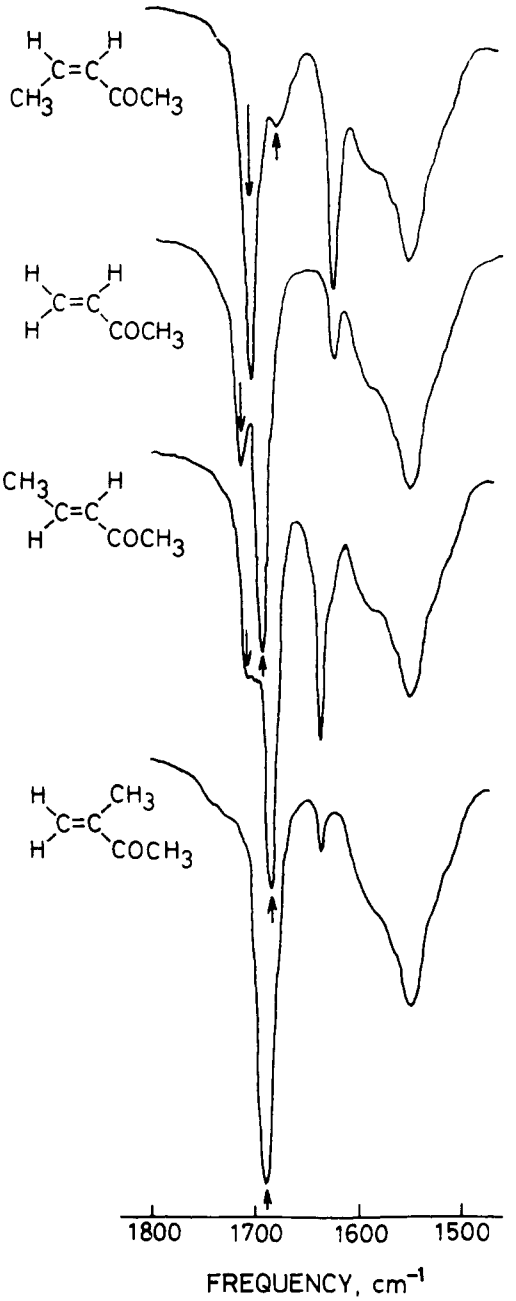


Figure 4. Infrared spectra of substituted methyl vinyl ketones. Concentration, 2.0 mol/l. in carbon tetrachloride. The upward arrows indicate the absorption peaks attributable to the stretching of the s-trans C=O group, whereas the downward arrows correspond to those of the s-cis C=O group.

Their relative endo selectivities decrease in the order of *cis*-β-CH_3 > H > *trans*-β-CH_3 > α-CH_3, and the exo products were obtained preferentially over the endo products in most α-methyl- and some *trans*-β-methyl-substituted olefins. A greater intermolecular attractive force is proposed for the methyl group in comparison with the COOH, COOR, CHO, $COCH_3$, and CN groups. The conformational change of dienophiles seems to be an important factor influencing the endo selectivity of methyl vinyl ketone derivatives.

Experimental Section

Reactants. Cyclopentadiene was obtained by cracking dicyclopentadiene at 170°, and was stored in a Dry Ice bath.

Acrolein, methacrolein, *trans*-crotonaldehyde, acrylic acid, methyl acrylate, methyl methacrylate, acrylonitrile, and methacrylonitrile were commercially obtained and distilled before use. Commercial *trans*-crotonic acid was recrystallized from water, mp 71–72°. The cis isomer of crotonic acid was obtained by a novel synthesis, isomerization of the trans isomer with sulfuric acid as catalyst. The mixture of commercial crotonic acid (100 g) and concentrated sulfuric acid (5 g) was heated gently in the distillation flask equipped with a helix-packed column and a cold finger. The fraction 165–175° was partially taken off from the totally condensing distillation head, and its ether solution was washed several times with $AgNO_3$ solution in order to remove vinylacetic acid and redistilled at high-reflux ratio through a spinning band column to give 15–28 g of pure *cis*-crotonic acid: bp 170–171°; nmr spectrum, 2.15 (3 H, d of doublets, J = 6.9, 0.15 Hz), 5.80 (1 H, d of multiplets, J = 11.5 Hz), 6.45 (1 H, d of q, J = 6.9, 11.5 Hz).

Anal. Calcd for $C_4H_6O_2$: C, 55.81; H, 7.02. Found: C, 55.73; H, 7.22.

The cis and trans isomers of *sec*-butyl crotonate were prepared by the esterification of corresponding acids and they were purified by distillation: cis, bp 64–65° (20 mm); trans, bp 165–166°. The commercial cis and trans mixtures of the crotononitrile were separated by fractional distillation through a spinning band column: cis, bp 108°; trans, bp 119°. Methyl vinyl ketone and methyl isopropenyl ketone were prepared by the aldol condensation of formalin with acetone and methyl ethyl ketone, respectively: MVK, bp 79–80°; MIPK, bp 98°. Methyl propenyl ketone was prepared from acetaldehyde and acetone.[14] The gas chromatographic analysis showed the presence of 16% cis and 76% trans ketones and 8% other impurities. The cis and trans isomers were fractionally distilled through a spinning band column: cis, bp 108°; trans, bp 120–121°. The cis isomer has never been reported in the past. We identified it by nmr and elemental analysis: nmr spectrum of 10% solution in $CDCl_3$, 2.11 (3 H, d, J = 6.6 Hz, $CH_3C{=}C$), 2.20 (3 H, s, CH_3CO), 6.20 (2 H, m, CH=CH).

Anal. Calcd for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.48; H, 9.55.

Diels–Alder Additions. Reaction temperatures, 25, 50, 100, and occasionally 60°, were maintained to within ±0.1° with a thermostat. Most of the reactions were conducted in ampoules containing 2.0×10^{-3} mol of a dienophile and 1.0×10^{-2} mol of cyclopentadiene and a small amount of hydroquinone, *ca.* 10 mol % of the cyclopentadiene. The time necessary to achieve convenient yields of products varied from 0.5 hr to several days, depending upon the temperature as well as the type of dienophiles.

Product Analyses. The reaction products from cyclopentadiene and appropriate substituted olefins were subjected to gas chromatography and the proportions of endo–exo isomers determined from the ratio of peak areas. The analyses were conducted with a Yanagimoto GCG-550T gas chromatograph. Most of the determinations employed a 2.25 m × 4 mm polyethylene glycol 20M column, although occasionally 1,2,3,4-tetrakis(2-cyanoethoxy)butane was used.

Product Identifications. The endo and exo isomers of norbornene derivatives were separated with a Shimadzu gas chromatograph Model GC-2C using a 3.75 m × 4 mm column packed with 15% polyethylene glycol 20M. Of all the samples examined, endo isomers showed longer retention times compared with the corresponding exo isomers. The stereochemical configurations of these norbornene derivatives were identified from the characteristic shieldings of the methyl protons attached to the 2 and 3 positions. The nmr spectra were measured on 10% solutions in $CDCl_3$ with a Japan Electron Optics C-60H nmr spectrometer using tetramethylsilane (TMS) as internal standard.

***endo*-2-Cyano-*endo*-3-methyl- and *exo*-2-cyano-*exo*-3-methylbicyclo[2.2.1]hept-5-ene (1cN and 1cX)** were prepared by the Diels–Alder reaction of *cis*-crotononitrile and cyclopentadiene (CPD) and separated by gas chromatography (vpc) at 180° (retention time, **1cN**, 7 min; **1cX**, 5 min). **1cN** was free from **1cX** isomer, and **1cX** was 97.9% pure, contaminated with 1.6% **1cN** and 0.5% dicyclopentadiene (DCPD); nmr spectrum, **1cN**, 1.01 (*endo*-3-CH_3, d, J = 7.2 Hz); **1cX**, 1.23 (*exo*-3-CH_3, d, J = 6.5 Hz); mass spectrum (same for both isomers), 133 (mol wt 133).

Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: **1cN**, C, 81.12; H, 8.46; N, 10.42. **1cX**, C, 81.07; H, 8.45; N, 10.32.

***endo*- and *exo*-2-cyanobicyclo[2.2.1]hept-5-ene (1N and 1X)** were prepared by the reaction of acrylonitrile and CPD and distilled through a spinning band column; bp **1N**, 90° (12 mm); **1X**, 79° (12 mm). **1X** was 94.3% pure, contaminated with 5.7% of **1X** isomer, and **1X** was free from **1N** isomer by vpc on a 2.25-m polyethylene glycol 20M at 180° (retention time, **1N**, 12 min; **1X**, 9 min).

Anal. Calcd for C_8H_9N: C, 80.63; H, 7.61; N, 11.75. Found: **1N**, C, 80.92; H, 7.65; N, 11.63. **1X**, C, 80.61; H, 7.64; N, 11.73.

***endo*-2-Cyano-*exo*-3-methyl- and *exo*-2-cyano-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (1tN and 1tX)** were prepared by the reaction of *trans*-crotononitrile and CPD and separated by vpc at 180° (retention time, **1tN**, 5.8 min; **1tX**, 4.7 min). **1tN** was 100% pure, and **1tX** was 98.7% pure, contaminated with 1.2% **1tN** isomer and 0.1% DCPD; nmr spectrum, **1tN**, 1.21 (*exo*-3-CH_3, d, J = 6.5 Hz); **1tX**, 0.94 (*endo*-3-CH_3, d, J = 6.6 Hz); mass spectrum (same for both isomers), 133 (mol wt 133).

Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: **1tN**, C, 80.97; H, 8.55; N, 10.46. **1tX**, C, 81.33; H, 8.55; N, 10.63.

***endo*-2-Cyano-*exo*-2-methyl- and *exo*-2-cyano-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (1αN and 1αX)** were prepared by the reaction of methacrylonitrile and CPD and separated by vpc at 180° (retention time, **1αN**, 8.6 min; **1αX**, 6.8 min). **1αN** was 80.7% pure, contaminated with 17.6% **1αX** isomer and 1.7% DCPD. **1αX** was 95.0% pure, contaminated with 1.8% **1αN** isomer and 3.2% DCPD; nmr spectrum, **1αN**, 1.56 (*exo*-2-CH_3, s); **1αX**, 1.23 (*endo*-2-CH_3, s); mass spectrum (same for both isomers), 133 (mol wt 133).

Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: **1αN**, C, 80.33; H, 8.14; N, 9.95. **1αX**, C, 75.75; H, 7.57; N, 9.17. Because these isomers had large tendency toward sublimation, it was very difficult to obtain exact elemental analysis data.

***endo*-2-Acetyl-*endo*-3-methyl- and *exo*-2-acetyl-*exo*-3-methylbicyclo[2.2.1]hept-5-ene (2cN and 2cX)** were prepared by the reaction of methyl *cis*-propenyl ketone and CPD and separated by vpc at 160° (retention time, **2cN**, 19 min; **2cX**, 16 min). **2cN** was 90.4% pure, contaminated with 1.2% **2cX** isomer and 8.4% **2tX**. **2cX** was 92.6% pure, contaminated with 5.8% **2cN** isomer and 1.6% **2tN**. The contamination of **2tN** or **2tX** isomers is due to the use of the isomeric mixture of methyl propenyl ketone: cis, 93.1%; trans, 6.9%; nmr spectrum, **2cN**, 1.13 (*endo*-3-CH_3, d, J = 7.2 Hz), 0.82 (*endo*-2-CH_3CO, s); **2cX**, 2.13 (*exo*-3-CH_3, d, J = 7.0 Hz); 0.97 (*endo*-2-CH_3CO, s); mass spectrum (same for both isomers), 150 (mol wt 150).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: **2cN**, C, 79.71; H, 9.62. **2tX**, C, 80.20; H, 9.29.

***endo*- and *exo*-2-acetylbicyclo[2.2.1]hept-5-ene (2N and 2X)** were prepared from methyl vinyl ketone and CPD and separated by vpc at 160° (retention time, **2N**, 9 min; **2X**, 7 min). **2N** was 90.0% pure, contaminated with 10.0% **2X** isomer, and **2X** was 69.8% pure, contaminated with 29.7% **2N** isomer and 0.5% DCPD; nmr spectrum, **2N**, 2.15 (*endo*-2-CH_3CO, s); **2X**, 2.24 (*exo*-2-CH_3CO, s); mass spectrum (same for both isomers), 136 (mol wt, 136).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: **2N**, C, 79.17; H, 8.92. **2X**, C, 79.31; H, 9.28.

***endo*-2-Acetyl-*exo*-3-methyl- and *exo*-2-acetyl-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (2tN and 2tX)** were prepared from methyl *trans*-propenyl ketone and CPD and separated by vpc at 160° (retention time, **2tN**, 11 min; **2tX**, 9 min). **2tN** was 98.7% pure, contaminated with 1.3% **2tX** isomer, and **2tX** was 99.0% pure, contaminated with 1.0% **2tN** isomer; nmr spectrum, **2tN**, 2.11 (*endo*-2-CH_3CO, s), 1.17 (*exo*-3-CH_3, d, J = 7.0 Hz); **2tX**, 2.20 (*exo*-2-CH_3CO, s), 0.93 (*endo*-3-CH_3, d, J = 6.8 Hz); mass spectrum (same for both isomers), 150 (mol wt 150).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: **2tN**, C, 79.67; H, 9.56. **2tX**, C, 79.98; H, 9.65.

***endo*-2-Acetyl-*exo*-2-methyl- and *exo*-2-acetyl-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (2αN and 2αX)** were prepared from methyl isopropenyl ketone and CPD and separated by vpc at 160° (retention time, **2αN**, 14 min; **2αX**, 12.5 min). **2αN** was 96.4% pure, contaminated with 3.1% **2αX** isomer and 0.5% DCPD. **2αX** was 90.4% pure, contaminated with 9.1% **2αN** isomer and 0.5% DCPD; nmr spectrum, **2αN**, 2.14 (*endo*-2-CH_3CO, s), 1.40 (*exo*-2-CH_3, s); **2αX**, 2.24 (*exo*-2-CH_3CO, s), 1.10 (*endo*-2-CH_3, s); mass spectrum (same for both isomers), 150 (mol wt, 150).

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Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: **2αN**, C, 80.11; H, 9.47. **2αX**, C, 80.24; H, 9.55.

endo-**2-Carbo-*sec*-butoxy-*endo*-3-methyl- and *exo*-2-carbo-*sec*-butoxy-*exo*-3-methylbicyclo[2.2.1]hept-5-ene (3cN and 3cX)** were prepared from *sec*-butyl *cis*-crotonate and CPD. The isomeric mixture of **3cN** and **3cX** was analyzed. Nmr spectrum, **3cN**, 0.84 (*endo*-3-CH_3, d, J = 6.8 Hz); **3cX**, 0.96 (*exo*-3-CH_3, d, J = 6.5 Hz); mass spectrum, 208 (mol wt, 208).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.86; H, 9.70.

endo-**2-Carbo-*sec*-butoxy-*exo*-3-methyl- and *exo*-2-carbo-*sec*-butoxy-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (3tN and 3tX)** were prepared from *sec*-butyl *trans*-crotonate and CPD. The isomeric mixture of **3tN** and **3tX** was analyzed.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.90; H, 9.72.

endo- **and *exo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene (3′N and 3′X)** were prepared from methyl acrylate and CPD and separated by vpc at 150° (retention time, **3′N**, 13.8 min; **3′X**, 12 min). **3′N** was 93.2% pure, contaminated with 5.4% **3′X** isomer and 1.4% DCPD. **3′X** was 90.7% pure, contaminated with 8.5% **3′N** isomer and 0.8% DCPD; nmr spectrum, **3′N**, 3.65 (*endo*-2-OCH_3, s); **3′X**, 3.73 (*exo*-2-OCH_3, s); mass spectrum (same for both isomers), 152 (mol wt 152).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: **3′N**, C, 71.03; H, 8.01. **3′X**, C, 71.06; H, 8.00.

endo-**2-Carbomethoxy-*exo*-3-methyl- and *exo*-2-carbomethoxy-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (3′tN and 3′tX)** were prepared from methyl *trans*-crotonate and CPD and separated by vpc at 150° (retention time, **3′tN**, 14 min; **3′tX**, 12.5 min). **3′tN** was 94.4% pure, contaminated with 5.6% **3′tX** isomer, and **3′tX** was 79.6% pure, contaminated with 20.4% **3′tN** isomer; nmr spectrum, **3′tN**, 3.66 (*endo*-2-OCH_3, s), 1.22 (*exo*-3-CH_3, d, J = 6.5 Hz); **3′tX**, 3.71 (*exo*-2-OCH_3, s), 0.92 (*endo*-3-CH_3, d, J = 7.0 Hz); mass spectrum (same for both isomers), 166 (mol wt, 166).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: **3′tN**, C, 72.31; H, 8.61. **3′tX**, C, 72.30; H, 8.52.

endo-**2-Carbomethoxy-*exo*-2-methyl- and *exo*-2-carbomethoxy-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (3′αN and 3′αX)** were prepared from methyl methacrylate and CPD and separated by vpc on 1,2,3,4-tetrakis(2-cyanoethoxy)butane at 120° (retention time, **3′αN**, 23 min; **3′αX**, 20 min). **3′αN** was 59.8% pure, contaminated with 32.9% **3′αX** isomer and 7.3% DCPD. **3′αX** was 75.7% pure, contaminated with 21.2% **3′αN** isomer and 3.1% DCPD; nmr spectrum, **3′αN**, 3.70 (*endo*-2-OCH_3, s), 1.10 (*exo*-2-CH_3, s); **3′αX**, 3.62 (*exo*-2-OCH_3), 0.92 (*endo*-2-CH_3); mass spectrum (same for both isomers), 166 (mol wt, 166).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: **3′αN**, C, 71.99; H, 8.52. **3′αX**, C, 72.49; H, 8.56.

endo- **and *exo*-2-formylbicyclo[2.2.1]hept-5-ene (4N and 4X)** were prepared from acrolein and CPD. The reaction products were oxidized with Ag_2O–NaOH followed by methylation by diazomethane to give **3′N** and **3′X**. The vpc analysis indicated the identity of these reaction products with **3′N** and **3′X**.

endo-**2-Formyl-*exo*-3-methyl- and *exo*-2-formyl-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (4tN and 4tX)** were prepared from *trans*-crotonaldehyde and CPD. The reaction products were treated as above and confirmed as such from the identity of the derived compounds with **3′tN** and **3′tX**.

endo-**2-Formyl-*exo*-2-methyl- and *exo*-2-formyl-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (4αN and 4αX)** were prepared from methacrolein and CPD. The reaction products were treated as above and confirmed from the identity of the derived compounds with **3′αN** and **3′αX**.

endo-**2-Carboxy-*endo*-3-methyl- and *exo*-2-carboxy-*exo*-3-methylbicyclo[2.2.1]hept-5-ene (5cN and 5cX)** were prepared from *cis*-crotonic acid and CPD. The reaction mixture was esterified with diazomethane. The isomeric mixture of methyl esters of **5cN** and **5cX** was analyzed.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.30; H, 8.51.

endo- **and *exo*-2-carboxybicyclo[2.2.1]hept-5-ene (5N and 5X)** were prepared from acrylic acid and CPD. The reaction mixture was esterified with diazomethane. The vpc analysis indicated the identity of these reaction products with **3′N** and **3′X**.

endo-**2-Carboxy-*exo*-3-methyl- and *exo*-2-carboxy-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (5tN and 5tX)** were prepared from *trans*-crotonic acid and CPD. The reaction mixture was treated as above and identified.

endo-**2-Carboxy-*exo*-2-methyl- and *exo*-2-carboxy-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (5αN and 5αX)** were prepared from methacrylic acid and CPD. The reaction mixture was treated as above and identified.

The Thermochemistry of 1,2-Dioxetane and Its Methylated Derivatives. An Estimate of Activation Parameters

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Abstract: Thermochemical data and activation parameters are calculated for the thermal decomposition of 1,2-dioxetane and its methylated derivatives. The calculations, based on a two-step mechanism, give a log A value of 12.4 for 3,3,4-trimethyl-1,2-dioxetane, which is in excellent agreement with the reported value of 12.2. The calculations indicate that increased methyl substitution increases the stability of 1,2-dioxetanes. The lifetime of 1,2-dioxetane is estimated to be 10 sec at 60° compared to 2.3 hr for tetramethyl-1,2-dioxetane at the same temperature. Light emission, associated with the decomposition of 1,2-dioxetanes, is discussed with respect to the calculated thermochemical data.

Numerous reports of 1,2-dioxetane intermediates have appeared in the literature.[1] In most instances, 1,2-dioxetanes were viewed as transient intermediates. Recently isolation of these four-ring peroxides has been reported.[1b,c,2,3] In carbon tetra-

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