[Ar] = [Bu_4NNO_3], showed that the incomplete conversion into mononitro derivatives was paralleled by the presence of unreacted starting substrate, so that at least 93% of the starting material could be accounted for.

In a number of cases it has been checked by GLC that the added amount of crown ether (1:1 molar ratio with respect to Bu_4NNO_3) can be found unchanged in the reacted mixture.

Acknowledgment. This work was supported in part by the Ministero della Pubblica Istruzione. I thank Professors G. Illuminati and L. Mandolini for their continuous interest and encouragement.

Registry No. 12C4, 294-93-9; 15C5, 33100-27-5; 18C6, 17455-13-9; 21C7, 33089-36-0; 24C8, 33089-37-1; $Bu_4N^+NO_3^-$, 1941-27-1; PhH, 71-43-2; PhMe, 108-88-3; m-$Me_2C_6H_4$, 108-38-3; $KClO_4$, 7778-74-7; KNO_2, 7758-09-0.

Reactions of Maleic Anhydride and Dimethyl Acetylenedicarboxylate (DMAD) with the Three Isodicyclopentadiene Isomers. Kinetic vs. Thermodynamic Control in Cycloadditions

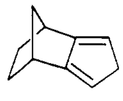
Paul D. Bartlett* and Chengjiu Wu

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received November 26, 1984

The cycloadducts of maleic anhydride and dimethyl acetylenedicarboxylate (DMAD) to the three isodicyclopentadiene isomers have been prepared and studied in terms of competing forward and reverse Diels–Alder reactions and 1,5-sigmatropic rearrangements. At moderate temperature, the maleic anhydride systems are thermodynamically controlled, whereas the DMAD cycloadditions are kinetically controlled. The cycloadduct of DMAD to isomer 3 undergoes a concerted norbornadiene–cycloheptatriene type rearrangement to 14 when heated above 100 °C. Quadricyclane derivatives have been prepared from the DMAD cycloadducts.

Some questions remain unanswered in the cycloaddition studies of the isodicyclopentadiene systems. For example, at elevated temperature where the equilibrium between dienes 1 and 2 is rapid, with most dienophiles only the cycloadducts of 2 are formed.[1,2] Since the amount of 2 in the reaction system is below the detectable limit even at the highest reaction temperature, a steady-state assumption and the knowledge of rates of sigmatropic rearrangement[3-6] of these dienes will lead to an estimate that diene 2 is at least 10^4 times more reactive than 1. Among the many dienophiles studied, dimethyl acetylenedicarboxylate (DMAD) is the only exceptional case, which, even at high reaction temperature, gives cycloadducts of 1 as the sole product.[1] A thorough examination of these systems thus seems necessary before any final explanation can be given. Because of the higher temperature which is essential for production of 2 from 1, particular attention has been paid to the problem of kinetic vs. thermodynamic control.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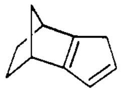
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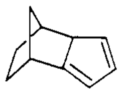
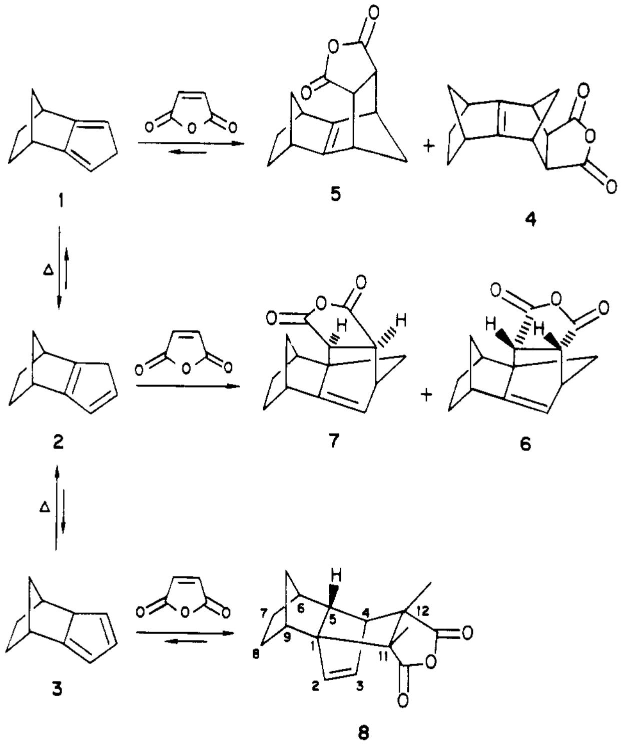

3

In this paper we report the cycloadducts of maleic anhydride and DMAD to the isomeric isodicyclopentadienes, with observations on the thermal and photochemical conversions of these cycloadducts. We also describe methods for preparing the cycloadducts of DMAD to 2.

Scheme I



Results

Cycloadditions of Maleic Anhydride. The reactions of maleic anhydride with the three isodicyclopentadiene isomers are summarized in Scheme I. Cycloadditions with isomer 1[7,8] and isomer 2[1] have been reported. Diene 3

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[1] Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. *J. Org. Chem.* **1982**, *47*, 4491.

[2] Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.

[3] Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

[4] Barlett, P. D.; Wu, C., unpublished.

[5] Washburn, W. N.; Hillson, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 4575.

[6] We thank Dr. W. N. Washburn for an advance preprint of ref 5.

[7] Watson, W. H.; Galloy, J.; Barlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

0022-3263/85/1950-4087$01.50/0

reacts with maleic anhydride at 0 °C quantitatively, giving one single product **8**. The distinctive ^{13}C and ^{1}H NMR spectra clearly indicate that this is a [2 + 4] cycloadduct of **3**. Each of the sp^2 carbons in **8** bears a hydrogen; the d and dd pattern of the two vinyl hydrogens indicates that only one of the vinyl H's is coupled with a vicinal hydrogen (H_4, $J = 2.7$ Hz). The two tertiary hydrogens on the anhydride ring bear the same d and dd feature; one of them is again coupled with the same vicinal hydrogen mentioned above (H_4, $J = 4.5$ Hz). That the maleic anhydride attacks the exo face of **3** is demonstrated by the ^{13}C chemical shifts of the two ethano-bridge carbons in the norbornyl section; the abnormal upfield shifting (22.2 and 28.1 ppm) indicates the unsymmetrical influence of a nearby double bond. All these structural descriptions were confirmed by an X-ray crystallographic analysis.[9]

Compound **8** is the fifth cycloadduct obtained from reactions of maleic anhydride with isodicyclopentadiene isomers. Isomer **1** reacts at both faces to give mainly **4** (anti-Alder rule product) and **5** (Alder rule product).[7,8] Isomer **2**, formed by sigmatropic rearrangement of **1** at 180 °C, gives cycloadducts **6** and **7**, both attached at the exo face.[1] Isomer **3** reacts with maleic anhydride regio- and stereospecifically, giving an Alder rule product at the exo face. This specificity can be explained by the stereochemistry of **3**: the two hydrogens of the ethano bridge prevent an endo attack while the H_6 of **3** and the methylene bridge hinder an exo attack in the anti-Alder mode.

Compared to **1**, isomer **3** reacts much more slowly with maleic anhydride. Our preliminary experiments showed that **3** is at least 30 times slower than **1** in the reaction. The reluctance of **3** in cycloaddition can be attributed to the starting material (interference of the H_6 of **3** with the dienophile molecule and the outward twisting of the π-lobes at the exo face) rather than to the product instability since an early transition state is usually involved in Diels–Alder reactions.[10] It has been shown that the methylene group offers hindrance even in the case of unsubstituted cyclopentadiene.[11]

Interconversions among Cycloadducts 4–8. Compound **8**, the cycloadduct obtained from maleic anhydride and **3**, is highly strained, having a cyclopentane ring trans-fused to the norbornyl framework. The bond angles of C_6–C_5–C_4 and C_9–C_1–C_{11} are 137.7° and 128.4°, respectively, much larger than the normal sp^3 angle. Compound **8**, heated at 170 °C, in solution (*m*-dichlorobenzene or Me_2SO-d_6), disappeared within 10 min; the ^{13}C and ^{1}H NMR spectra became a superposition of those of **6** and **7** with a ratio of 1:1. After 8 h at 170 °C, the ratio of **6** to **7** approaches 10:1. Apparently the thermally unstable **8** underwent a retro-Diels–Alder reaction to diene **3** which rearranged rapidly to isomer **2** by a 1,5-hydrogen shift and was then re-captured by the maleic anhydride in the equilibrium to give **6** and **7**.

Similar results were obtained when pure **4** and **5** were heated separately in *m*-dichlorobenzene solution. Both **4** and **5** were transformed completely into a mixture of **6** and **7** within 40 min at 170 °C; this process is then followed by a slow conversion of **7** to **6** to reach a final equilibrium ratio of 9:91 at about 12 h. In the heating of compound **5**, a temporary buildup of **4** in the first 30 min is also observed. The rearrangements of **4** and **5** during heating are traced by ^{1}H NMR and illustrated in Figure 1, A and B. Compounds **8**, **7**, **6**, and **4** have characteristic absorptions at 5.95, 5.63, 5.53, and 0.55 ppm, respectively, and these were used for quantitative purposes. It is thus established that the thermostabilities of these cycloadducts are increased in the following order: **8** < **5** < **4** < **7** < **6**.

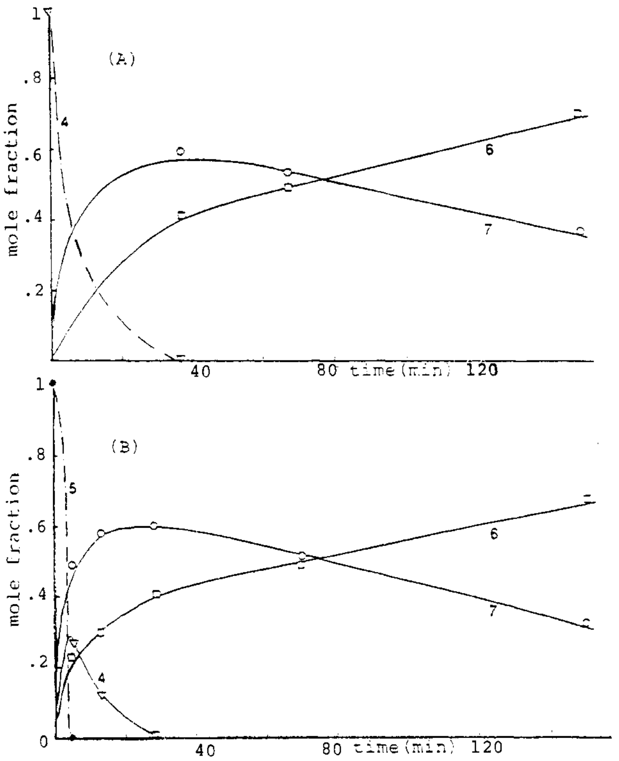

Figure 1. Rearrangement of **4** and **5** during heating at 169 °C: (A) heating of **4**; (B) heating of **5**.

The above observations emphasize the reversibility of moderate-temperature Diels–Alder reactions and the importance of the problem of thermodynamic vs. kinetic controls. Retro-Diels–Alder reactions have long been recognized in the behavior of unreactive dienophiles in which higher temperatures are required.[12] In the reaction of TCNE with the three isodicyclopentadiene isomers, we noticed that the retro-Diels–Alder reaction is significant even at room temperature; at temperatures above 150 °C, all the cycloadducts of **1** were converted into those of **2**.[13] Therefore, the overwhelming formation of the cycloadducts of **2** in the reaction of **1** with many unreactive dienophiles at moderate temperature is not merely a competitive result of extraordinary reactivity of **2** over **1** but a thermodynamic equilibrium of the cycloadducts of **1** and **2**. To test this point further, it is advantageous to have a system in which the reverse reaction is depressed. Dimethyl acetylenedicarboxylate (DMAD) turned out to be a good choice in this respect. Since formation of an alkyne from an alkene is 10 kcal/mol more endothermic than formation of ethylene from ethane,[14] the retro-Diels–Alder reaction is relatively inhibited, in the case of DMAD.

Reactions of DMAD with the Three Diene Isomers. Diene **1** reacts with DMAD at 0 °C to give one endo cycloadduct **9**,[1,15] as shown in Scheme II and Tables I and II. Compound **9** is stable in solution at 170 °C even for 4 days; no formation of **10**, the cycloadduct from **2**, is ever

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[8] Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218; **1981**, *103*, 2910.

[9] Watson, W. H.; Galloy, J.; Wu, C.; Barlett, P. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1418.

[10] Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

[11] Sustmann, R.; Böhm, M.; Sauer, J. *Chem. Ber.* **1979**, *112*, 833.

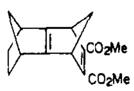
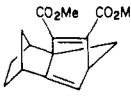
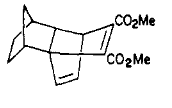
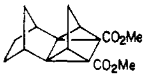
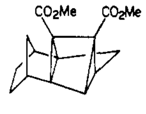
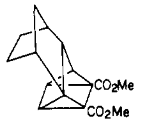
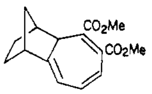
[12] For review, see: Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415.

[13] Bartlett, P. D.; Wu, C. *J. Org. Chem.* **1984**, *49*, 1880.

[14] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; pp 294–295.

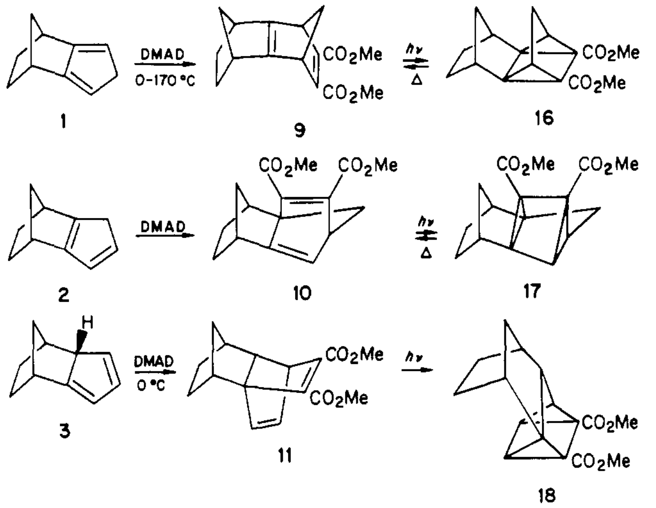
[15] Washburn and Hillson[5] successfully separated an exo cycloadduct of DMAD and diene **1** as a minor product (5%).

Table I. ^{13}C NMR Data of the Seven $C_{10}H_{18}O_4$ Isomers[a] (in $CDCl_3$)

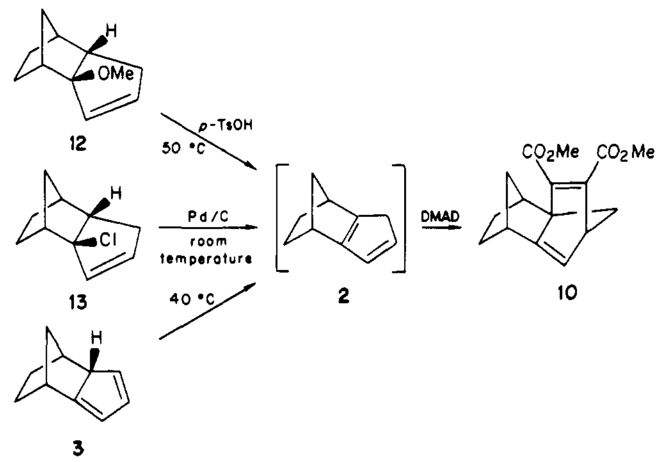
 9	 10	 11	 16	 17	 18	 14
166.0 (s), 2 C	167.6 (s)	166.3 (s)	171.0 (s), 2 C	171.0 (s)	171.4 (s)	167.6 (s)
	167.3 (s)	164.9 (s)		170.8 (s)	170.6 (s)	166.7 (s)
158.7 (s), 2 C	164.6 (s)	159.8 (s)	51.4 (q), 2 C	52.0 (q)	60.9 (s)	153.4 (s)
	155.4 (s)	159.5 (s)		51.7 (q)	58.3 (s), 2 C	134.0 (d)
150.3 (s), 2 C	148.3 (s)	144.6 (d)	50.4 (s), 2 C	43.9 (s)		133.6 (s)
	122.7 (d)	133.1 (d)		43.3 (s)	51.5 (q), 2 C	127.7 (s)
69.9 (t)	75.4 (s)	93.5 (d)	40.7 (d), 2 C	41.0 (d)		124.0 (d)
52.0 (q), 2 C	73.8 (t)	73.6 (s)		36.5 (t)	46.8 (t)	116.0 (d)
	53.2 (d)	54.7 (d)	39.1 (t)	36.1 (d)	39.0 (d)	52.4 (q)
48.5 (t)	52.0 (q)	51.9 (q)	36.8 (d), 2 C	35.4 (d)	35.4 (d)	52.0 (q)
42.9 (d), 4 C	51.8 (q)	51.8 (q)		33.3 (s)	34.4 (t, s) 2 C	48.3 (d)
	43.6 (t)	47.2 (t)	34.2 (t)	31.3 (d)		43.7 (d)
22.3 (t), 2 C	37.7 (d)	43.0 (d)	29.6 (s), 2 C	29.2 (s)	33.9 (d)	40.5 (t)
	37.1 (d)	36.6 (d)		28.7 (t)	32.3 (s)	39.6 (d)
	30.8 (t)	28.4 (t)	28.7 (t), 2 C	27.1 (t)	31.0 (d)	31.4 (t)
	23.9 (t)	22.0 (t)		23.7 (t)	20.7 (t)	27.9 (t)

[a] The related ^{13}C spectrum of 13 is given in ref 16, where it is designated as 4-Cl.

Scheme II



Scheme III



detected. This proved that the retro-Diels–Alder reaction is absent in this case. However, to establish fully that the DMAD–isodicyclopentadiene system is kinetically controlled we need to demonstrate the availability of reaction of DMAD with 2.

From our recent studies on the electrophilic reactions of the isodicyclopentadiene isomers,[16] we now have intermediates which can be used (Scheme III) to generate isomer 2 thermally under mild conditions and without the presence of isomer 1 as a precursor. In the presence of excess DMAD, diene 2 can be generated by acidification of the allylic ether 12 at 50 °C and captured to give 10 as the only product in 82% yield. The spectral features of 10 closely resemble those reported for exo cycloadducts of 2 with various dienophiles.[1,2] Compound 10 is stable enough to withstand distillation or to pass through a GC column at 225 °C. Dehydrochlorination of the allylic chloride 13 under neutral conditions by Pd/C is an alternative method to give 10 by way of 2.

It has also been observed[4] that the sigmatropic conversion 3 → 2 is rapid enough relative to the reaction of 3 with DMAD so that warming of a mixture of 3 and DMAD at controlled relative concentrations can yield a mixture of 10 and 11 in about a 1:3 ratio. This mixture can be further separated by HPLC. It is thus established that the system (1 + DMAD) at moderate temperature is kinetically controlled, in contrast to many other related cycloadditions.

Cycloaddition of DMAD with diene 3 gives only one cycloadduct 11 (exo), its NMR spectra bearing close resemblances to those of the well-defined maleic anhydride cycloadduct 8. The cycloaddition is again very slow; at 0 °C it takes 4 days to complete.

Because 9, 10, and 11 are all formed by apparently irreversible Diels–Alder reactions, there is no direct test of which adduct is the most stable thermodynamically.

In each case we can recognize a source of destabilization: 9 has the unfavorable double-bond ring junction, 10 has the torque resulting from a ring junction with one sp^2 and one sp^3 carbon atom, and 11 has a five-membered ring fused in the trans manner to a norbornane unit.

Since among these compounds only 11 showed any tendency to react thermally, we undertook a study of its thermal behavior as well as the photochemical reactions of the three isomers.

Thermal Rearrangement of 11. When 11 was heated in solution, in a polar or nonpolar solvent at moderate temperature (>100 °C), an irreversible, quantitative re-

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(16) Wu, C.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 733.

Table II. ^{1}H NMR Data of the Seven $C_{10}H_{18}O_4$ Isomers (in $CDCl_3$)

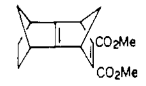
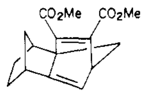
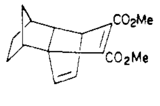
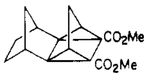
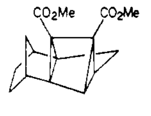
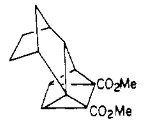
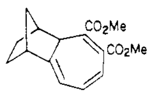
 9	 10	 11	 16	 17	 18	 14
3.70, s, 6 H	6.13, d, 1 H (J = 3.0 Hz)	6.76, d, 1 H (J = 5.1 Hz)	3.70, s, 6 H	3.80, s, 3 H	3.72, s, 3 H	6.74, br s, 1 H (part of ABX)
3.02, br s, 2 H			2.70, m, 2 H	3.67, s, 3 H	3.67, s, 3 H	
2.47, dt, 1 H (J = 7, 1.8 Hz)	3.93, dt, 1 H (J = 3.0, 1.6 Hz)	6.34, dd, 1 H (J = 5.1, 1.8 Hz)	2.68, t, 2 H (J = 1.2 Hz)	2.54, s, 2 H	2.90, dd, 1 H (J = 4.5, 2.4 Hz)	6.71, d, 1 H (part of ABX)
	3.87, s, 3 H			2.50, s, 1 H		
2.14, dt, 1 H (J = 7, 1.8 Hz)	3.79, s, 3 H	4.05, dd, 1 H (J = 1.8, 1.2 Hz)	2.06, dm, 1 H (J = 15 Hz)	2.37, m, 1 H	2.57, m, 1 H	6.19, m, 1 H (part of ABX)
	3.02, d, 1 H (J = 1.8 Hz)			2.13, dt, 1 H (J = 12.6, 1.5 Hz)	2.40, m, 1 H	3.82, s, 3 H
1.45, m, 3 H	2.88, m, 2 H	3.66, s, 3 H	1.87, dm, 1 H (J = 15 Hz)		1.03–2.03, series of m, 9 H	3.76, s, 3 H
1.13, dt, 1 H (J = 8.4, 1.5 Hz)	2.13, br s, 2 H	3.60, s, 3 H		1.98, dd, 1 H (J = 12.6, 1.2 Hz)		2.96, m, 1 H
	0.7–2.0, series of m, 5 H	2.79, m, 2 H	1.68, m, 4 H			2.70, m, 1 H
0.53, m, 2 H		2.36, m, 1 H	1.46, dt, 1 H (J = 12, 1.2 Hz)	0.86–1.42, series of m, 4 H		2.23, m, 1 H
		1.1–1.6, series of m, 6 H				1.20–1.90 series of m, 6 H
			1.12, dt, 1 H (J = 12, 1.2 Hz)			

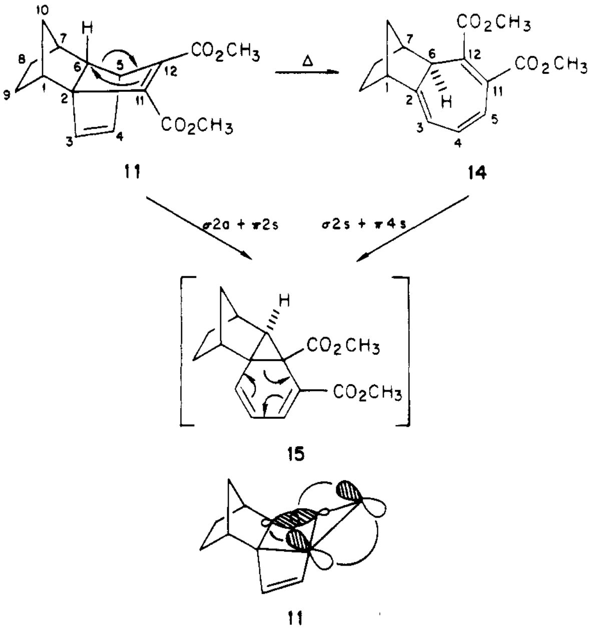
Table III. First-Order Rate Constants for the Thermal Rearrangement of 11 in Solution

temp, °C	solvent	10^4k_1, s^{-1}
	For 11	
108.2	*sec*-butylbenzene-d_{14}	0.393
118.4	*sec*-butylbenzene-d_{14}	1.15
127.4	*sec*-butylbenzene-d_{14}	2.63
138.3	*sec*-butylbenzene-d_{14}	7.21
138.6	*sec*-butylbenzene-d_{14}	7.77
138.6	Me_2SO-d_6	7.53
	For 11-d_1	
138.3	*sec*-butylbenzene-d_{14}	6.08

Table IV. Activation Parameters for the Thermal Rearrangement of 11 in *sec*-Butylbenzene-d_{14}

log A	$\Delta E,^\ddagger$ kcal/mol	$\Delta H,^\ddagger$ kcal/mol	$\Delta S,^\ddagger$ eu	kH/kD (138.3 °C)
13.12	30.6	29.8	-11.3	1.18

Scheme IV



arrangement occurred. The product 14, having the same molecular weight as 11, can be identified as a norbornanocycloheptatriene[17] derivative, as shown in Scheme III, by its ^{1}H and ^{13}C NMR. The norbornyl framework is retained, and one of its ethano-bridge positions is occupied by an sp^2 carbon; the three double bonds are conjugated, and the three vinyl hydrogens are separated from the rest of the protons. Deuterium labeling by starting from 6-deuterio-3 suggests that the methyl carboxylate substituted double bond in 14 is adjacent to the deuterium substituted carbon (C_6). X-ray crystallographic analysis[18] of 14 confirmed the above structural assignment and, importantly, revealed that the hydrogen atom at C_6 is now pointing endo; i.e., the exo configuration of H_6 in compound 11, which is inherited from diene 3, has been inverted during rearrangement.

The rearrangement from 11 to 14 was followed kinetically by ^{1}H NMR. First-order kinetics was observed at various temperatures up to 90% conversion. The kinetic data are shown in Tables III and IV. The Arrhenius plot is strictly linear. There is a large negative activation entropy together with a low activation enthalpy; and no polar solvent effect on rate (the rate in Me_2SO-d_6 is the same as in *sec*-butylbenzene-d_{14}). These two indications, together with the stereospecific inversion of configuration, combined to support the concertedness of the rearrangement.[19]

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[17] The tropylium salt of the parent compound, norbornanocycloheptatriene, has recently been reported: Thummel, R. P.; Chayangkoon, P. *J. Org. Chem.* **1983**, *48*, 596.

[18] Watson, W. H.; Kashyap, R. P.; Wu, C.; Bartlett, P. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1854.

There are very few reported examples of thermal norbornadiene–cycloheptatriene rearrangements.[20-23,26] The usual mechanism of rearrangement involves a norcaradiene intermediate.

Norcaradiene can be formed from norbornadiene in a 1,3-sigmatropic process, illustrated in Scheme IV, where in **11** the old bond from C-6 to C-5 is broken and the new bond from C-11 to C-6 is formed with inversion at C-6, as required for a concerted process with conservation of orbital symmetry.[27] The resulting norcaradiene **15** can now isomerize concertedly to the cycloheptatriene **14** is a disrotatory six-electron electrocyclic process in which the old single bond from C-2 to C-11 is broken and all configurations are retained, an overall geometry confirmed by the X-ray crystallographic study of **14**.

Formation of the Quadricyclane Derivatives from 9–11. Photochemical cyclization of the substituted norbornadienes **9–11** in benzene leads to the substituted quadricyclanes **16–18** in good yields; each of them has been separated and characterized, as shown in Tables I and II. Heating of **16** and **17** in solution gives back the starting materials **9** and **10**, respectively. This orbital-symmetry-forbidden process[24,25] is slow even at 170 °C. However, rearrangement of **18** at 170 °C gives compound **14**, showing that the rearrangement from **11** to **14** is a faster process than from **18** to **11**.

The central double bond in **9** is sensitive to triplet oxygen and autoxidizes in air to give an epoxide.[1] Compared to **9**, the isomers **10** and **11** are much more stable toward autoxidation. The reversible interconversion between **10** and **17** being free of this susceptibility to autoxidation, may be of interest in the storage of solar energy.

Of the three fused norbornadienes **9**, **10**, and **11**, why is **11** the only one to undergo the cycloheptatriene rearrangement? There is no obvious single feature making **11** unique in this respect; but the ability of the "migrating" carbon to undergo this concerted reaction with inversion is obviously critical to the whole process, and the ability of the cooperating deformations to work together to attain this strained transition state may well be the critical difference between the isomers.

Experimental Section

The ^1H NMR spectra were obtained on a Varian EM-390 90-MHz spectrometer. The ^{13}C NMR spectra were determined on a JEOL FX-60 (15 MHz) spectrometer. The IR spectra were recorded on a Perkin-Elmer 197 spectrophotometer. GC analyses were performed on a Perkin-Elmer Sigma-2000 chromatograph, using SE-30 or Carbowax 1000 packed columns. Preparative GC separations were performed on a Varian 920 Aerograph, using 15-ft Carbowax packed columns.

HPLC separations were performed on a Waters 204 liquid chromatograph, using a 7.8 mm × 30 cm μ-Porasil column.

The GC–MS data were determined on a Finnigan OWA 1020 GC–MS–DS; the ionization voltage is 70 eV. High-resolution mass spectral determinations were performed by the Analytical Service Lab at University of Texas (Austin). Elemental analyses were performed by Schwarzkopf Microanalytical Lab. Melting points are uncorrected.

Preparations of the isodicyclopentadiene isomers,[3] compounds **4**,[7] **5**,[7] **6**,[1] **7**,[1] **9**,[1] **12**,[16] and **13**[16] have been described elsewhere.

Cycloaddition of 3 with Maleic Anhydride, Compound 8. A solution of 300 mg (3.0 mmol) of maleic anhydride in 1 mL of CH_2Cl_2 was slowly added into a stirred mixture of 300 mg (2.3 mmol) of **3** and 1 mL of CH_2Cl_2 which was cooled in an ice bath. After 8 h at 0 °C, all **3** had reacted, and only one product was formed as indicated by ^1H and ^{13}C NMR. After removal of CH_2Cl_2, the product was recrystallized in a 1:1 ether–pentane mixture, giving 400 mg of **8** (yield 77%). The x-ray crystallographic results have been reported elsewhere.[9]

Compound 8: mp 100–101 °C; ^1H NMR ($CDCl_3$) δ 6.13 (d, 1 H, J = 6 Hz), 5.95 (dd, 1 H, J = 6, 2.7 Hz), 3.78 (dd, 1 H, J = 4.5, 7 Hz), 3.52 (m, 1 H, J = 4.5 Hz), 3.40 (d, 1 H, J = 7 Hz), 2.73 (br s, 1 H), 2.27 (m, 1 H), 1.1–1.9 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.8 (s), 170.6 (s), 134.4 (d), 128.8 (d), 73.8 (d), 67.4 (s), 58.0 (d), 47.9 (d), 45.9 (t), 45.6 (d), 39.8 (d), 36.5 (d), 28.1 (t), 22.2 (t); IR (neat) ν_{max} 3045, 2945, 2855, 1845, 1765, 1690, 1620, 1440, 1340, 1240, 1210, 1075, 1045, 910, 750, 700. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.11; H, 6.03.

Interconversions among the Five Cycloadducts of Maleic Anhydride. A solution of 60 mg of **8** in 400 μL of *m*-dichlorobenzene was heated in a refluxing *tert*-butylbenzene bath (169 °C) for about 10 min. All ^{13}C NMR signals of **8** had disappeared, and the spectrum became a superimposition of those of **6** and **7**.

A solution of 50 mg of **4** or **5** in 400 μL of *m*-dichlorobenzene was heated in a refluxing *tert*-butylbenzene bath (169 °C); its composition was checked by ^1H NMR over some time intervals and is presented in Figure 1.

Cycloaddition of 2 with DMAD, Compound 10. (a) From Allyl Ether 12. A mixture of 1.0 g (6.7 mmol) of **12**, 20 mg (0.1 mmol) of *p*-TsOH, and 4.8 g (33.8 mmol) of DMAD was heated at 50 °C and under nitrogen for 48 h. The mixture was then dissolved in 20 mL of CH_2Cl_2 and passed through a 10-cm column packed with silica (230–400 mesh) to remove free acid. After removal of excess DMAD, vacuum distillation gave 1.5 g (82% yield) of **10** as a yellowish liquid, bp 170 °C (1 torr): ^1H NMR ($CDCl_3$) δ 6.13 (d, J = 3.0 Hz, 1 H), 3.93 (dt, J = 3.0, 1.6 Hz, 1 H), 3.87 (s, 3 H), 3.79 (s, 3 H), 3.02 (d, J = 1.8 Hz, 1 H), 2.88 (m, 2 H), 2.13 (s, 2 H), 0.7–2.0 (series of m, 5 H); ^{13}C NMR ($CDCl_3$) δ 167.6 (s), 167.3 (s), 164.6 (s), 155.4 (s), 148.3 (s), 122.7 (d), 75.4 (s), 73.8 (t), 53.2 (d), 52.0 (q), 51.8 (q), 43.6 (t), 37.7 (d), 37.1 (d), 30.8 (t), 23.9 (t); IR (neat) ν_{max} 2945, 2870, 1710, 1640, 1610, 1430, 1325, 1260, 1210, 1200, 1140, 1120, 1080, 1070, 1040, 790; GC–MS, *m/e* (relative intensity), 274 (M^+, 15.1), 259 (11.4), 242 (39.5), 215 (37.4), 185 (43.6), 183 (43.8), 155 (86.6), 141 (21.4), 128 (80.3), 115 (69.6), 104 (100), 91 (53.6), 77 (74.1); high-resolution MS, *m/e* (M^+), calcd 274.1205, obsd 274.192.

(b) From 3. A mixture of 0.35 g (2.6 mmol) of diene **3** and 0.70 g (4.9 mmol) of DMAD in 40 mL of CH_2Cl_2 was refluxed under nitrogen for 20 h. The product is a mixture of **10** and **11** in an approximate 1:3 ratio, as indicated by ^1H NMR. Preparative HPLC by CH_2Cl_2 gave 110 mg of **10** (15% yield) identical with that obtained from the previous method.

(c) From Allyl Chloride 13. To a mixture of 0.5 g (3.0 mmol) of **13** and 1.3 g (9 mmol) DMAD in 10 mL of ether under nitrogen was slowly added 1.0 g of 5% Pd on charcoal. The slurry was stirred at room temperature for 20 h. After filtration, short path vacuum distillation at 170 °C (1 torr) gave 0.2 g (24%) of distillate which contains **10** as the major component. Pure **10** can be obtained by preparative HPLC, identical with that obtained by the previous methods.

Cycloaddition of 3 with DMAD, Compound 11. To an ice-cooled solution of 130 mg (1.0 mmol) of **3** in 2 mL of CH_2Cl_2 was added 160 mg (1.2 mmol) of DMAD. The reaction mixture was kept in a refrigerator for 5 days for complete consumption of **3**. Only one product was formed as indicated by ^1H and ^{13}C NMR. Preparative TLC (1:2 ether/pentane) gave 190 mg (70% yield) of **11** as a yellowish liquid: ^1H NMR ($CDCl_3$) δ 6.76 (d, 1 H, J = 5.1 Hz), 6.34 (dd, 1 H, J = 5.1, 1.8 Hz), 4.05 (dd, 1 H, J = 1.8, 1.2 Hz), 3.66 (s, 3 H), 3.60 (s, 3 H), 2.79 (m, 2 H), 2.36 (m, 1 H), 1.1–1.6 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 166.3 (s), 164.9 (s), 159.8 (s), 159.5 (s), 144.6 (d), 133.1 (d), 93.5 (d), 73.6 (s), 54.7 (d),

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(19) Marchand, A. P. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. I, Chapter 1.

(20) Woods, W. F. *J. Org. Chem.* **1958**, *23*, 10.

(21) Herndon, W. C.; Lowry, L. L. *J. Am. Chem. Soc.* **1964**, *86*, 1922.

(22) Lustgarten, R. K.; Richey, K. G., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6393.

(23) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Borolin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241.

(24) This and related rearrangements are reviewed by Gajewski, J. J. In "Hydrocarbon Thermal Isomerizations", Academic Press: New York, 1981; Chapter 7.

(25) Kabakoff, D. S.; Bünzh, J. C. G.; Oth, J. F. M.; Hammond, W. B.; Berson, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1510.

(26) Edman, J. R. *J. Org. Chem.* **1967**, *32*, 2920; **1968**, *33*, 3808.

(27) As pointed out by referee 1 any rearrangement *without* inversion at C_6 would result in a norcaradiene prohibitively strained by trans-fusion of a cyclopropane ring to the norbornane.

51.9 (q), 51.8 (q), 47.2 (t), 43.0 (d), 36.6 (d), 28.4 (t), 22.0 (t); IR (neat) ν_{max} 2950, 2870, 1710, 1620, 1540, 1440, 1310, 1295, 1265, 1200, 1175, 1060, 990, 815, 760; GC–MS (solid inlet), *m/e* (relative intensity), 274 (M^+, 0.8), 260 (3.2), 245 (7.5), 229 (7.8), 219 (15.9), 201 (43.5), 188 (34.1), 173 (49.9), 156 (74.9), 143 (55.3), 130 (87.1), 117 (56.0), 104 (63.9), 90 (66.3), 55 (1.00); high-resolution MS, *m/e* (M^+) calcd 274.1205, obsd 274.1195.

Rearrangement of 11. Compound 14. (a) Preparation of 14. A solution of 1.32 g (10 mmol) of diene **3** and 2.32 g (16 mmol) of DMAD in 10 mL of CH_2Cl_2 was kept at 0 °C under nitrogen for 5 days. The reaction was complete as the total disappearance of **3** in ^1H NMR. After removal of CH_2Cl_2 and excess DMAD by evacuating at 130 °C for 1 h, the residue was kept overnight in the refrigerator to give 2.6 g (93% yield) of yellowish crystals which were almost pure **14**. Recrystallization in hexane–carbon tetrachloride gave 2.0 g of **14** as colorless crystalls: mp 91–92 °C; ^1H NMR ($CDCl_3$) δ 6.74 (br s, 1 H, part of ABX), 6.71 (d, 1 H, part of ABX), 6.19 (m, 1 H, part of ABX), 3.82 (s, 3 H), 3.76 (s, 3 H), 2.96 (m, 1 H), 2.70 (m, 1 H), 2.23 (m, 1 H), 1.20–1.90 (series of m, 6 H); ^1H NMR (*sec*-butylbenzene-d_{14}) δ 6.83 (dd, J = 12.0, 1.0, Hz, 1 H, H_4), 6.50 (dd, J = 12.0, 6.0 Hz, 1 H, H_3), 6.00 (dd, J = 6.0, 1.0 Hz, 1 H, H_2), 3.64 (s, 3 H), 3.48 (s, 3 H), 2.75 (br s, 2 H), 2.18 (br s, 1 H), 0.90–2.0 (series of m, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.6 (s), 166.7 (s), 153.4 (s), 134.0 (d), 133.6 (s), 127.7 (s), 124.0 (d), 116.0 (d), 52.4 (q), 52.0 (q), 48.3 (d), 43.7 (d), 40.5 (t), 39.6 (d), 31.4 (t), 27.9 (t); IR (neat) ν_{max} 2940, 2865, 1720, 1640, 1590, 1545, 1430, 1280, 1250, 1190, 1160, 1085, 1045, 1025, 1000, 765, 755, 730; GC–MS, *m/e* (relative intensity) 274 (M^+, 4.3), 259 (9.7), 243 (16.6), 233 (37.0), 215 (77.5), 199 (8.6), 187 (39.6), 183 (64.5), 155 (100), 143 (22.9), 128 (86.8), 115 (56.3), 77 (21.4), 59 (45.6); high-resolution MS, *m/e* (M^+) calcd 274.1205, obsd 274.1210. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.21; H, 6.74.

(b) Preparation of 14-d_1. Starting from **3**-d_1, the **14**-d_1 is obtained in 80% yield. In the ^1H NMR, the δ 2.23 peak is missing; in the ^{13}C NMR, the δ 48.3 line is split into three with a $^1J_{CD}$ of 22.4 Hz.

(c) Kinetics of Rearrangement. A 0.5 M solution of **11** in *tert*-butylbenzene-d_{14} or Me_2SO-d_6 was sealed in a 5-mm NMR tube under nitrogen. Compound **11** was purified by preparative HPLC before use. The sample was heated in a bath; the temperature of which was controlled by refluxing solvents for certain time periods, and the ^1H NMR was determined at room temperature. The relative amounts of **11** and **14** were measured by the integral intensities of their vinyl protons at δ 6.33 and 6.50, respectively. With the residual protons of the deuterated solvents as an internal standard, the total amount of **11** plus **14** was unchanged during the whole course of rearrangement. The kinetic data are reported in Tables III and IV.

Preparation of the Norbornanoquadricyclanes, 16–18. General Procedure. An 0.5 M solution of the tetracyclic norbornadiene **9**, **10**, or **11** in benzene was placed in a 10-mm quartz NMR sample tube under nitrogen and irradiated in a Rayonet RMR 400 Photochemical Reactor for 12–24 h until the ^{13}C NMR signals of the starting material disappeared. After removal of benzene, the products were purified by preparative TLC, using 1:2 ether/pentane as solvent.

Compound **16** was obtained from **9** in 72% yield as colorless crystals, mp 37–38 °C: ^1H NMR ($CDCl_3$) δ 3.70 (s, 6 H), 2.70 (m, 2 H), 2.68 (t, 2 H, J = 1.2 Hz), 2.06 (dm, 1 H, J = 15 Hz), 1.87 (dm, 1 H, J = 15 Hz), 1.68 (m, 4 H), 1.46 (dt, 1 H, J = 12, 1.2 Hz), 1.12 (dt, 1 H, J = 12, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 171.0 (s, 2 C), 51.4 (q, 2 C), 50.4 (s, 2 C), 40.7 (d, 2 C), 39.1 (t, 1 C), 36.8 (d, 2 C), 34.2 (t, 1 C), 29.6 (s, 2 C), 28.7 (t, 2 C); IR (neat) ν_{max} 2950, 2860, 1720, 1440, 1340, 1300, 1240, 1220, 1195, 1050, 1040, 1035, 1030, 940, 815, 715; MS, *m/e* (relative intensity) 274 (M^+, 4.9), 259 (1.9), 246 (37.0), 243 (12.7), 231 (9.9), 214 (93.3), 199 (15.6), 187 (87.7), 171 (20.0), 155 (93.8), 142 (31.6), 128 (10.00), 116 (72.6), 104 (75.1), 91 (48.8), 78 (92.3), 65 (94.5), 59 (56.2); high-resolution MS, *m/e* (M^+) calcd 274.1205, obsd 274.1200. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.98; H, 6.74.

Compound **17** was obtained from **10** as a yellowish liquid; the yield is 60%: ^1H NMR ($CDCl_3$) δ 3.80 (s, 3 H), 3.67 (s, 3 H), 2.54 (s, 2 H), 2.50 (s, 1 H), 2.37 (m, 1 H), 2.13 (dt, 1 H, J = 12.6, 1.5 Hz), 1.98 (dd, 1 H, J = 12.6, 1.2 Hz), 1.49 (m, 2 H), 0.86–1.42 (series of m, 4 H); ^{13}C NMR ($CDCl_3$) δ 171.0 (s), 170.8 (s), 52.0 (q), 51.7 (q), 43.9 (s), 43.3 (s), 41.0 (d), 36.5 (t), 36.1 (d), 35.4 (d), 33.3 (s), 31.3 (d), 29.2 (s), 28.7 (t), 27.1 (t), 23.7 (t); IR (neat) ν_{max} 2940, 2860, 1710, 1430, 1370, 1275, 1200, 1170, 1140, 1090, 1010, 965, 870, 780, 740; MS, *m/e* (relative intensity) 274 (M^+, 7.3), 259 (7.7), 242 (28.6), 227 (7.7), 215 (40.4), 199 (16.1), 185 (73.4), 171 (16.3), 155 (74.3), 143 (53.6), 130 (77.0), 117 (75.6), 104 (64.2), 89 (79.1), 77 (76.1), 55 (100); high-resolution MS, *m/e* (M^+) calcd 274.1205, obsd 274.1208.

Compound **18** was obtained from **11** as a viscous liquid in 70% yield: ^1H NMr ($CDCl_3$) δ 3.72 (s, 3 H), 3.67 (s, 3 H), 2.90 (dd, 1 H, J = 4.5, 2.4 Hz), 2.57 (m, 1 H), 2.40 (m, 1 H), 1.03–2.03 (series of m, 9 H); ^{13}C NMR ($CDCl_3$) δ 171.4 (s), 170.6 (s), 60.9 (s), 58.3 (s, 2 C), 51.5 (q, 2 C), 46.8 (t), 39.0 (d), 35.9 (d), 35.4 (d), 34.4 (t and s), 33.9 (d), 32.3 (s), 31.0 (d), 20.7 (t); IR (neat) ν_{max} 2950, 2870, 1720, 1440, 1370, 1300, 1270, 1250, 1225, 1200, 1160, 1140, 1115, 990, 960, 880, 820, 750; GC–MS, *m/e* (relative intensity) 274 (M^+, 2.4), 259 (11.6), 243 (12.3), 233 (26.6), 227 (12.3), 214 (54.5), 205 (7.5), 199 (26.9), 187 (50.1), 184 (27.5), 155 (74.0), 143 (62.4), 129 (64.3), 118 (100.0), 104 (50.6), 91 (34.1), 85 (57.6), 78 (52.8), 64 (63.6); 59 (35.7); high-resolution MS, *m/e* (M^+) calcd 274.1205, obsd 274.1200.

Thermal Rearrangement of 16–18. A solution of 50 mg of each of the compounds **16–18** in *m*-dichlorobenzene was heated to 170 °C under argon, and the compositions were checked by ^1H NMR. The starting materials remained unchanged within 1 h. After heating for 24 h, the spectra of **9**, **10**, and **14** replaced those of **16**, **17**, and **18**, respectively.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for support of this research.

Registry No. **1**, 6675-72-5; **2**, 75725-33-6; **3**, 89689-33-8; **3**-*6-d*, 90969-39-4; **4**, 73321-32-1; **5**, 77982-64-0; **6**, 82918-62-5; **7**, 82950-40-1; **8**, 91785-97-6; **9**, 82918-66-9; **10**, 90969-38-3; **11**, 90969-37-2; **12**, 94706-22-6; **13**, 94706-24-8; **14**, 93972-30-6; **14**-*6-d*, 97674-83-4; **16**, 97674-80-1; **17**, 97674-81-2; **18**, 97674-82-3; DMAD, 762-42-5; maleic anhydride, 108-31-6.