BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2993—3000 (1971)

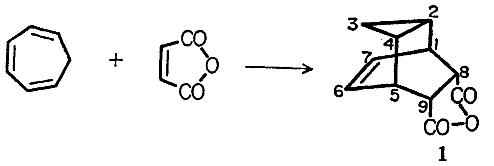
Re-examination of the Cycloaddition of Cycloheptatriene with Maleic Anhydride

Hiroyuki Ishitobi, Hiroshi Tanida, Kazuo Tori, and Teruji Tsuji
Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka

(Received May 28, 1971)

Cycloaddition of cycloheptatriene to maleic anhydride was re-examined and found to produce, in addition to the reported main product *anti*-tricyclo[3.2.2.$0^{2,4}$]non-6-ene-*endo*-8,*endo*-9-dicarboxylic anhydride (**1**), the exo, exo isomer of this compound (**4**) and bicyclo[3.2.2]nona-2,6-diene-*endo*-8,*endo*-9-dicarboxylic anhydride (**5**). Evidence for these structures involving the orientation of the cyclopropane ring in **1** and **4** and the configuration of the carboxylic anhydride was provided by PMR spectroscopy using the intramolecular nuclear Overhauser effect and paramagnetic induced shift due to tris(dipivalomethanato)europium(III). The structure assignment by Alder and Jacobs for **1** was found to be correct, but not the one by Schenk *et al.* The difference in free energies of activation leading to **1** and **4** was determined.

An addition reaction of cycloheptatriene to maleic anhydride was first reported by Kohler and his coworkers.1) For this adduct, the structure of *anti*-tricyclo[3.2.2.$0^{2,4}$]non-6-ene-*endo*-8,*endo*-9-dicarboxylic anhydride (**1**) was assigned by Alder and Jacobs.2) Although the structure of the ring system seems to be unequivocal from the data on chemical transformations, conclusive evidence has not yet been obtained for the *anti* orientation of the cyclopropane ring and the *endo*



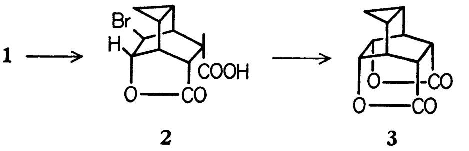
1

---

1) E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Amer. Chem. Soc.*, **61**, 1057 (1939).

2) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

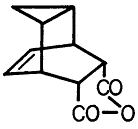
configuration of the carboxylic anhydride group.[3,4] An important result by Alder and Jacobs[2] favourable to the *endo* configuration of the carboxylic group is the fact that the adduct could be lactonized to the bromolacto acid (**2**) by treatment with bromine in water and, furthermore, to the dilactone (**3**). It was, however, pointed out that such a reaction causes Wagner-Meerwein rearrangements whereby even an *exo* acid forms lactone.[5,6] More recently, Schenk and his co-workers found that the photosensitized addition between cycloheptatriene and maleic anhydride gave mainly Alder's adduct, in addition to two minor compounds, and they assigned the *exo* configuration for the carboxylic anhydride group on the grounds that treatment of the adduct with a basic iodine-potassium iodide solution did not cause iodolactonization.[7,8] However, such a result is worthless for a stereochemical determination unless it is proven that in the treatment one isomer is positive and the other negative. However, this other isomer is still unknown. Prematurely accepting the Alder and Jacobs's structure, one of us (K.T.) used the adduct as a model for the investigation of anisotropic long-range shielding effects of a cyclopropane ring in PMR spectroscopy.[9]



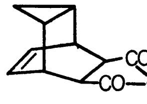
2 **3**

Accordingly, we undertook a re-examination of the cycloaddition reaction and a determination of the configuration of the adduct, mainly by means of PMR spectroscopy. It was found that the reaction produces, besides the reported adduct, another carboxylic anhydride isomer and a bicyclo[3.2.2]nona-2,6-diene derivative, the last compound indicating a new behavior of cycloheptatriene in cycloaddition.

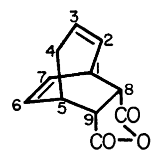
Products. The reaction mixtures were prepared at the indicated reaction temperature by mixing a slight excess of cycloheptatriene and a 0.1 M solution of maleic anhydride in xylene. The reaction at 120°C took about 3 hr for completion. Sampling from the reaction mixture was carried out at given time intervals in order to analyze the products by VPC. The analysis revealed the formation of three products which were isolated for structure determination by a combination of recrystallization and elution chromatography. Relative yields of these products were determined by VPC as a function of reaction temperature and are presented in Table 1. The melting point of the predominant product (**1**), 100.5—101°C, was identical with that reported by Kohler[1] and Alder[2] for their adduct and that by Schenk *et al.* for their most important product.[7] Hydrolysis of the second major product (**4**), mp 112—113°C, in methanol containing a drop of sulfuric acid, followed by epimerization with sodium methoxide in methanol, yielded a *trans*-dicarboxylic ester (**6**), which was identical with the compound obtained by the cycloaddition of cycloheptatriene to fumaryl chloride followed by methanolysis.[2]



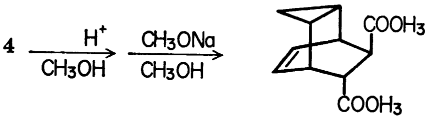
1



4

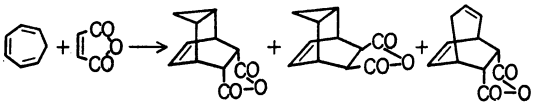


5



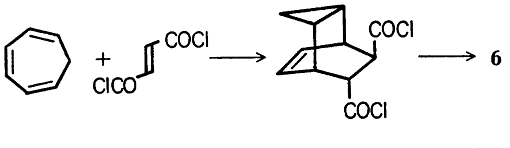
6

Table 1. Reaction temperature-dependence of product ratio



1 **4** **5**

Temp (°C)	Reaction time (hr)	**1** (%)	**4** (%)	**5** (%)	log **1**/**4**
80	2.0	90.20	9.30	~0.5	0.987
80	4.0	91.26	8.24	~0.5	1.044
120	1.0	88.16	11.18	0.66	0.897
120	2.0	88.19	11.32	0.49	0.892
120	3.0	87.59	11.70	0.73	0.874
149.5	0.5	87.72	13.66	0.62	0.798
149.5	1.0	86.12	12.96	0.92	0.822
176.5	0.5	82.03	16.85	1.12	0.687
176.5	1.0	83.83	15.01	1.16	0.747



Since **6** was also obtained from the adduct of Alder and Jacobs, the compounds of mp 100—101°C and 112—113°C are concluded to be *exo* and *endo* carboxylic anhydride isomers and to have an identical orientation concerning the cyclopropane ring. The standard procedure of iodolactonization[7,10] was found to be unsuccessful for both **1** and **4**, so that the assignment of

---

[3] A. S. Onishchenko, "Diene Synthesis," Israel Program for Scientific Translations, Jerusalem (1964), pp. 373—375.

[4] M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, **1965**, 4417.

[5] R. B. Woodward and H. Baer, *J. Amer. Chem. Soc.*, **70**, 1161 (1948).

[6] C. D. Ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 3583 (1955).

[7] G. O. Schenk, J. Kuhls, and C. H. Krauch, *Ann. Chem.* (Justus Liebigs), **693**, 20 (1966).

[8] Iodolactonization in the absence of Wagner-Meerwein rearrangement has been demonstrated. cf. 5).

[9] K. Tori and K. Kitahonoki, *J. Amer. Chem. Soc.*, **87**, 386 (1965).

[10] H. Stockmann, *J. Org. Chem.*, **26**, 2025 (1961).

configuration of the carboxylic anhydride by Schenk *et al.* is inconclusive. Bromolactonization with **1** proceeded smoothly with the formation of colorless crystals, but the reaction with **4** gave a viscid tar. The structure of the bromolactone from **1** and the possibility of Wagner-Meerwein rearrangement in this reaction were not investigated. Confirmatory evidence for the tricyclic nature, the orientation of the cyclopropane ring, and the configuration of the carboxylic anhydride group in the structures of **1** and **4** was obtained from their PMR spectroscopic studies.

The minor third product (**5**) showed a melting point, 112—113°C, identical with that recorded by Schenk *et al.* for their bicyclic adduct.[7] Iodolactonization of **5** gave an iodolactone, whose melting point was the same as that reported.[7] The bicyclic structure of **5** was evident on integrating the vinyl proton signals in its PMR spectrum. The thermal conversion of **1** into **5** was observed on heating 1 at 220°C, but not under the mild conditions employed for the present cycloadditon.[11] To our knowledge, **5** is the first cycloadduct from cycloheptatriene which is formed without precedence of the norcaradiene transition state or intermediate.

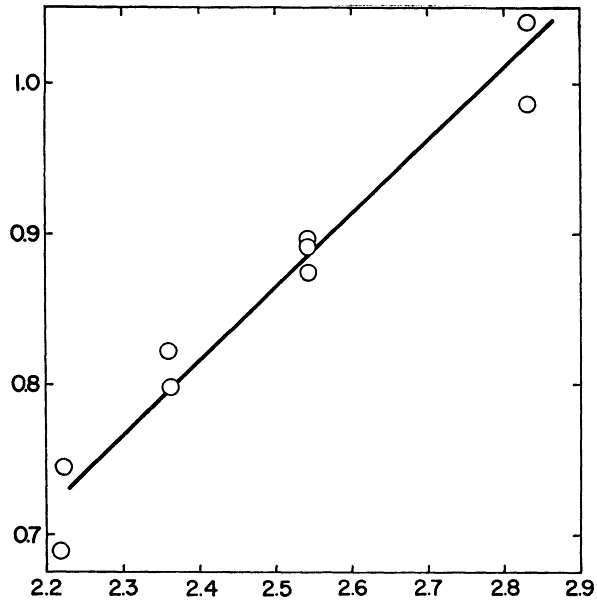
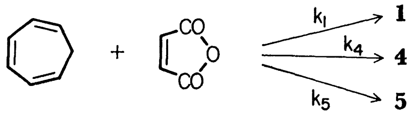


Fig. 1. Arrhenius plots of product ratios, **1**/**4**.

Kinetic Treatment. Since the relative yields of products in Table 1 were confirmed to be independent of the reaction time within maximum experimental error of 0.9%, they are kinetically controlled ones. If we assume that the formation of all three products in a given run follows rate laws of the same form, the yield ratios are equal to those of the specific rate coefficients, $k_1:k_4:k_5$. Since the ground state reactants leading to the transition states in the independent pathways (k_1, k_4, and k_5) are identical, $\log(k_1/k_4)$ is directly proportional to the free energy difference between the two transition states in the k_1 and k_4 pathways.



The k_5 pathway is omitted from this treatment because of experimental errors which are unavoidable owing to the very small yield of **5**. The temperature dependence of the product ratio, expressed in the Arrhenius form gives

$$\log(k_1/k_4) = \log(A_1/A_4) + (E_4-E_1)/2.303RT \qquad (1)$$

for the ratio of the pre-exponential factors and for the difference in empirical activation energy from the intercepts and slope, respectively, of plots of $\log(k_1/k_4)$ *vs.* 1/T. The difference in entropy of activations is given by

$$\Delta S_1^{\neq} - \Delta S_4^{\neq} = 2.303R\log(A_1/A_4) \qquad (2)$$

while the difference in enthalpy of activation is identical with the difference in the Arrhenius activation energy.[12] Regression analysis of logarithms of the relative yields of **1** and **4** on 1/T gave a good linear relationship with a slope of 0.481×10^3 (correlation coefficient 0.9760) as shown in Fig. 1. The equations gave 2.20±0.18 kcal/mole for $\Delta H_1^{\neq}-\Delta H_4^{\neq}$ and -1.6 ± 0.5 cal/deg for $\Delta S_1^{\neq}-\Delta S_4^{\neq}$. Since the relative yields in Table 1 were

TABLE 2. CHEMICAL SHIFT (δ in ppm downfiled from TMS) AND COUPLING CONSTANT (J in Hz) IN $CDCl_3$ AND C_6D_6 (in parentheses)

Compd.	δ						J		
	$H_{1(5)}$	$H_{2(4)}$	H_{3s}	H_a	$H_{6(7)}$	$H_{8(9)}$	$J_{2,3a}$	$J_{2,3s}$	$J_{3a,3s}$
1	3.43 (3.02)	1.13 (0.46)	0.25 (−0.12)	0.35 (−0.07)	5.88 (5.38)	3.27 (2.56)	7.3	4.0	(−)6.1
4	3.41 (2.88)	1.10 (0.70)	0.14 (−0.26)	0.22 (−0.32)	5.95 (2.23)	3.09 (2.22)	7.5	4.0	(−)5.5
7	2.57 (2.12)	1.11 (0.38)	0.86 (~0.3)	0.65 (~0.1)	~1.34 (0.75) (0.95)	3.28 (2.42)	7.5	3.4	(−)6.5
8	2.62 (2.11)	0.97 (0.55)	0.62 (0.03)	0.46 (−0.15)	~1.33 ~1.49 (~0.76) (~0.52)	3.11 (2.13)	7.6	3.4	(−)6.0

---

11) T. Tsuji, H. Ishitobi, and H. Tanida, This Bulletin, **44**, 2447 (1971).

12) Substantially the same treatment was carried out for the reaction of cyclopentadiene with some dienophiles. J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

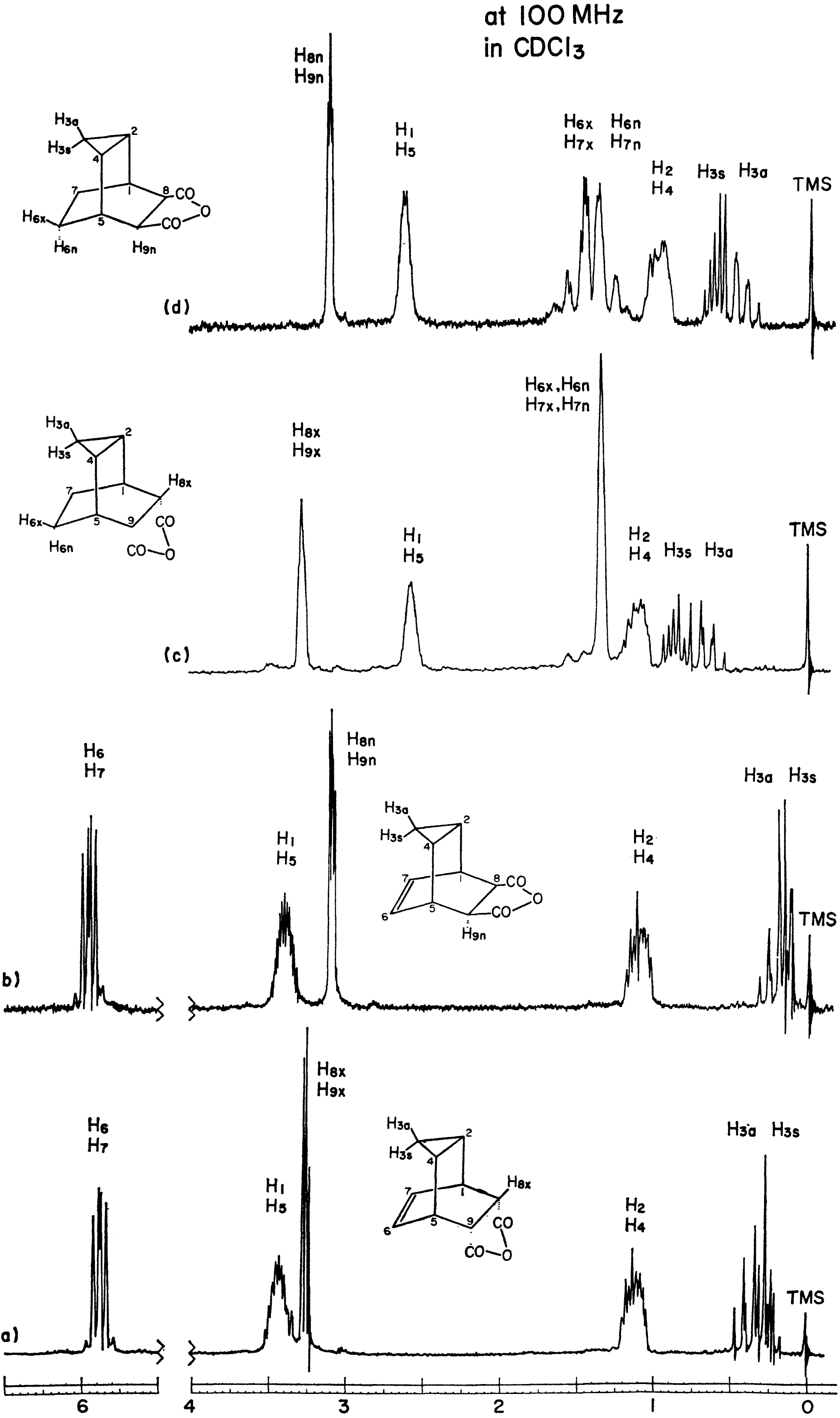


Fig. 2. The 100-MHz PMR spectra of (a) **1**, (b) **4**, (c) **7**, and (d) **8** in $CDCl_3$.

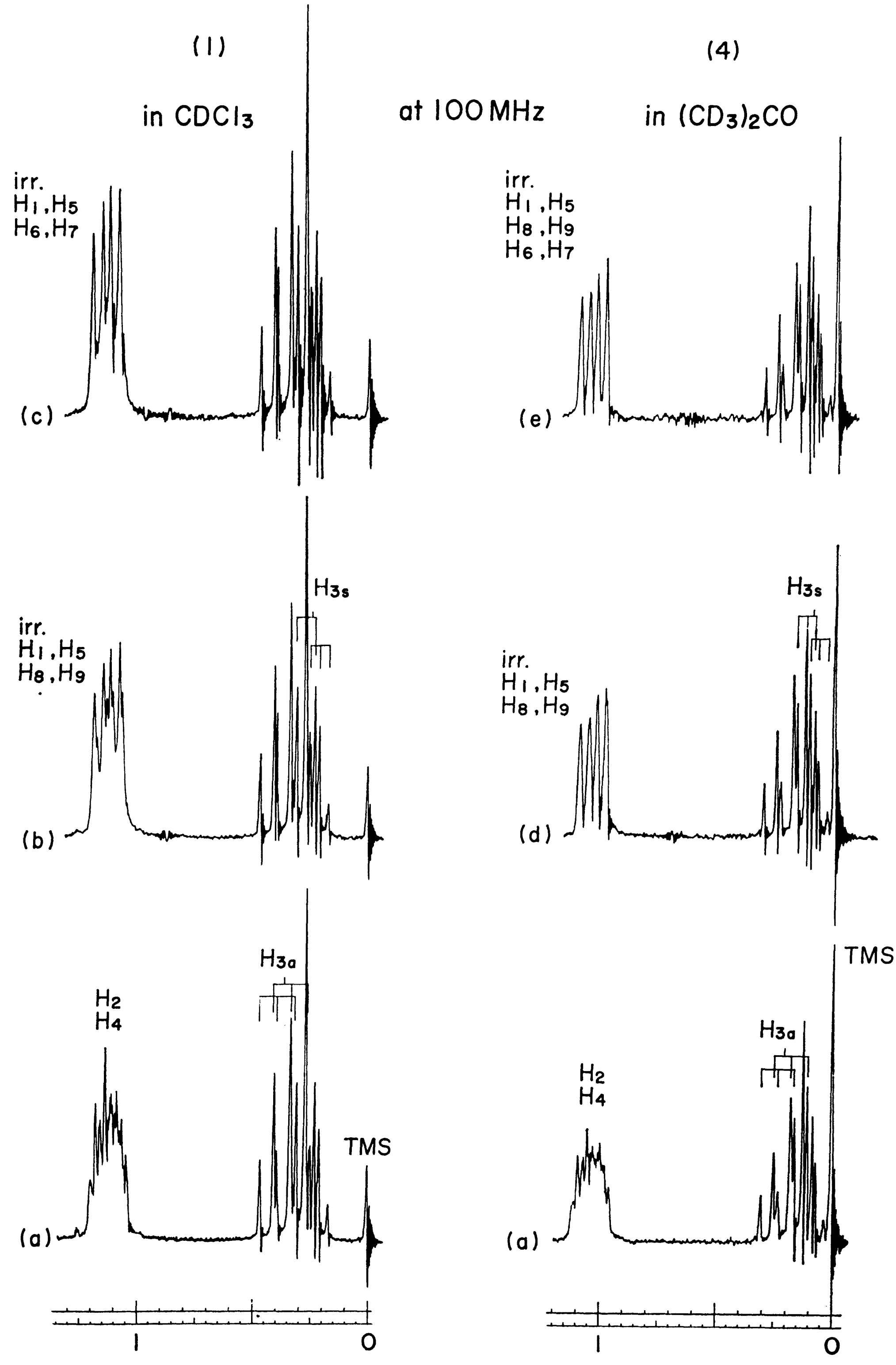


Fig. 3. The 100-MHz PMR (a), PMDR (d), and PMTR (b, c, e) spectra of **1** in $CDCl_3$ and of **4** in acetone-d_6.

constant during the reaction periods with in ±0.9%, the values for $\log(k_1/k_4)$ are reliable for 0.02—0.06 units.

It has been reported by Diels and Alder[13] that cyclopentadiene and 1,3-cyclohexadiene show extreme stereospecificity in their additions with maleic anhydride by the formation of a single endo adduct. We traced the reaction with 1,3-cyclohexadiene by means of VPC and confirmed the absence of the exo adduct in amounts greater than 0.2%. Therefore, the decreased stereospecificity of cycloheptatriene presently observed is very notable.

PMR studies. The 100-MHz PMR spectra of **1**, **4**, and their hydrogenation products, **7** and **8**, in

---

[13] O. Diels and K. Alder, *Ann. Chem.* (Justus Liebigs), **460**, 98 (1928). Also, see M. C. Kloetzel "Organic Reactions," Vol. IV, John Wiley & Sons, Inc., New York, N. Y. (1948), p. 1.

$CDCl_3$ are shown in Fig. 2. The spectra of these compounds were also measured in benzene-d_6. The data obtained are listed in Table 2. Signals due to H_{3s} and H_{3a} were assigned according to the known general sequence of the *J* values between cyclopropane ring protons.[14] The assignment of other signals though simple was confirmed by spin-decoupling experiments.

The anisotropic long-range shielding effect of a cyclopropane ring is well understood,[14] and it is apparent that the cyclopropane rings in **1** and **4** are *syn* to their double bonds in view of the abnormally high-field positions of their olefinic-proton signals. Accordingly, **1** and **4** are determined to be *endo*-8,*endo*-9- and *exo*-8,*exo*-9-isomers, respectively, from the fact that the $H_{8(9)}$ signal of **7** appears at a lower field than that of **8** (see Table 2). The anisotropic shielding effect of the C-6: C-7 double bond[15] upon H_{3s} and H_{3a} and that of the two carbonyl groups[16] upon $H_{6(7)}$ are also consistent with the molecular configurations.

However, the use of chemical shift difference to determine molecular structure is sometimes risky, particularly for bridged bicyclic compounds.[17,18] Therefore, intramolecular nuclear Overhauser effect (NOE)[19] measurements and paramagnetic shifts induced by tris(dipivalomethanato)europium(III). $Eu(DPM)_3$,[20] have been applied to assign the configurations of the cyclopropane and the acid-anhydride rings of **1** and **4**.

The NOE measurements on **1**, **4**, **7**, and **8** in $CDCl_3$ are summarized in Table 3. The nuclear Overhauser effects observed for the H_{3s} signals on saturating the $H_{6(7)}$ signals and *vice versa* by double irradiation evidence the *syn* configurations of the cyclopropane rings to the double bonds. The fact that the NOE's between the $H_{2(4)}$ and $H_{8(9)}$ signals were observed for **1** and **7**, but not for **4** and **8**, show that the configurations of the acid-anhydride rings are as illustrated by their formulas. Further, the five-bond long-range spin-couplings[21] observed between H_{3a} and $H_{8(9)}$ ($|J|=0.2$ Hz) in **4** and **8** are consistent with their assigned configurations. Figure 3 shows some results with double and triple resonance experiments on **1** and **4**; the experiments on **4** are shown with the spectra taken in acetone-d_6 because the H_{3s} and H_{3a} signals appeared as the first-order patterns in this solvent.

Table 3. Nuclear overhauser effect values (%)

Observed signal	Saturted signal	Compound **1**	**4**	**7**	**8**
$H_{1(5)}$	$H_{2(4)}$	6	6	9	8
$H_{1(5)}$	$H_{6(7)}$	8	10	15	[a]
$H_{2(4)}$	$H_{1(5)}$	8	7	[a]	[a]
$H_{2(4)}$	$H_{6(7)}$	nil	nil	[a]	[a]
$H_{2(4)}$	$H_{8(9)}$	10	nil	[b]	nil
H_{3s}	$H_{6(7)}$	5	5	[b]	[a]
$H_{6(7)}$	$H_{1(5)}$	11	10	[a]	[a]
$H_{6(7)}$	$H_{2(4)}$	nil	nil	[a]	[a]
$H_{6(7)}$	H_{3s}	3	3	[a]	[a]
$H_{8(9)}$	$H_{2(4)}$	8	nil	7	nil
$H_{8(9)}$	$H_{6(7)}$	nil	nil	nil	[a]

a) Unmeasurable
b) Positive but undeterminable

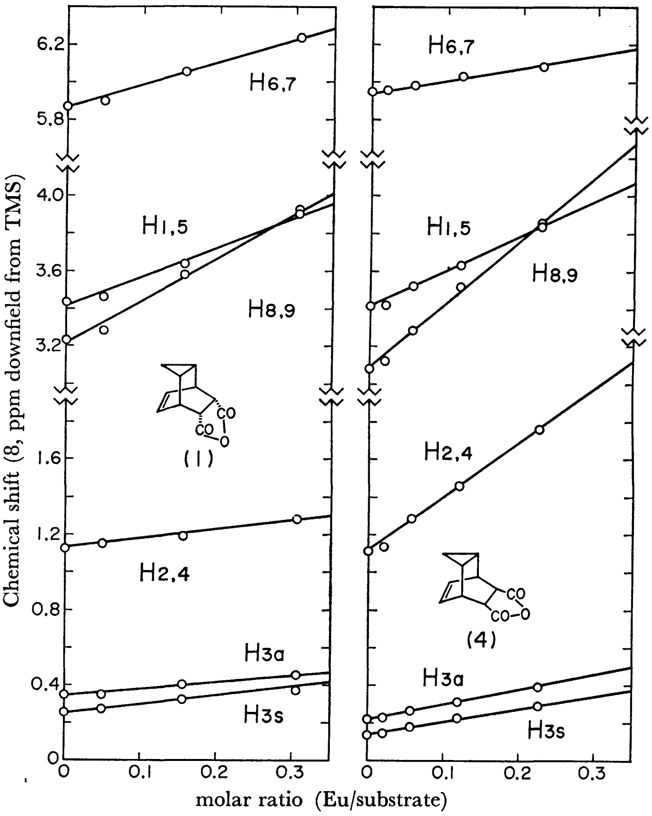


Fig. 4. Paramagnetic induced shift measurements for **1** and **4** using $Eu(DPM)_3$ in $CDCl_3$.

Much interest has been shown in the application of paramagnetic shifts induced by lanthanide complexes such as $Eu(DPM)_3$ in the PMR spectra of molecules having substituents with lone-pair electrons.[20] The paramagnetic shifts caused by $Eu(DPM)_3$ has been considered to result mainly from the pseudocontact shift.[20,22] Therefore, the stereostructure of a compound

Table 4. S-Values for $Eu(DPM)_3$ in $CDCl_3$
(in ppm; +sign denotes a downfield shift)

Compd.	$H_{1(5)}$	$H_{2(4)}$	H_{3s}	H_{3a}	$H_{6(7)}$	$H_{8(9)}$
1	+1.51	+0.49	+0.49	+0.31	+1.14	+2.26
4	+1.90	+2.93	+0.80	+0.93	+0.67	+3.37

---

[14] a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Oxford (1969), p, 98; b) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N.Y. (1969), p. 71.

[15] J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**. 2357 (1967), and references therein.

[16] J. W. ApSimon, P. V. Demarco, D. W. Mathieson, W. G. Craig, A. Karim, L. Saunders, and W. B. Whalley, *ibid.*, **26**, 119 (1970), and references therein.

[17] K. Tori, A. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, **1966**, 9.

[18] a) R. G. Foster and M. C. McIvor, *J. Chem. Soc.*, *B*, **1969**, 188; b) R. G. Foster and M. C. McIvor, *Org. Mag. Res.*, **1**, 203 (1969).

[19] F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

[20] a) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971); b) K. Tori, Y. Yoshimura, and R. Muneyuki, *Tetrahedron Lett.*, **1971**, 333, and references therein.

[21] K. Tori and M. Ohtsuru, *Chem. Commun.*, **1966**, 886.

[22] D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965).

Table 5. Benzene induced solvent shift
($\Delta\delta_{C_6D_6-CDCl_3}$ in ppm; −sign denoted an upfield shift)

Compd.	$H_{1(5)}$	$H_{2(4)}$	H_{3s}	H_{3a}	$H_{6(7)}$	$H_{8(9)}$
1	−0.41	−0.67	−0.37	−0.42	−0.50	−0.71
4	−0.53	−0.40	−0.40	−0.54	−0.72	−0.87
7	−0.45	−0.73	∼−0.55	∼−0.55	−0.39 −0.59	−0.86
8	−0.51	−0.42	−0.59	∼−0.61	−0.73 −0.81	−0.98

can sometimes be determined by a consideration of paramagnetic shift parameters, *S*-values,[23] measured for each proton signal.[24] The *S*-value is represented by the equation $\delta_E=\delta+S\cdot Eu(DPM)_3/substrate$ (molar ratio), where δ_E and δ are the chemical shifts of a proton in complexed and uncomplexed molecules, respectively.[23]

Examinations of Dreiding models show that S-values for $H_{2(4)}$ and $_{6(7)}$ in **1** should be respectively smaller and larger than those in **4**. Figure 4 shows the relationships between the chemical shifts of proton in **1** and **4** and the molar ratios of $Eu(DPM)_3$ added to the substrates. The *S*-values obtained are listed in Table 4.

Table 4 shows that the S-value of $H_{2(4)}$ is considerably larger in **4** than in **1**, and the value of $H_{6(7)}$ is smaller in **4** than in **1**. The *S*-values of H_{3s} and H_{3a} in both compounds are small, as was expected. These facts confirm the stereostructutes of **1** and **4**. It should be noted that the complexing ability of the acid-anhydride function with $Eu(DPM)_3$ is fairly weak. The difference in the *S*-values of $H_{8(9)}$ between **1** and **4** cannot immediately be explained.

The benzene induced shift, $\Delta\delta_{C_6D_6-CDCl_3}$,[25] also supports the structures of the present compounds, because thay have an acid-anhydride function. Table 5 lists the benzene-induced shifts for **1**, **4**, **7**, and **8**. The high-field shift values of $H_{2(4)}$ for **1** and **7** are larger than those for **4** and **8**, respectively, whereas the corresponding shift values of $H_{6(7)}$ show opposite trends. These facts are consistent with the structure of the compounds.

Experimental

All melting points were determined in capillary tubes and are corrected. Infrared spectra were determined with a Nippon Bunko IR-S spectrometer. VPC analysis was carried out on a Hitachi-Perkin-Elmer gas chromatograph F-6D equipped with a hydrogen flame ionization detector, using a 1 m×3 mm stainless steel column packed with 5% XE 60 on Chromosorb W.

The 100-MHz PMR spectra were taken with a Varian HA-100 spectrometer using about 5% (w/v) carefully degassed solutions in $CDCl_3$, benzene-d_6, and(or) acetone-d_6 in the frequency-swept and internal $CHCl_3$-locked mode. Calibration of the charts was carried out by direct readings of resonance frequencies, using a Hewlett-Packard HP-5212A electronic counter to an accuracy of ±0.1 Hz. PMDR and PMTR experiments were performed using the spectrometer and two Hewlett-Packard HP-200ABR audiooscillators. Chemical shifts are expressed in δ, ppm downfield from tetramethylsilane as an internal standard with an accuracy of ±0.01 ppm, and coupling constants are in Hz with an accuracy of ±0.1 Hz.

Reaction of Maleic Anhydride with Cycloheptatriene. A solution of 24.4 g of cycloheptatriene and 20 g of maleic anhydride in 100 m*l* of xylene was refluxed for 3 hr. VPC analysis of the reaction solution, operated at 180°C with a flow pressure of 1.3 kg/cm^2, showed three peaks at retention times of 6 min 30 sec, 7 min 20 sec, and 11 min and with relative areas of 11 : 1 : 88. The solvent was evaporated under reduced pressure and the residue was recrystallized from ligroin to give 27 g of *anti*-tricyclo[3.2.2.0^{2,4}]non-6-ene-*endo*-8,*endo*-9-dicarboxylic anhydride (**1**) in 69.7% yield, mp 100.5—101°C (lit.,[2] mp 101°C), corresponding to the peak at 11 min. The mother liquor was concentrated to dryness and subjected to elution chromatography on 150 g of silica gel using ether-pentane to give 3.8 g of a mixture of the two minor products in a ratio of 13 : 1 as the first fraction eluted. Absence of of the *endo* product in this mixture was confirmed by VPC. The mixture was recrystallized twice from hexane to afford 2.1 g (5.4%) of *anti*-tricyclo[3.2.2.0^{2,4}]non-6-ene-*exo*-8,*exo*-9-dicarboxylic anhydride (**4**), mp 112—113°C, which corresponded to the peak at 6 min 30 sec; IR (CCl_4) 1870, 1782, and 1220 cm^{-1} (C=O), NMR ($CDCl_3$) τ 9.85 (m, 2H at C-3), 8.85 (m, 2H at C-2 and 4), 6.95 (t, J=1.5 Hz, 2H at C-8 and 9), 6.6 (m, 2H at C-1 and 5), and 3.08 (d-d, J=5 and 3.3 Hz, 2H at C-6 and 7).

Found: C, 69.74; H, 5.46%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%.

Catalytic reduction in a mixed solution of acetic acid and acetic anhydride (15 : 1) gave *anti*-tricyclo[3.2.2.0^{2,4}]nonane-*exo*-8,*exo*-9-dicarboxylic anhydride, which was recrystallized from ligroin to give a pure sample, mp 153—154°C.

Found: C, 68.54; H, 6.25%. Calcd for $C_{11}H_{12}O_3$: C. 68.73; H, 6.29%.

Quantitative Products Distribution. Cycloheptatriene sealed in a thin-walled glass capillary, a clean iron bar and 3 m*l* of a 0.1 M solution of maleic anhydride dissolved in xylene were placed in a heavy-walled glass ampoule and sealed. The ampoule was immersed in a constant temperature bath (±0.03°C). After temperature equilibrium had been reached, the cycloheptatriene capillary was crushed with the iron bar and the reaction allowed to proceed. Analysis of the products was carried out by VPC, and relative yields of the three adducts were determined by integration of the component peaks with a planimeter with correction for the relative sensitivity of the detector. The control experiments showed that the proportions of adducts were strictly independent both of the yields of the products and of initial proportions of the reactants. The reaction time necessary for detection of the products by VPC varied from 10 min at at 176.5°C to 1 hr at 80°C, but further heating did not affect the relative proportions of the product. Table 1 gives the

---

[23] A. F. Cockerill and D. M. Rackham, *Tetrahedron Lett.*, **1970**, 5149.

[24] J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, **1970**, 1506.

[25] P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967).

data thus obtained.

Dimethyl anti-*Tricyclo*[3.2.2.0^{2,4}]*non-6-en-8,9*-trans-*dicarboxylate (6).* A solution of 300 mg of the anhydride (**4**) and 0.3 m*l* of concentrate sulfuric acid in 8 m*l* of methanol was refluxed for 2.5 hr. After the usual work-up, the *exo-exo* dimethylcarboxylate obtained was dissolved in 8 m*l* of basic methanol, prepared by dissolving 60 mg of sodium into methanol and then refluxed for 5 hr. After removal of the solvent the reaction product was diluted with water and extracted with ether. Evaporation of the ether gave 280 mg of **6** which was identical with an authentic sample[2)] obtained by quenching cycloheptatriene-fumaryl chloride adduct with methanol.

Iodolactonization of Adducts. A mixture of 1.0 g of the bicyclic adduct (**5**), 1.8 g of sodium bicarbonate and 30 ml of water was stirred for 20 min at room temperature, and then 13.5 m*l* of a iodine-potassium iodide solution (prepared by dissolving 5 g of iodine and 15 g potassium iodide into 50 m*l* of water) was added to the mixture. During the course of the reaction the initially suspended **5** gradually dissolved and the red colour of the mixture faded. After 4 hr the reaction mixture was made acidic with hydrochloric acid and extracted with dichloromethane. The extract was washed with aqueous sodium thiosulfate and water, and dried over sodium sulfate. After removal of the solvent, 1.3 g of the iodolactone was recrystallized from benzene to give a pure sample, mp 147°C (lit,[7)] 147—148°C).

Similar attempts to prepare iodolactones from **1** and **4** failed, the red colour of iodine remaining almost unchanged even after treatment for 24 hr.

Bromolactonization of the Tricyclic Adducts. A solution of 500 mg of the *endo* tricyclic adduct and 230 mg of sodium hydroxide in 7.5 m*l* of water was stirred for 30 min under ice-cooling, and bromine was added slowly until the colour of the bromine persisted. The resulting milky solution was further stirred for 30 min and acidified with hydrochloric acid to give 450 mg of the bromolactone which was recrystallized from ether-hexane to give a pure sample mp 197—198°C (lit,[2)] 185°C).

Found: C, 46.29; H, 3.93; Br, 27.55%. Calcd for $C_{11}H_{11}O_4Br$: C, 46.02; H, 3.86; Br, 27.84%.

The same procedure for the *exo* anhydride resulted in the formation of a high molecular product.