Studies of the Transition-state Structure by the Method of Volumetric Steric Effects. Part 4.† Transition State in Diels–Alder Reactions of (*E*)-1-Alkyl(alkoxy)-buta-1,3-dienes with Alkyl Acrylates‡

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A method of studying transition-state structures by analysis of volumetric steric effects is proposed. The method is used to reveal features of the steric structure of the transition state in Diels–Alder reactions. The structure has been found to change from one approximating the structure of the prereactional complex to that resembling the half-chair adduct as the diene substituent changes from methyl to t-butyl. As this takes place, no intermediate half-boat adduct is formed. An increase in steric hindrance during the change in the substituent is regarded as the driving force responsible for the transition-state shift along the reaction co-ordinate. This is consistent with the Hammond postulate. The C=O and C=C groups of the dienophile in the *endo*-transition state are in the *s-cis*-conformation.

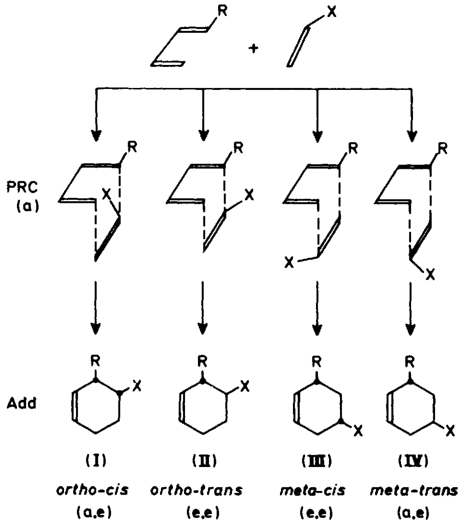
The idea that steric hindrance attributable to the valence non-bonding atoms drawing closer together is accompanied by a decrease in the volume of the reacting system was clearly formulated by Gonikberg and his co-workers from kinetic studies[6–8] and Allinger by conformational analysis.[9,10] This effect was explained by overlap of the van der Waals spheres of the repulsing atoms in the transition state (TS) or in the stable molecules. Later studies have shown that the overlap model fails to account for all the experimental evidence available. The volumetric effects attending steric hindrance [the volumetric steric effects (VSE)] were attributed to the decreased free volume of the system, resulting from the restriction of the internal mobility in the molecule or TS.[11,12]

The existence of VSE is demonstrated by two rules. The first, Gonikberg–Kitaigorodsky's rule,[6] states 'the more hindered a chemical reaction, the greater the decrease in volume in the formation of a TS and, accordingly, the greater acceleration of this reaction under pressure'. According to the second, Allinger's conformational rule,[10] the sterically hindered isomer or conformation will have a smaller volume than the sterically unhindered one. Owing to the fact that the two rules are supported by a great body of data, VSE can be regarded as a fairly reliable characteristic of steric hindrance.

At the earlier stages of the development of stereochemistry VSE were successfully applied to the determination of the configuration of cyclohexane derivatives by use of the Auwers–Skita rule[13] through comparison of the isomer densities. However, with the appearance of more efficient physical methods for the study of molecular structure the above technique has been abandoned. Nevertheless, it is believed that it deserves further development and may be used to advantage in those cases where other physical methods are unsuitable, particularly in stereochemical TS studies.

Information on the VSE in the TS is provided by the activation volumes $\Delta V^{\ddagger}$ or the selectivity volumes $\Delta V_{\mathrm{sel}}^{\ddagger} = V_{\mathrm{a}}^{\ddagger} - V_{\mathrm{b}}^{\ddagger}$, where $V_{\mathrm{a}}^{\ddagger}$ and $V_{\mathrm{b}}^{\ddagger}$ are the volumes of the isomeric TS. They can be found from the dependence of the reaction rate constant or selectivity on pressure.

This paper uses the VSE method to gain information on features of the steric structure of the TS in Diels–Alder reactions. Using this method a study is made of the effect of pressure on the isomeric composition of products resulting from the reaction of 1-substituted buta-1,3-diene with mono-substituted olefins. This permits the values of $\Delta V_{\mathrm{sel}}^{\ddagger}$ to be obtained. The reaction involves the four pathways in the Scheme. The Scheme gives adduct structures and plane-parallel models corresponding to each pathway. These models should describe the system's structure at the moment when the reagents begin interacting, *i.e.* when the interacting atoms of the molecules become separated by a distance equal to the sum of their van der Waals radii. This state located immediately at the foot of the energy barrier can be termed 'a prereactional complex' (PRC). As the system shifts along the reaction co-ordinate, its steric structure gradually changes, the final product having a cyclohexene structure in a half-chair conformation. The following two reaction pathways are feasible: (a) initially a half-boat adduct (Add-hb) is formed, which is then converted into a half-chair adduct (Add-hch); (b) the system passes directly to Add-hch without formation of Add-hb. Energy profiles corresponding to these two cases are shown in Figure 1.



Scheme. 1,2- and 1,3-substituents are designated *ortho* and *meta* for convenience. Conformations are in parentheses

Let us now consider relations between the volumes of the isomeric structures for each of the limiting states, *viz.*, PRC and Add-hch. It is accepted that the relation between the volumes of the isomers is solely governed by differences in their VSE. In the case of PRC model (**Ia**) is expected to have a smaller volume

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† For parts 1—3 see refs. 1—3.

‡ Preliminary short communications, refs. 4 and 5.

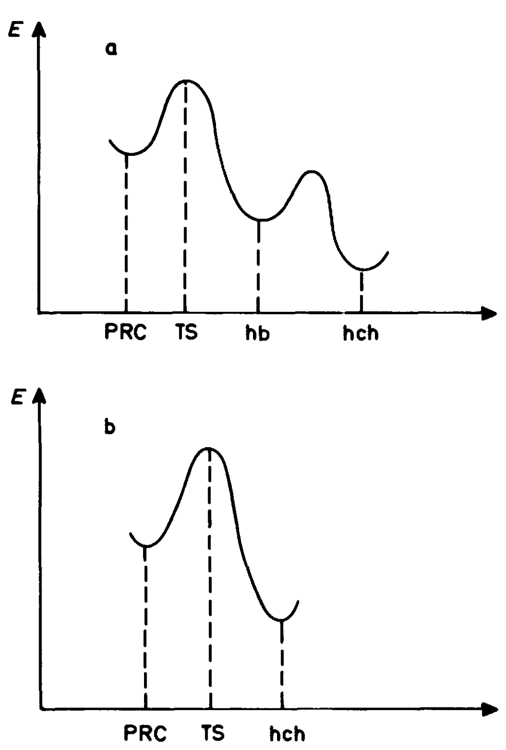

Figure 1. Possible reaction energy profiles: PRC, prereactional complex; TS, transition state; hb, half-boat; hch, half-chair

than (**IIa**) since in (**Ia**) the substituent X interacts sterically with the diene atoms whereas in (**IIa**) this type of interaction is not observed. Thus $V_{(\mathbf{Ia})} < V_{(\mathbf{IIa})}$ and, similarly, $V_{(\mathbf{IIIa})} < V_{(\mathbf{IVa})}$.

It is evident from comparison of models (**Ia**) and (**IIIa**) that $V_{(\mathbf{Ia})} < V_{(\mathbf{IIIa})}$ due to the fact that in the former X and R are nearer to one another than in the latter. Similarly, $V_{(\mathbf{IIa})} < V(_{(\mathbf{IVa})}$.

We now consider similar relations for Add-hch. It is recognized that the axial group is more sterically hindered than the equatorial, which is also the case for the *ortho*-position compared with the *meta*-position. Then $V_{(\mathrm{I})} < V_{(\mathrm{II})}$, $V_{(\mathrm{III})} > V_{(\mathrm{IV})}$, $V_{(\mathrm{I})} < V_{(\mathrm{III})}$ and $V_{(\mathrm{II})} \gtrless V_{(\mathrm{IV})}$. The last case is uncertain due to the competition of the two effects. The results of the comparison performed are presented in Table 1.

It is evident that in the first and third cases the inequality signs for PRC and Add-hch are the same; therefore, one can expect the same sign for the TS [see column TS (interpolated) in Table 1]. For the second case PRC and Add-hch will have different signs. This fact has important practical implications in that comparison of these signs with that of the experimentally obtained quantity $\Delta V_{\mathrm{sel}}^{\ddagger}$ permits the conclusion to be drawn whether the steric structure of TS is closer to the structure of the plane-parallel model of PRC or Add-hch. A conclusion about the proximity of the structure of the TS to that of Add-hch can be also drawn in the fourth case when $(V_{\mathrm{ot}}^{\ddagger} - V_{\mathrm{mt}}^{\ddagger}) > 0$. With the opposite sign no definite conclusion can be made. For Add-hb, it should be borne in mind that with respect to the steric arrangement of atoms this structure is very close to the PRC so that our approach will fail to reveal any differences between the TS structures that are very much the same as those of PRC or Add-hb.

Thus, studies of the effect of pressure on the isomeric composition of adducts in the reaction of 1-substituted butadiene with monosubstituted olefins or carbonyl derivatives and comparison of the signs of the derived values of $\Delta V_{\mathrm{sel}}^{\ddagger}$ with those of the inequalities of Table 1 provide evidence for the details of the steric structure of the TS. It will be shown below that additional information to this effect can be obtained by examining how $\Delta V_{\mathrm{sel}}^{\ddagger}$ changes in a reaction series.

A number of Diels–Alder reactions have been studied earlier. In the case of reaction of 1-vinylcyclopentene with methyl acrylate[1] the TS has been shown to have a structure intermediate between those of the PRC and Add-hch. Reactions of *trans*-piperylene with methyl acrylate,[2] (*E*)-1-methoxy-, and (*E*)-1-ethoxy-butadiene with alkyl glyoxylates and acetaldehyde[3] have shown the TS structure to resemble that of PRC. This paper reports reactions of *trans*-piperylene with n-propyl and t-amyl acrylates, of (*E*)-1-isopropylbuta-1,3-diene with methyl and n-propyl acrylates, (*E*)-1-t-butylbuta-1,3-diene with methyl acrylate in heptane at 80 °C and pressures up to 6 kbar. (*E*)-1-Methoxybuta-1,3-diene was treated with methyl acrylate in anisole at 30 °C. The isomeric composition of the adducts was determined by g.l.c.

Results and Discussion

Selectivity Volumes.—Table 2 lists the isomeric concentration ratios α at various pressures. For the reaction of isopropylbutadiene with propyl acrylate the values of α_2 and α_4 were not calculated as the peak of the *meta-trans* isomer on the gas-liquid chromatogram was distorted by the presence of an impurity. It is evident that even for a broad range of pressures the maximum variation of α does not exceed 50%. It is rather a modest value due to the small values of $\Delta V_{\mathrm{sel}}^{\ddagger}$ (3 cm^3 mol^{-1} maximum) as shown by calculation. The calculation from the slope of the tangent to the curve $\ln \alpha = f(p)$ at $p = 0$ by equation (1)

$$\partial \ln \alpha / \partial p = -\Delta V_{\mathrm{sel}}^{\ddagger}/RT \qquad (1)$$

involves random errors commensurate with the values to be calculated. To diminish their effect on $\Delta V_{\mathrm{sel}}^{\ddagger}$, the latter were calculated by use of a least-squares techniques with the aid of equation (2) which has, along with $\Delta V_{\mathrm{sel}}^{\ddagger}$, only one adjustable

$$\lg \alpha_p = \lg \alpha_0 - \frac{\Delta V_{\mathrm{sel}}^{\ddagger}}{T} \times \Phi \qquad (2)$$

parameter, $\lg\alpha_0$. Here the indices p and 0 relate to the elevated and atmospheric pressures, respectively, and Φ is given by equation (3).

$$\Phi = [(1 + a)p - (a/b)(1 + bp)\ln(1 + bp)]/R\ln 10 \qquad (3)$$

For Diels–Alder reactions[14] $a = 0.170$ and $b = 4.94 \times 10^{-3}$ bar^{-1}. Equation (2) was obtained by starting with the relation $\alpha = k_{\mathrm{A}}/k_{\mathrm{B}}$ for two competing reactions of the same kinetic order and the linear free-energy dependence (4) where k_p and k_0

$$\lg k_p = \lg k_0 - \frac{\Delta V_0^{\ddagger}}{T}\Phi \qquad (4)$$

are the rate constants, $\Delta V^{\ddagger}$ is the activation volume, and Φ is the pressure function common to the related reactions.[14]

To check for the validity of equation (2) at the adopted form of Φ and given values of a and b, use was made of the tests of linearity and error randomness as well as an accuracy index proposed elsewhere.[14,15]

Some clarifying remarks concerning the test of error randomness should be made. As proposed by us earlier,[14] this test is described by the condition by which, when using a least-squares technique according to equation (5), there will be an

Table 1. Results of analysis of selectivity volumes*

	PRC	Add-hch	TS (interpolated)
1	$(V_{oc} - V_{ot})_a < 0$	$(V_{oc} - V_{ot}) < 0$	$(V_{oc}^{\ddagger} - V_{ot}^{\ddagger}) < 0$
2	$(V_{mc} - V_{mt})_a < 0$	$(V_{mc} - V_{mt}) > 0$	$(V_{mc}^{\ddagger} - V_{mt}^{\ddagger})$?
3	$(V_{oc} - V_{mc})_a < 0$	$(V_{oc} - V_{mc}) < 0$	$(V_{oc}^{\ddagger} - V_{mc}^{\ddagger}) < 0$
4	$(V_{ot} - V_{mt})_a < 0$	$(V_{ot} - V_{mt}) \gtrless 0$	$(V_{ot}^{\ddagger} - V_{mt}^{\ddagger})$?

* o = *ortho*, m = *meta*, c = *cis*, t = *trans*.

Table 2. Effect of pressure on isomer ratios in the products of the Diels–Alder reactions studied*

Diene	Dienophile	Pressure (kbar)	Ratio			
			$\alpha_1 = \frac{oc}{ot}$	$\alpha_2 = \frac{mc}{mt}$	$\alpha_3 = \frac{oc}{mc}$	$\alpha_4 = \frac{ot}{mt}$
Piperylene	Propyl acrylate	0.001	0.96	0.96	6.81	6.82
		1.961	1.12	1.07	7.82	7.49
		3.923	1.18	1.12	8.08	7.71
		5.884	1.28	1.26	8.35	8.22
Piperylene	t-Amyl acrylate	0.001	0.79	0.90	4.93	5.62
		1.961	0.92	1.01	5.47	5.98
		3.923	1.01	1.06	5.92	6.25
		5.884	1.13	1.17	6.38	6.59
Isopropylbutadiene	Methyl acrylate	0.001	1.18	1.16	8.41	8.25
		1.961	1.39	1.20	9.41	8.12
		3.923	1.55	1.25	9.96	8.02
		5.884	1.65	1.31	10.1	8.04
Isopropylbutadiene	Propyl acrylate	0.001	1.09		7.49	
		1.961	1.26		8.07	
		3.923	1.39		8.44	
		5.884	1.48		8.45	
t-Butylbutadiene	Methyl acrylate	0.001	1.54	1.45	8.09	7.63
		1.961	1.83	1.38	10.0	7.57
		3.923	1.99	1.38	10.8	7.52
		5.884	2.23	1.40	11.6	7.26
Methoxybutadiene†	Methyl acrylate	0.001	3.07			
		1.961	3.29			
		3.923	3.72			
		5.884	4.35			

* 80 °C, unless otherwise stated. † 30 °C.

$$\lg \alpha_p = \lg \alpha_0 - \frac{V_{sel}^{\ddagger}}{T}\Phi + B\Phi^2 \qquad (5)$$

equal probability of obtaining both $B > 0$ and $B < 0$. In our work this condition is considered to be satisfied if ω_{expt}, *i.e.* the frequency of the realization of the case when $B > 0$, calculated from the experimental data, falls within the statistically estimated interval of the practicable values of ω_{theor} at the probability $\tilde{p} = 0.5$, number of experiments N, and significance level $p_0 = 0.05$. At $5 \leqslant N \leqslant 50$ ω_{theor} can be calculated from equation (6) where $N_{max.}$ is retrieved from Table A of ref. 16.

$$\omega_{theor} = 0.5 \pm (N_{max.}/N - 0.5) \qquad (6)$$

For $N > 50$ we have equation (7).

$$\omega_{theor} = 0.5 \pm 0.98/\sqrt{N} \qquad (7)$$

Equation (7) is obtained by substituting $\tilde{p} = 0.5$ and the quantile of the standard normal distribution $u_{(1-p_0/2)} = 1.96$ at $p_0 = 0.05$ in the general equation (8).[17] This equation is somewhat more precise than equation (27) of ref. 14.

$$\omega_{theor} = \tilde{p} \pm u_{(1-p_0/2)}\sqrt{\tilde{p}(1 - \tilde{p})/N} \qquad (8)$$

Table 3 presents the test of linearity, where the sign (+) designates its fulfilment and (±) a doubtful case. Standard deviations S_2, when calculations are performed by use of equation (2), and the resulting accuracy indices are also given in Table 3. It is evident that out of 23 reactions only two are rated as doubtful, the accuracy indices being good or excellent in all cases. The value of ω_{expt} for $B > 0$ is 0.479 and $\omega_{theor} = 0.5 \pm 0.197$, so that the test of error randomness is satisfied.

The values of $\Delta V_{sel}^{\ddagger}$ for the reactions studied as well as the reaction of piperylene with methyl acrylate,[2] calculated from data up to 6 kbar, are given in Table 4.* The standard deviations for $\Delta V_{sel}^{\ddagger}$ are given in parentheses, and are calculated from

$$\delta\Delta V_{sel}^{\ddagger} = S_2 T/\sqrt{[\Sigma\Phi^2 - (\Sigma\Phi)^2]/l} \qquad (9)$$

equation (9) where l is the number of experimental points.[15] Table 4 is composed of three sections; the first shows reactions of various dienes with methyl acrylate, the second of piperylene with various acrylates, and the third the remaining reactions.

As stated above, $V_{oc}^{\ddagger} - V_{ot}^{\ddagger}$ and $V_{oc}^{\ddagger} - V_{mc}^{\ddagger}$ should be negative. The results obtained demonstrate that this requirement

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* Table 4 lists values refined with respect to those in preliminary communications,[4,5] which, however, do not affect the conclusions made.

Table 3. Check for the applicability of equation (2) to the Diels–Alder reactions studied

Reaction	α	S_2	Test of linearity	Accuracy index	Sign of *B*
Piperylene + methyl acrylate	1	0.0058	+	Excellent	+
	2	0.0039	+	Excellent	+
	3	0.0104	+	Excellent	−
	4	0.0075	∓	Excellent	−
Piperylene + propyl acrylate	1	0.0094	+	Excellent	−
	2	0.0099	+	Excellent	+
	3	0.0133	+	Good	−
	4	0.0061	+	Excellent	−
Piperylene + t-amyl acrylate	1	0.0052	+	Excellent	+
	2	0.0062	+	Excellent	+
	3	0.0016	+	Excellent	+
	4	0.0012	+	Excellent	+
Isopropylbutadiene + methyl acrylate	1	0.0078	+	Excellent	−
	2	0.0043	+	Excellent	+
	3	0.0101	+	Excellent	−
	4	0.0022	+	Excellent	+
t-Butylbutadiene + methyl acrylate	1	0.0067	+	Excellent	−
	2	0.0080	+	Excellent	+
	3	0.0153	+	Good	−
	4	0.0056	+	Excellent	−
Isopropylbutadiene + propyl acrylate	1	0.0057	+	Excellent	−
	3	0.0085	+	Excellent	−
Methoxybutadiene + methyl acrylate	1	0.0217	∓	Good	+

Table 4. Experimentally obtained selectivity volumes (cm^3 mol^{-1}) at 80 °C.

		Stereoselectivity		Regioselectivity	
		$V_{oc}^‡ - V_{ot}^‡$	$V_{mc}^‡ - V_{mt}^‡$	$V_{oc}^‡ - V_{mc}^‡$	$V_{ot}^‡ - V_{mt}^‡$
Piperylene	Methyl acrylate	−3.10 (0.16)	−3.01 (0.11)	−0.83 (0.28)	−0.74 (0.20)
Isopropylbutadiene	Methyl acrylate	−2.99 (0.21)	−1.09 (0.12)	−1.65 (0.27)	+0.24 (0.06)
t-Butylbutadiene	Methyl acrylate	−3.16 (0.18)	+0.34 (0.22)	−3.11 (0.41)	+0.39 (0.15)
Piperylene	Methyl acrylate	−3.10 (0.16)	−3.01 (0.11)	−0.83 (0.28)	−0.74 (0.20)
Piperylene	Propyl acrylate	−2.45 (0.25)	−2.26 (0.27)	−1.75 (0.36)	−1.56 (0.16)
Piperylene	t-Amyl acrylate	−3.09 (0.14)	−2.21 (0.17)	−2.24 (0.04)	−1.36 (0.07)
Isopropylbutadiene	Propyl acrylate	−2.73 (0.15)		−1.10 (0.23)	
Methoxybutadiene	Methyl acrylate	−2.57* (0.50)			

* 30 °C.

is met in all cases. To acquire further information on the TS structure we shall consider $V_{mc}^‡ - V_{mt}^‡$ and $V_{ot}^‡ - V_{mt}^‡$.

Alkylbutadiene Series.—In this series $V_{mc}^‡ - V_{mt}^‡$ is negative in the first two reactions and positive in the third. $V_{ot}^‡ - V_{mt}^‡$ is negative for the reaction of piperylene with methyl acrylate and positive for the other reactions. Thus the data of Table 1 suggest that for the first reaction the steric structure of the TS is close to that of the PRC whereas for the third it is closer to that of the adduct. At the same time, for the second reaction our approach yields conflicting conclusions in that the sign of $V_{mc}^‡ - V_{mt}^‡$ points to the proximity of the TS structure to that of the PRC whereas that of $V_{ot}^‡ - V_{mt}^‡$ shows that it resembles the adduct. Such a contradiction can be readily reconciled if one takes a TS structure intermediate between the two limiting cases and takes into account the fact that a change in the sign of both $\Delta V_{sel}^‡$ quantities, as the reacting system shifts along the reaction co-ordinate, can take place at various values of this co-ordinate. Thus the growing radical in the diene brings about a change in the steric structure of the TS, corresponding to its shift along the reaction co-ordinate towards Add-hch.

The same conclusion is supported by examining changes in the values of $\Delta V_{sel}^‡$ as the radical grows in the diene in that the two quantities, *i.e.* $V_{mc}^‡ - V_{mt}^‡$ and $V_{ot}^‡ - V_{mt}^‡$, increase regularly (shifting towards the positive values). According to Table 1, this means that the TS shifts along the reaction co-ordinate towards Add-hch.

Without regard to the TS shift along the reaction co-ordinate it would be impossible to understand the difference in the effect

Table 5. Effect of radical size in 1-alkylbutadiene on the rate of reaction with maleic anhydride.[20]

Alkyl	Temperature (°C)	Rate constant ($l\ mol^{-1}\ h^{-1}$)
Methyl	25	0.92
t-Butyl	40	0.009
t-Butyl	50	0.021

of radical growth in the diene on $V_{oc}^{\ddagger} - V_{ot}^{\ddagger}$ and $V_{mc}^{\ddagger} - V_{mt}^{\ddagger}$. As this takes place, the former quantity remains practically unaltered, whereas the latter changes considerably. It could be expected, though, that the radical would produce a steric effect on the proximal *ortho*-substituents and no effect on the distant *meta*-substituents. Considering the TS shift along the reaction co-ordinate towards Add-hch allows a simple explanation of this fact. The *meta*-substituents, as opposed to their *ortho*-counterparts, undergo noticeable steric displacements, which can be readily seen with the aid of a three-dimensional model. This will be accompanied by the above mentioned changes of $V_{mc}^{\ddagger} - V_{mt}^{\ddagger}$ towards the positive side.

The increase of the positive values of $\Delta V_{sel}^{\ddagger}$ with growing radical can be attributed to the fact that there arises a steric repulsive interaction of the methoxycarbonyl group with the hydrogen atom at C(1) of the diene in the TS for the *meta-trans*-isomer, this interaction increasing as the system shifts along the reaction co-ordinate.

The results have another important implication. Owing to the fact that the features of Add-hch become noticeable in the TS, this means that the reaction does not occur through the intermediate formation of Add-hb, *i.e.* reaction pathway 'b' rather than 'a' of Figure 1 will take place.

The question arises concerning the driving force of the TS shift along the reaction co-ordinate. Unfortunately, we have no direct kinetic data on the reactions under investigation. However, by analogy with the data of Table 5 on the condensation of our dienes with maleic anhydride,[18] the growth of the radical can be assumed to result in a substantial deceleration of the reaction rate because of increased steric hindrance. (Qualitatively this effect has also been directly observed by us in terms of lower conversions in equal times.) According to the Hammond postulate, an increased energy barrier is expected to lead to the TS being shifted along the reaction co-ordinate towards the product, which is consistent with our data.

Acrylate Series.—For this whole series the values of $\Delta V_{sel}^{\ddagger}$ are negative, which suggests the structure of the TS is close to that of the PRC. This is in accord with the Hammond postulate which states that in the case of exothermic reactions, a class to which Diels–Alder reactions belong, one can expect the appearance of 'an early' TS. However, as shown in the preceding section, for some reactions the steric structure of the TS is already characterized by features typical of the final adduct, which is likely to take place in the early bonding stages. Thus, with respect to the description of the steric structure, the Hammond postulate may or may not be valid. At the same time, it can be seen that this postulate correctly indicates a direction of structural changes under the effect of an additional factor, in our case steric hindrance.

Consideration of $V_{oc}^{\ddagger} - V_{mc}^{\ddagger}$ suggests that with the growth of the radical in the alkyl acrylate one can observe a steady increase of this quantity. This fact can be attributed to the steric repulsion of the diene-contained methyl and the dienophile-contained alkoxyl radical, which increases as the radical becomes larger. It follows then that in the *endo*-TS the alkoxy group of the dienophile is located adjacent to the methyl of the diene and, hence, the dienophile C=O and C=C groups will be in the *s-cis*-conformation (Figure 2). There exists no such clear dependence for the *trans*(*exo*)-orientation.

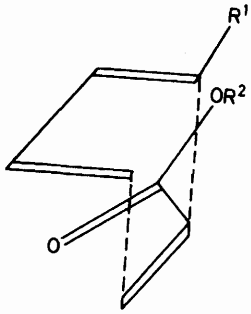

Figure 2. Dienophile conformation in the TS

Concerning the stereoselectivity volumes, the growing radical in the acrylate brings about no increase in $\Delta V_{sel}^{\ddagger}$. This suggests the absence of any noticeable repulsive interaction between the alkyl group of the acrylate and the diene system in the *endo*-position, which agrees with the conclusion as to the *s-cis*-conformation of the dienophile in the *endo*-TS. Thus our results for steric structure of the TS in Diels–Alder reactions demonstrate the prospect of the application of the VSE method to TS studies in some chemical processes.

Experimental

The methods of studying the reactions of 1-alkylbutadienes with acrylates and isomer peak assignments are described elsewhere.[19] G.l.c. of anisole, 1-methoxybutadiene, and its adducts with methyl acrylate was carried out on a Chrom-2 instrument (flame ionization detector; carrier gas N_2; capillary column 0.25 mm × 80 m with polypropylene glycol 1 025). 1-Methoxybutadiene was obtained by the published techniques,[20] b.p. 50 °C at 165 mmHg, n_D^{20} 1.4618, $E:Z = 85:15$. Anisole had b.p. 154.0—154.5 °C at 754 mmHg, n_D^{20} 1.5173, impurity content 0.1% maximum as shown by g.l.c.

Concentrations of components were chosen such that the initial pressure rise did not affect the experimental results. In the interaction of alkylbutadienes with alkyl acrylates concentrations of diene were 1.5—3M and dienophile 1—1.5M. In the reaction of 1-methoxybutadiene with methyl acrylate the concentrations of diene and dienophile were 0.25 and 0.2M, respectively. The reactions were carried out in sealed Teflon ampoules placed in a thermostatted pressure vessel. All the experiments were performed twice. 3—5 Chromatograms were obtained for each experiment.

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