C, 7.17% H, and 0.34% S; theoretical $(C_9H_8)_n$ = 93.06% C and 6.94% H). Gel permeation chromatography in tetrahydrofuran vs. polystyrene standards showed the polymer to have molecular weight distributions from about 230 (dimer) to 10 000 (86 indene units); mid range of the distribution was at 1150 (10 units). Therefore, 50% of polymer was oligomeric with degree of polymerization (n) being 2–6, and 50% with 6–86.

Synthesis and Purification of 4-Nitrophthalic Anhydride. Crude 4-nitrophthalic acid (50 g, 84% purity), isolated from nitration/oxidation of indene by evaporation of product mixture to dryness, was heated under reflux in the presence of o-xylene (225 mL) and 3.8 g of charcoal (Darco, G-60) until a theoretical amount of water had been collected in a Dean-Stark trap (3–5 h). Dehydration was at out under nitrogen atmosphere. At the end of the dehydration, the mixture was cooled to about 90 °C and the hot product mixture was vacuum filtered through a 0.6 × 9-cm bed of celite. The filtrate was chilled (0–5 °C) and allowed to crystallize overnight. Filtration, followed by washing with n-hexane, produced 28.5 g (74%) of xylene-free 4-nitrophthalic anhydride, mp 107–114 °C, which was 97.5% pure (GLC). Starting with a purer product, 57.3 g (96.2% 4-nitrophthalic acid) from a run comparable to experiment 1, led to recovery of 46.8 g (85%) of 4-nitrophthalic anhydride of 99.4% purity, mp 114–117 °C (lit.[13] mp 117–119 °C). The NMR and IR spectra of product were identical with that of authentic sample.

Acknowledgment. We thank Dr. E. W. Albaugh and Mr. J. C. Suatoni for determining the molecular weight distributions of polyindene and nitrated polyindenes.

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Regiospecific Intramolecular Cyclization in 7-Keto-*endo*-2-*cis*-decalylcarbinyl Methanesulfonate

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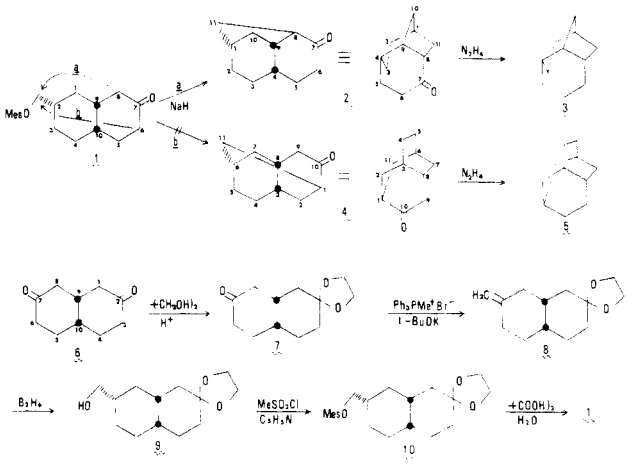
Many tricyclic compounds including natural sesquiterpenes have been synthesized via base-catalyzed intramolecular cyclizations of bicyclic keto tosylates and mesylates, which involves nucleophilic attack of α-ketocarbanion on the sulfonate-substituted, potentially cationic carbon atom.[1] In each of these syntheses, structure around the carbonyl group as well as relative orientation of the carbanion and the sulfonate-bearing carbon atom was so designed that only one product was expected to form on cyclization. Thus, the precursors were constructed under the strategies either that the carbonyl group was situated adjacent to a bridgehead in order to be enolizable only in one direction[1a,c,d,f,g] or that, although both of the α-carbon atoms could ionize, one of them cyclized to a much more stable tricyclic structure than the other did.[1b,e,h,i]

Scheme I



During our attempts to carry out independent syntheses of tricycloundecane isomers, cyclization of 7-keto-*endo*-2-*cis*-decalylcarbinyl mesylate (**1**) was examined. However, this substrate, in contrast to those studied so far,[1] could cyclize via either of the two carbanion centers C-6 and C-8. The former carbanion would afford 2,4-bishomobrendan-7-one (tricyclo[6.2.1.$0^{4,9}$]undecan-7-one, **2**), while the latter would afford tricyclo[4.4.1.$0^{3,8}$]undecan-10-one (**4**). There seems to exist no reason for the preferential formation of one carbanion over the other, and the resulting ketones **2** and **4** should have similar thermodynamic stabilities because[2] the corresponding hydrocarbons were calculated[3] to possess comparable heats of formation ($\Delta H°_f$ = −25.94 and −26.10 kcal/mol for **3** and **5**, respectively). Nevertheless, our experimental results were quite contrary to our expectation because 2,4-bishomobrendan-7-one (**2**) was formed selectively.

The keto mesylate **1** was prepared from *cis*-decalin-2,7-dione (**6**)[1b,4] via the route shown in Scheme I. The ethylene ketal **7** was used for the Wittig methylenation since the known diethyl ketal[1b] was partly hydrolyzed under the present reaction conditions. Hydroboration of **8** gave exclusively one hydroxymethyl isomer, which most probably had the endo structure **9** because of the established preferable exo attack of diborane on bridged olefins.[5] This configurational assignment is consistent with the successful cyclization of **1**.

The product of sodium hydride catalyzed cyclization of **1** showed only one major peak (92% of the combined peak areas), together with several unidentified minor constituents, upon preparative VPC. Golay column GC–MS indicated that the isolated major fraction was comprised of only a single component corresponding to a tricycloundecanone. IR and ^{13}C NMR spectra demonstrated an asymmetrical molecular structure with the ketone function in a six-membered ring. Wolff–Kishner reduction of the above product mixture gave 2,4-bishomobrendane (**3**)[6] (93%) and several unknowns, but no tricyclo[4.4.1.$0^{3,8}$]undecane (**5**)[7] at all.

We consider the cause for the observed regioselectivity in the cyclization of **1** to be ascribed mainly to the difference in the entropies of activation for the two transition states **2t** and **4t** leading to **2** and **4**, respectively. If we take the conformer **1g** as the ground state for the cyclization, **2t** has almost the same skeletal conformation as that of **1g**. In contrast to this, the process leading to **4** is required to pass through **4t**, and the conformation of **1g** should be altered greatly in order to reach it. Accordingly, the entropy of activation for **4t** should have a large negative value as compared with that for **2t**, and this

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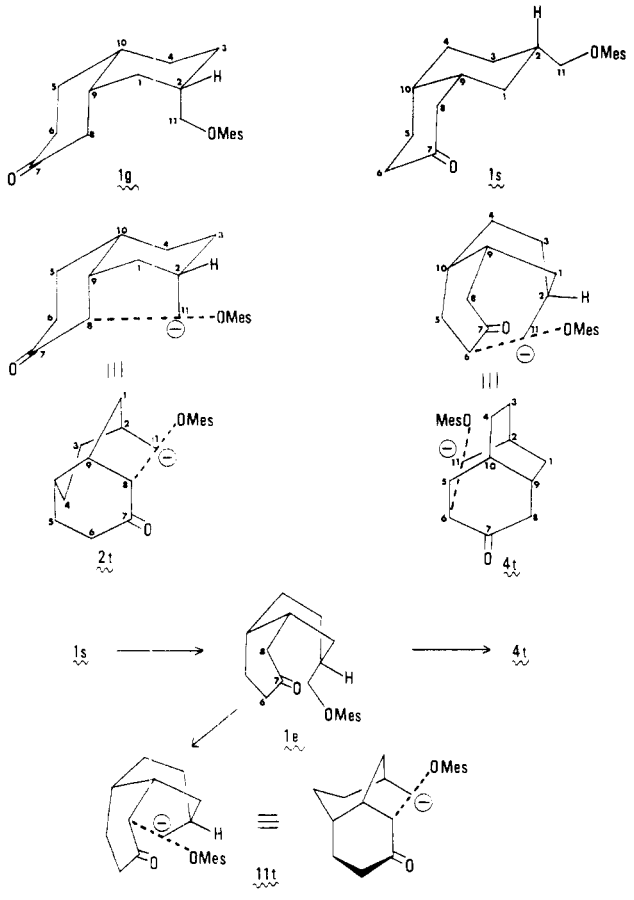

reflects on the difference in the free energies of activation for the two cyclizations.[8] An interpretation with a similar concept in terms of a "closer proximity" effect[1d] was given for the selective cyclization of a 5-keto-*exo*-1-*cis*-decalyl tosylate[1d] as well as the iodo ketone formed in situ in the thermolysis of 1-homoadamantyl hypoiodite.[2]

We took **1g**, instead of the most stable conformer **1s**, as the ground state for the cyclization to **2** because the transition state (**11t**) from **1s** to **2** is fairly strained compared with that (**2t**) from **1g** and gives an unstable conformer of **2** corresponding to **11t**. In addition, this process seems to predict rather the preferable formation of **4** over **2**, in opposition to the experimental result.

In order to facilitate an estimation of the relative ease in **1s** with which either the cyclization to **2** or to **4** occurs, the ground state **1s** is assumed to be excited at first to a less stable conformer **1e**. In **1e**, both C-6 and C-8 are situated in a similar spatial orientation with respect to the C-11 cationic center.[9] Therefore, the transition states **4t** and **11t** might be expected according to this analysis to have similar stabilities. On the other hand, the product **4** is more stable than the strained conformer of **2** to be formed from **11t**. Thus, if we start at **1s** going through **1e**, the cyclization via **4t** should be more likely to occur than that via **11t**.

Experimental Section

***cis*-Decalin-2,7-dione Monoethylene Ketal (7).** A mixture comprising 71.5 g (0.43 mol) of *cis*-decalin-2,7-dione (**6**),[1b,3] 17.0 g (0.27 mol) of ethylene glycol, 0.5 g of crystalline *p*-toluenesulfonic acid, and 800 mL of benzene was heated for 3 h, while the water that formed was continuously removed by means of a water separator.[10]

The reaction mixture was washed successively with 5% sodium carbonate solution and water, dried over anhydrous sodium sulfate, and concentrated. The residue was fractionally distilled to give 36.0 g (40% yield) of *cis*-decalin-2,7-dione monoethylene ketal (**7**): bp 115–117 °C (0.2 mmHg); IR (neat) 1710 ($\nu_{C=O}$), 1160, 1120, 1090, 1050 (O–C–O) cm^{-1}; mass spectrum, *m/e* (rel intensity) 210 (18, M$^+$), 154 (13), 139 (18), 112 (19), 99 (100), 86 (20), 55 (11), 41 (11).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.7; H, 8.7.

7-Methylene-*cis*-decalin-2-one Ethylene Ketal (8). A Wittig reagent was prepared by adding dropwise 37.0 g (0.33 mol) of potassium *tert*-butoxide to a solution of 98.2 g (0.27 mol) of methyltriphenylphosphonium bromide in 500 mL of dimethyl sulfoxide. A solution of 47.5 g (0.23 mol) of *cis*-decalin-2,7-dione monoethylene ketal (**7**) in 150 mL of dry ether was added dropwise in a period of 1.5 h to the above Wittig reagent solution kept at 10–15 °C, and the reaction was stirred overnight at ambient temperature.

The reaction mixture was diluted with 500 mL of a saturated sodium chloride solution and extracted with three 100-mL portions of *n*-hexane. The combined hexane extracts were washed with water and dried over anhydrous sodium sulfate. Concentration of the solution and fractional distillation of the residue gave 19.3 g (40% yield) of 7-methylene-*cis*-decalin-2-one ethylene ketal (**8**): bp 88–89 °C (0.25 mmHg); IR (neat) 3070 ($\nu_{=C=H_2}$), 1660 ($\nu_{C=CH_2}$), 1190, 1170, 1120, 1090, 1050 (O–C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3–2.4 (complex m, 14 H), 3.91 (s, 4 H, OCH_2CH_2O), 4.59 (d, J = 5 Hz, 2 H, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ_C 27.2 (t), 28.1 (t), 30.3 (t), 34.4 (t and d), 35.6 (t and d), 39.9 (t), 64.1 (t and t), 108.7 (t, $=CH_2$), 109.8 (s, $C(OCH_2)_2$), 146.3 (s, $C=CH_2$); mass spectrum, *m/e* (rel intensity) 208 (34, M$^+$), 153 (27), 106 (16), 99 (100), 91 (18), 86 (26), 80 (15), 79 (21), 77 (17), 55 (22), 53 (17), 42 (18), 41 (34), 39 (26).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.1; H, 9.6.

***endo*-7-(Hydroxymethyl)-*cis*-decalin-2-one Ethylene Ketal (9).** To a mixture consisting of 19.0 g (0.091 mol) of 7-methylene-*cis*-decalin-2-one ethylene ketal (**8**), 3.45 g (0.091 mol) of sodium borohydride, and 100 mL of dry tetrahydrofuran was added dropwise with efficient stirring at ambient temperature in a period of 2 h a solution of 19.0 g (0.13 mol) of boron trifluoride etherate in 30 mL of tetrahydrofuran, and the reaction was heated under reflux for an additional 3.5 h.

To the reaction mixture kept at 0–5 °C was added dropwise 30 mL of 3 N sodium hydroxide solution and then 30 mL of 30% hydrogen peroxide, and the mixture was stirred for an additional 1 h at 40–50 °C.

The cooled reaction mixture was mixed with 200 mL of a saturated sodium chloride solution and extracted with three 100-mL portions of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. Concentration of the ether solution and fractional distillation of the residue gave 17.7 g (86% yield) of *endo*-7-(hydroxymethyl)-*cis*-decalin-2-one ethylene ketal (**9**): bp 119–120 °C (0.04 mmHg); IR (neat) 3700–3100, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–1.8 (complex m, 15 H), 2.19 (s, 1 H, OH), 3.36–3.56 (m, 2 H, CH_2OH), 3.90 (d, J = 3 Hz, 4 H, OCH_2CH_2O); ^{13}C NMR ($CDCl_3$) δ_C 23.8 (t), 24.1 (t), 30.0 (t), 31.0 (t), 35.2 (t), 35.4 (d), 35.9 (d), 40.0 (t), 41.4 (d), 63.5 (t), 64.5 (t), 68.5 (t), 108.9 (s, $C(OCH_2)_2$); mass spectrum, *m/e* (rel intensity) 226 (31, M$^+$), 195 (69), 99 (10), 86 (39), 79 (20), 67 (25), 55 (34), 42 (21), 41 (50), 39 (23). Golay column GC–MS showed the sample to consist of a single isomer (96% of the combined peak areas) contaminated with a few minor constituents.

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.8; H, 9.9.

***endo*-7-(Methanesulfonyloxy)methyl-*cis*-decalin-2-one Ethylene Ketal (10).** A solution of 11.3 g (0.05 mol) of *endo*-7-(hydroxymethyl)-*cis*-decalin-2-one ethylene ketal (**9**) and 20 mL of dry pyridine in 130 mL of methylene chloride was kept at −10 to −7 °C, and 9.7 g (0.085 mol) of methanesulfonyl chloride was added dropwise to the solution in a period of 20 min. The reaction was set aside overnight at −10 °C.

After being mixed with 200 mL of water, the reaction mixture was extracted with three 50-mL portions of methylene chloride. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. The methylene chloride was evaporated off, and the residue was purified by passing through an alumina-packed column using benzene as eluent to give 13.3 g (88% yield) of viscous, oily *endo*-7-(methanesulfonyloxy)methyl-*cis*-decalin-2-one ethylene ketal (**10**): IR (neat) 1360, 1180 ($\nu_{S=O}$), 1100, 1040, 950, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (complex m, 15 H), 2.99 (s, 3 H, CH_3SO_2), 3.90 (d, J = 2 Hz, OCH_2CH_2O), 4.03 (m, 2 H, CH_2OSO_2); ^{13}C NMR ($CDCl_3$) δ_C 23.7 (t and t), 29.4 (t), 30.6 (t), 35.0 (t and d), 35.7 (d), 37.0 (q), 38.3 (d), 39.8 (t), 63.5 (t), 64.4 (t), 75.0 (t), 108.5 (s, $C(OCH_2)_2$); mass spectrum, *m/e* (rel intensity) 208 (19), 153 (11), 99 (100), 93 (10), 91 (14), 86 (21), 79 (18), 77 (13), 67 (11), 55 (18), 53 (12), 42 (13), 41 (27), 39 (20).

Anal. Calcd for $C_{14}H_{24}O_5S$: C, 55.24; H, 7.95; S, 10.5. Found: C, 55.3; H, 8.1; S, 10.8.

***endo*-7-(Methanesulfonyloxy)methyl-*cis*-decalin-2-one (1).**

To a solution of 12.9 g (0.042 mol) of *endo*-7-(methanesulfonyloxy)-methyl-*cis*-decalin-2-one ethylene ketal (**10**) in 120 mL of ether was added 12.6 g (0.1 mol) of oxalic acid dihydrate and 40 mL of water, and the resulting mixture was stirred at ambient temperature for 7 h.

The reaction mixture was mixed with 150 mL of water and extracted with three 50-mL portions of ether. The combined ether extracts were washed with 50 mL of 5% sodium carbonate solution and then with water and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 8.5 g (78% yield) of crude *endo*-7-(methanesulfonyloxy)methyl-*cis*-decalin-2-one (**1**): IR (neat) 1710 ($\nu_{C=O}$), 1350, 1180 ($\nu_{S=O}$), 960, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.6 (complex m, 15 H), 3.00 (s, 3 H, CH_3SO_2), 3.9–4.1 (m, 2 H, CH_2OSO_2); ^{13}C NMR ($CDCl_3$) δ_C 22.9 (t), 26.0 (t), 29.5 (t), 29.6 (t), 34.1 (d), 37.1 (d), 37.9 (q), 38.4 (d), 40.9 (t), 47.4 (t), 74.3 (t), 211.5 (s, C=O); mass spectrum, *m/e* (rel intensity) 164 (41), 107 (41), 106 (100), 99 (47), 93 (53), 91 (62), 79 (78), 77 (46), 67 (53), 55 (42), 53 (50), 41 (97), 39 (97).

2,4-Bishomobrendan-7-one (2). A solution of 10.2 g (0.039 mol) of the crude *endo*-7-(methanesulfonyloxy)methyl-*cis*-decalin-2-one (**1**) obtained above in 100 mL of benzene was added at ambient temperature with efficient stirring to a suspension of 4.7 g (0.20 mol) of sodium hydride in 100 mL of benzene, and the resulting mixture was heated under reflux with stirring for 6 h.

The reaction mixture was filtered, and the filtrate was concentrated. The concentration residue was absorbed on a silica gel packed column and eluted with *n*-hexane to afford 3.4 g (53% yield) of crude 2,4-bishomobrendan-7-one (**2**). Golay column GC–MS showed the sample to be of 92% purity. VPC fractionation yielded a pure sample: IR (neat) 1710 ($\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.8 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 24.2 (t), 28.3 (t), 31.6 (t), 32.5 (t), 33.1 (d), 33.4 (d), 34.7 (t), 39.1 (t), 41.1 (d), 50.2 (d), 217.2 (s, C=O); mass spectrum, *m/e* (rel intensity) 164 (93, M^+), 109 (65), 107 (34), 93 (41), 91 (35), 80 (50), 79 (92), 77 (41), 67 (100), 66 (39), 53 (42), 41 (93), 39 (94).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.3; H, 9.7.

After the 2,4-bishomobrendanone **2** had been eluted, the silica gel column was further eluted with ether. Evaporation of the solvent left 3.4 g (33% recovery) of the starting keto methanesulfonate **1**.

Wolff–Kishner Reduction of the Cyclization Product. A sample (0.1 g, 0.61 mmol) of the crude 2,4-bishomobrendan-7-one (**2**) obtained above was reduced in the usual manner with 0.2 g (4.0 mmol) of 100% hydrazine hydrate and 0.2 g of potassium hydroxide in 20 mL of diethylene glycol to give 0.035 g (38% yield) of the reduction product. The sample was shown upon Golay GC–MS to contain five constituents, of which the major one (93%) agreed with 2,4-bishomobrendane (**3**).[5] The absence of tricyclo[4.4.1.0^{3,8}]undecane (**5**) in the above sample was confirmed by comparison of the GC–MS behaviors of the sample with those of an authentic specimen of **5**.[6]

Registry No.—**1**, 68423-44-9; **2**, 68423-45-0; **3**, 51027-87-3; **6**, 20917-92-4; **7**, 68423-46-1; **8**, 68423-47-2; **9**, 68423-48-3; **10**, 68423-49-4; ethylene glycol, 107-21-1; methyltriphenylphosphonium bromide, 1779-49-3; methanesulfonyl chloride, 124-63-0.

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(8) If we take **1s** as the ground state for **4t**, separately from that (**1g**) for **2t**, the same conclusion holds true (Curtin–Hammett principle). Cf. E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 238.

(9) A similar conformational situation with respect to the relative orientation of the two competitive carbanions (C-5 and C-7) and the sulfonate was encountered with 6-keto-*exo*-1-*cis*-decalyl tosylate [C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Am. Chem. Soc.*, **89**, 4133 (1967)], and here again the selectivity was exhibited toward the cyclization via the C-5 anion. The cause was attributed in this case to an electronic effect arising from a better orbital overlap with C-5 than with C-7 between the vacant p orbital formed on the leaving of the tosylate and the anionic p orbital. However, no such preference in the electronic factor is found with our **4t** and **11t** because of conformational mobility of the mesyloxy group.

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High-Pressure Kinetics of Electron Donor–Acceptor Complex Formation and Cycloaddition with Tetracyanoethylene and Ethyl Vinyl Ether

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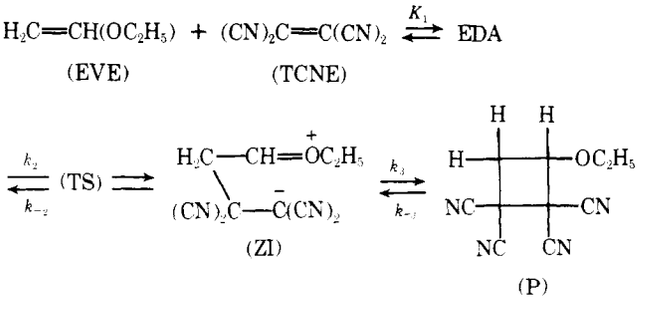
The cycloaddition of tetracyanoethylene (TCNE) to electron-rich olefins such as enol ether is supposed to take place through a zwitterionic intermediate or transition state, as supported by a strong dependency on solvent polarity,[1] incomplete stereospecificity,[2] and acetal formation in alcoholic solvents.[3] Strong evidence for the high polarity of the transition state was also obtained from high-pressure kinetics which gives the volume of activation. The overall values of the volume of activation for the cycloaddition of TCNE with enol ether are largely negative,[4] and even the cycloreversion has a negative volume of activation,[5,6] despite the bond-breaking process. These mechanistic studies so far, however, have not evaluated the role of the colored electron donor–acceptor complex (EDA complex) which appears immediately after the mixing of TCNE and enol ether, and which fades with the formation of the cycloadduct.

In the case of the Diels–Alder reaction between TCNE and 9,10-dimethylanthracene, the EDA complex was proved to be a true intermediate by the fact that the overall enthalpy of activation was negative.[7] The present work determines the volume change of each reaction step, both the EDA complex formation and the cycloaddition, in the reaction between TCNE and ethyl vinyl ether (EVE) in chloroform, based on the reaction scheme that the EDA complex is part of the pathway to the cycloaddition.

The disappearance of the EDA complex is too fast to be followed by conventional method under high pressure. The technical difficulty has restricted the high-pressure study of thermal reactions in which such short-lived species occur. The

Scheme I



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