fluorocarbons[7] that association due to hydrogen bonding between molecules of partially fluorinated methanes occur in the liquid state, the above mentioned minimum could correspond to a shift in the equilibrium constant of the reaction polymers ⇄ monomers as the temperature is raised.

(c) **Heat Capacity of the Solid.**—An examination of the heat capacity of the solid state for various halogenated methanes reported in the literature indicates that except for methane[12] no λ-type transitions are observed. Carbon tetrafluoride,[13] carbon tetrabromide,[14] carbon tetrachloride[15] and bromomethane[16] show sharp transitions, characteristic of a first-order effect, while chloromethane[17] and trichlorofluoromethane[18] show no transitions.

The nature of the λ-type transition in chlorodifluoromethane cannot be ascertained solely on the basis of the heat capacity. This transition appears anomalous in comparison with other halogenated methanes, however, it should be pointed out that due to kinetic effects a first-order transition may be masked, resulting in what appears to be a λ-type transition.

Derived Thermodynamic Functions

The heat capacity and derived thermodynamic functions for chlorodifluoromethane at selected temperatures are given in Table VI.

TABLE VI

THERMODYNAMIC FUNCTIONS OF CHLORODIFLUOROMETHANE

Temp., °K.	C_p, cal./mole/deg.	S, cal./mole/deg.	$(H - H_0)/T$, cal./mole/deg.	$-(F - H_0)/T$, cal./mole/deg.
		Solid		
15	2.470	1.1393	0.8120	0.3273
20	3.905	2.039	1.395	0.644
30	6.970	4.236	2.747	1.489
40	9.015	6.536	4.097	2.439
50	10.235	8.697	5.219	3.478
Transition in solid occurs 50–75°K. (entropy of transition is 0.272 cal./mole/deg.)				
80	12.080	14.215	8.648	6.567
90	12.845	15.681	8.185	7.496
100	13.645	17.070	8.688	8.382
110	14.442	18.395	9.175	9.220
115.73	14.900	19.131	9.447	9.684
		Liquid		
115.73	22.142	27.647	17.963	9.684
120	22.100	28.449	18.111	10.338
140	21.904	31.841	18.666	13.175
160	21.856	34.760	19.066	15.694
180	21.978	37.341	19.382	17.959
200	22.104	39.663	19.649	20.014
220	22.184	41.774	19.875	21.899
232.50	22.234	42.996	20.001	22.995
232.50 (vapor)	....	63.781	40.786	22.995
232.50 (ideal gas)	....	63.919	....	....

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[12] K. Clusius, *Z. physik. Chem.*, **B3**, 65 (1929).

[13] A. Eucken and E. Schroder, *ibid.*, **B41**, 307 (1938).

[14] J. G. Marshall, K. R. Hart and L. A. K. Staveley, *Nature*, **168**, 519 (1951).

[15] J. F. Hicks, J. G. Hooley and C. C. Stephenson, THIS JOURNAL, **66**, 1064 (1944).

[16] C. J. Egan and J. D. Kemp, *ibid.*, **60**, 2097 (1938).

[17] G. H. Messerly and J. G. Aston, *ibid.*, **62**, 886 (1940).

[18] D. W. Osborne, C. S. Garner, R. N. Doescher and D. M. Yost, *ibid.*, **63**, 3496 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK STATE COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, AND ALDRICH CHEMICAL CO.]

Addition of Methyl Radical to *cis* and *trans* Isomers

BY A. R. BADER, R. P. BUCKLEY, F. LEAVITT AND M. SZWARC

RECEIVED MAY 14, 1957

The addition of methyl radicals to a series of *cis* and *trans* isomers has been studied. The kinetic data permit us to conclude that different transition states represent the addition to a *cis* and a *trans* isomer. This means that the transition state is rigid in respect to the central C–C bond. The difference in the reactivities of *cis* and *trans* isomers is satisfactorily accounted for. It is explained by the difference in the resonance energies of the respective transition states. Finally an attempt is made to solve the problem from which direction the radical approaches a C=C double bond. It is suggested tentatively that the most probable approach of a radical is along the C=C axis.

The object of the present investigation is to study the differences in the reactivities of *cis* and *trans* isomers and to explain the observed variations in reactivities in terms of structural changes of the molecule resulting from the isomerization process. To obtain the desired information we investigated the addition of methyl radicals to the respective isomers, *i.e.*, the reactions described by the general equation

$$\mathrm{CHX{:}CHX + CH_3 \longrightarrow \cdot CHX{\cdot}CHX{\cdot}CH_3}$$

These reactions are simple, easy to investigate, and their product—the radical $\cdot$CHX$\cdot$CHX$\cdot$CH$_3$— is common for both isomers.[1]

Although the addition to either isomer results in the same product, the transition states of the respective processes need not be the same. If the internal rotation in the transition state is free, then the reactions involving the *cis* or the *trans* isomer would both proceed through the same transition state. On the other hand, if the internal rotation is restricted, then the two reactions would proceed through different transition states. The results, discussed later in this paper, show that the addition of radicals to *cis* and to *trans* isomers proceeds through different transition states. Hence, it appears that the internal rotation in respect to the central C–C bond is restricted in the transition state.

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[1] See, *e.g.*, F. R. Mayo and K. E. Wilzbach, THIS JOURNAL, **71**, 1124 (1949).

Experimental

The following pairs of isomers were investigated: the 2-butenes, the di-*t*-butylethylenes, the stilbenes, maleo- and fumaronitrile, and diethyl maleate and diethyl fumarate.

The *cis*- and *trans*-2-butene were acquired commercially from Philips Petroleum Co. The purity of both gases exceeds 99%, and before use they were subjected to a trap to trap vacuum distillation and a thorough deaeration.

The two isomeric di-*t*-butylethylenes were prepared by Dr. Walter H. Puterbaugh working in Dr. Melvin Newman's laboratories.[2] The *cis* isomer was prepared by the catalytic hydrogenation of di-*t*-butylacetylene using platinum on alumina catalyst. The *trans* isomer was prepared by the pyrolysis of 2,2,5,5-tetramethyl-3-hexyl acetate. Both isomers were carefully purified by a repeated distillation. The *cis* isomer boils at 143°, n^{20}_D 1.4269, and its infrared spectrum shows the typical *cis*-hydrogen absorption band at 13.7 μ and no absorption at 10.3 μ (trans-hydrogen) and at 7.7 and 8.0 μ. The *trans* isomer boils at 125.1°, n^{20}_D 1.4117, and its freezing point is $-4.8°$. Its infrared spectrum shows the typical *trans* absorption band at 10.3 μ. All these constants agree well with those reported by Howard, *et al.*,[3] and by Hennion and Banigan.[4]

Commercial *trans*-stilbene was recrystallized and melted sharply at 124°. The *cis* isomer was prepared by the decarboxylation[5] of α-phenylcinnamic acid, m.p. 174°. The product was treated several times with hexane at low temperatures to remove small amounts of *trans*-stilbene, and was then redistilled twice, b.p. 100–101° (2 mm.), n^{25}_D 1.6188.

Commercial fumaronitrile was recrystallized and melted sharply at 96°. Maleonitrile was prepared by the method of Linstead and Whalley.[6] The product, purified by distillation *in vacuo* and crystallization from ethanol, melted at 30–32°.

Finally, diethyl maleate and diethyl fumarate were acquired commercially, and purified by fractional distillation.

The rates of addition of methyl radicals were determined by the method described previously.[7,8] The results are presented in the form of k_2/k_1, where the subscripts refer to the two reactions

$$CH_3 + \text{solvent} \longrightarrow CH_4 + \text{solvent radical} \quad (1)$$

$$CH_3 + \text{olefin} \longrightarrow CH_3\cdot\text{olefin} \quad (2)$$

In most experiments isoöctane was used as a solvent; however, in a few cases the solubilities of the respective compounds in isoöctane were too low, and then methyl ethyl ketone was used as the alternative solvent. The solvents were purified by careful distillation, attention being paid to remove all the peroxides which were present in the commercial ketone.

Results

The addition of methyl radicals was investigated at temperatures varying from 55 to 85°. The values of k_2/k_1 obtained for each compound at the required temperatures are listed in Table I. Each of these values represents an average of at least 3 or 4 experiments, in which the concentration of the investigated olefin was varied. In all cases, with the exception of the 2-butenes and the di-*t*-butylethylenes, no significant trend in k_2/k_1 was observed as the concentration of the olefin was varied by a factor of about 4. The trends observed in the case of the 2-butenes and *cis*-di-*t*-butylethylene were ascribed to the abstraction of a hydrogen atom from the olefinic compound by a methyl radical. Consequently, the respective values of k_2/k_1 for these compounds were obtained by the method of extrapolation to zero concentration,[9] illustrated in the case of *cis*-di-*t*-butylethylene by Fig. 1.

Table I

Compound	k_2/k_1 at 54.1°	64.9°	74.8°	85.2°
Solvent, isoöctane				
Butene-2-*cis*[a]	4.2	3.4	....	3.1
Butene-2-*trans*[a]	8.3	6.9	....	6.2
Di-*t*-butylethylene-*cis*[a]		1.9		
Di-*t*-butylethylene-*trans*	....	~0.4	....	....
Stilbene-*cis*	26.3	29.0	17.5	22
Stilbene-*trans*	123	104.5	102.5	85
Diethyl maleate	405	333	266	228
Diethyl fumarate	2655	1998	1453	1092
Solvent, methyl ethyl ketone				
Diethyl maleate[b]	27.6	22.9	23.8	16.8
Diethyl fumarate[b]	241	205	185	149
Maleic anhydride	....	388	....	283
Chloromaleic anhydride	....	560	....	440
Dichloromaleic anhydride	....	~40	....	~20
Maleonitrile	....	175	....	159
Fumaronitrile	249	179	194	169

[a] These results were obtained by extrapolation to zero concentration. [b] These results differ slightly from the results published earlier (F. Leavitt, V. Stannett and M. Szwarc, *Chemistry and Industry*, **28**, 985 (1957). We believe that the difference in the results is due to some impurities present in the solvent. The present results were repeated and confirmed.

While most of the compounds were investigated in isoöctane solution, the low solubilities of fumaronitrile, of maleic anhydride and of its derivatives forced us to use methyl ethyl ketone as a solvent for the latter compounds. The results obtained in methyl ethyl ketone are also listed in Table I. At 65° the k_1 value for the latter solvent is approximately 10 times greater than the corresponding k_1 values for isoöctane.[10] Consequently, in order to compare the relative reactivities of compounds studied in methyl ethyl ketone with those studied in isoöctane solution, the respective k_2/k_1 values have to be multiplied by approximately a factor of 10.

Table II

Compound	$E_2 - E_1$, kcal./mole	$-\Delta E$, kcal./mole	$\Delta(\Delta H^0 f)$, kcal./mole	A_2/A_1
Butene-2-*cis*	~ −2			~0.2
Butene-2-*trans*	~ −2			~0.4
		~0	+1.2[a]	
Stilbene-*cis*	−1.0			5
Stilbene-*trans*	−2.4			3
		−1.4	+6[b]	
Diethyl maleate[c]	−4.6			0.4
Diethyl fumarate[c]	−7.1			0.04
		−2.5	+4.2[b]	

$$\Delta E = (E_2 - E_1)_{cis\text{-isomer}} - (E_2 - E_1)_{trans\text{-isomer}}$$

$$\Delta(\Delta H_f) = \Delta H_f \text{ of } cis\text{-isomer} - \Delta H_f \text{ of } trans\text{-isomer}$$

[a] E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 269 (1946). [b] R. B. Williams, This Journal, **64**, 1395 (1942). [c] The activation energies determined in methyl ethyl ketone are −3.3 and −3.5 kcal./mole for diethyl maleate and diethyl fumarate, respectively. Their significance is discussed in the later part of this paper.

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(2) We take this opportunity to express our gratitude to Dr. Newman and Dr. Puterbaugh for their help in this investigation.

(3) F. L. Howard, *et al.*, This Journal, **68**, 2121 (1946).

(4) G. F. Hennion and T. F. Banigan, Jr., *ibid.*, **68**, 1202 (1946).

(5) T. W. J. Taylor and C. E. J. Crawford, *J. Chem. Soc.*, 1130 (1934).

(6) R. P. Linstead and M. Whalley, *ibid.*, 4844 (1952).

(7) M. Levy and M. Szwarc, This Journal, **77**, 1949 (1955).

(8) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

(9) R. P. Buckley, F. Leavitt and M. Szwarc, This Journal, **78**, 5557 (1956).

(10) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

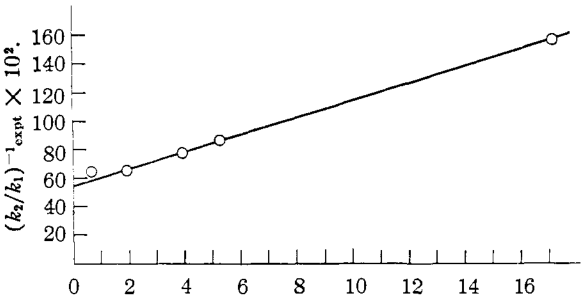

Fig. 1.—*cis*-Di-*t*-butylethylene.

The activation energies and the corresponding A_2/A_1 factors were obtained in the usual way. The Arrhenius plots are illustrated by Fig. 2 and the results are summarized in Table II. The latter table also includes the differences in the heats of formation of the respective pairs of isomers as well as the differences in the corresponding activation energies. As will be shown later an equality $-\Delta E = \Delta(\Delta H_f)$ is required if the reactions involving one or the other isomer would proceed through the same transition state; while the data listed in Table II show clearly that this is not the case.

Discussion

Let us consider two pairs of reversible reactions leading to the same product, namely

$$A + X \rightleftarrows Y$$

and

$$B + X \rightleftarrows Y$$

Let us denote by k_A', k_A, k_B and k_B' the respective rate constants, and by K_A and K_B the corresponding equilibrium constants. These constants are related by the equations[11]

$$K_A = k_A/k'_A$$

and

$$K_B = k_B/k'_B$$

and hence

$$(k_B/k'_B)/(k_A/k'_A) = K_e \qquad \text{(a)}$$

where K_e denotes the equilibrium constant for the reaction

$$A \rightleftarrows B$$

Accepting premises of the transition state theory, we express the various rate constants in terms of the corresponding free energies of activation. Thus

$$k_A = (kT/h)\kappa_A \exp(-\Delta F^{\ddagger}_A/RT)$$
$$k'_A = (kT/h)\kappa_A \exp(-\Delta F^{\ddagger}_A{}'/RT)$$

and so forth. Here all the symbols have the conventional meaning, κ_A and κ_B are the respective transmission coefficients which must be identical for k_A and k_A' and again identical, although not necessarily the same as the previous one, for k_B and k_B'.

Substitution of these expressions to equation (a) leads to the result

$$K_e = \exp(-\Delta F/RT) \exp\{-(\Delta F^{\ddagger}_B - \Delta F^{\ddagger}_B{}' - \Delta F^{\ddagger}_A + \Delta F^{\ddagger}_A{}')/RT\}$$

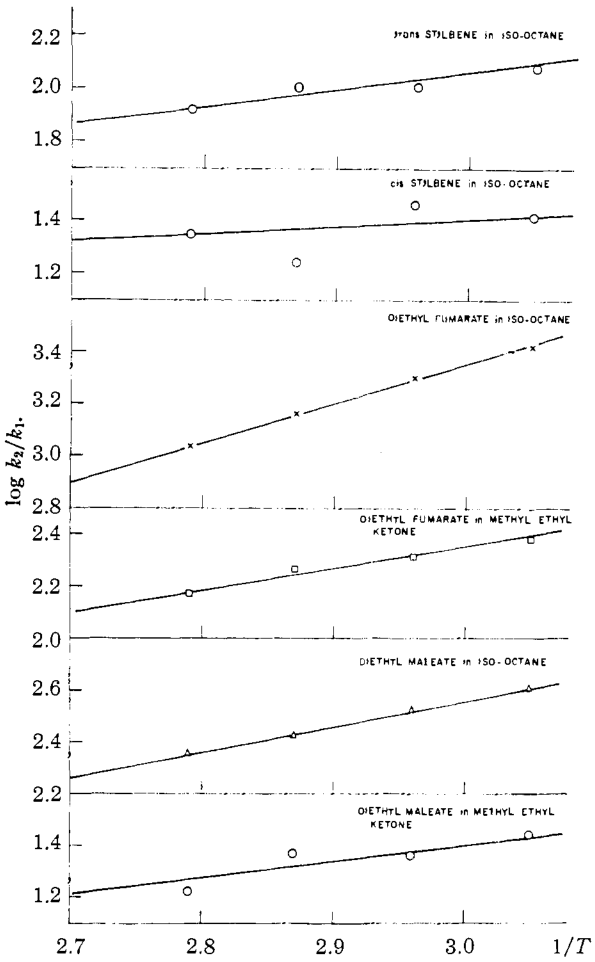

Figure 2.

If both reactions $Y \rightarrow A + X$ and $Y \rightarrow B + X$ proceed through the same transition state, then

$$\Delta F^{\ddagger}_A{}' = \Delta F^{\ddagger}_B{}'$$

and therefore

$$\Delta F = \Delta F^{\ddagger}_B - \Delta F^{\ddagger}_A$$

This means that the difference of the corresponding activation energies should be equal to the difference in the heats of formation of the respective isomers A and B, *i.e.*

$$E_B - E_A = \Delta H_F(A) - \Delta H_F(B) \qquad \text{(b)}$$

if the reactions involving the *cis* and the *trans* isomers proceed through the *same* transition state.

The experimental results obtained for the 2-butenes, for the stilbenes and for diethyl maleate and diethyl fumarate show clearly that the required relation

$$(E_2 - E_1)_{trans\ \text{isomer}} - (E_2 - E_1)_{cis\ \text{isomer}} = \Delta H_f(cis\ \text{isomer}) - \Delta H_f(trans\ \text{isomer})$$

does not hold. All the required data are given in Table II, which includes also the differences in the heats of formation of the investigated isomers calculated from their heats of hydrogenation (determined by Williams) or from their heats of combustion. It is striking that in the case of the stilbenes and of the fumarate and the maleate it is the thermodynamically *more* stable isomer which is

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[11] It is assumed that the activities are identical with the corresponding concentrations, the infinitely diluted solution being the reference state.

more reactive. Such a result is exactly contrary to the expectation based on the assumption that both reactions proceed through the same transition state. The conclusion is, therefore, obvious: the additions of a radical to *cis* and to *trans* isomer proceed through different transition complexes which appear to be rigid.

It is desirable to point out at this juncture that the determination of rate constants of the respective reactions at one temperature only does not furnish information which is sufficient for elucidation of the structure of the transition state. The ratio of the rate constants of the addition is given by the equation

$$k_{cis}/k_{trans} = (\kappa_{cis}/\kappa_{trans}) \exp -(\Delta F^{\ddagger}_{cis} - \Delta F^{\ddagger}_{trans})/RT$$

Since the ratio of the transmission coefficients $(\kappa_{cis}/\kappa_{trans})$ remains an unknown quantity the difference of $\Delta F^{\ddagger}_{cis} - \Delta F^{\ddagger}_{trans}$ cannot be evaluated by determining the ratio of k_{cis}/k_{trans} only.

All the conclusions discussed above are based on the data derived from the experiments carried out in isoöctane solution. In our discussion we assumed tentatively that the solvation effects can be neglected, and thus the reactions were treated as if they proceed in the gas phase. We believe that the solvation effects are insignificant in a hydrocarbon solvent particularly when the reacting species are non-polar molecules like the butenes and the stilbenes. However, for a reaction studied in a polar solvent like methyl ethyl ketone and involving polar species like fumarates or maleates, the solvation effects cannot be neglected. Fortunately, they affect only slightly the rate constants since any decrease in the activation energy due to the heat of solvation is to some extent compensated by the decrease in the entropy of solvation due to some freezing of motion of the surrounding solvent molecules. However, the effect of the solvation on the activation energy of the addition reaction might be quite considerable and prevent any intelligible discussion of the differences in the activation energies of isomeric compounds. For example, at 65° the ratio k_2/k_1 for diethyl maleate and diethyl fumarate are 22.9 and 176 if the reaction is carried out in methyl ethyl ketone, while the corresponding values in isoöctane are 333 and 2000, respectively. Hence, the change of solvent decreases uniformly the ratio k_2/k_1 for both isomers by approximately the same factor, namely, 11–15. On the other hand, the difference in activation energies $E_2 - E_1$ were found to be -4.6 and -7.1 kcal./mole, respectively, for the maleate and the fumarate in isoöctane, while in methyl ethyl ketone both values were determined at approximately -3 kcal./mole.

Knowing now that the additions to *cis* and to *trans* isomers proceed through different transition states, we can turn our attention to the next problem, namely, how to account for the difference in the reactivities of the *cis* and *trans* isomers. The behavior of the stilbenes seems to be most easily explicable. The models of both isomers demonstrate clearly that the *trans* isomer is approximately planar, while the planes of the phenyl groups in the *cis* isomer are nearly perpendicular to the plane of the C=C double bond. Hence, the transition state, which resembles the benzyl type radical formed from the stilbenes on addition of a methyl radical to one of the central C=C atoms, gains its resonance energy in the *trans* isomer, but considerable resonance energy is lost in the *cis* isomer.[12] This loss in the resonance energy is reflected in the lower reactivity of the *cis* isomer and manifested by the higher activation energy of the addition reaction to this isomer.

A similar situation is encountered in the case of diethyl maleate and diethyl fumarate. The models of these esters show again that in diethyl maleate the interference between the carboxylic groups prevents their coplanar configuration, while the coplanar configuration is feasible in diethyl fumarate. Again, the loss of the resonance energy causes the thermodynamically less stable maleate to be less reactive, and hence its reaction with methyl radicals requires higher activation energy (see Table II).

The effect of coplanarity on the reactivity of *cis* and *trans* isomers was discussed previously by Mayo and Lewis[13] who studied the copolymerization of *cis* and *trans* isomers with other monomers. They were first to advance the explanation outlined in the preceding paragraph and stressed that the high reactivity of maleic anhydride is due to the presence of the five-membered ring which forces this molecule into a planar configuration. We investigated, therefore, the reactivity of this compound and found it to be even more reactive than diethyl fumarate (see Table I), fully confirming Lewis and Mayo's hypothesis.[14]

If the substituting groups in an olefin are linear or spherically symmetrical, then, the concept of rotation does not apply to them. Hence, in contradistinction to the previous compounds, there is no reason to expect any difference in reactivities of such *cis* and *trans* isomers. We would expect, therefore, that *cis* and *trans* isomers containing linear or spherically symmetrical substituents should be equally reactive. This expectation is fully borne out by the studies of reactivities of maleonitrile and fumaronitrile (see Table I). It appears that for these isomers the activation energies[15] of the addition as well as the respective rate constants are approximately the same.

An attempt was made to extend our investigations to *cis*- and *trans*-dichloroethylenes. Unfortunately, some side reactions, taking place in the solution containing these compounds, prevented us from obtaining the required results.

The 2-butenes exemplify compounds in which the substituting groups, *i.e.*, methyls, are approximately spherically symmetrical. Hence, in agreement with our hypothesis the same activation energy should be required for the addition of methyl radicals to either of these isomers. This seems to be the case (see Table II), although one has to stress

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(12) Since we have shown that the transition state is rigid and no internal rotation takes place along the middle C–C bond, the configuration of the transition state should resemble somewhat that of the initial state.

(13) F. M. Lewis and F. R. Mayo, THIS JOURNAL, **70**, 1533 (1948).

(14) Lewis and Mayo based their conclusion on the ratio of relative reactivities. In view of our discussion this observation is not sufficient.

(15) These activation energies were measured in a polar solvent, *i.e.*, methyl ethyl ketone. This introduces some difficulties in interpretation, see p. 10.

that the experimental data obtained for these two compounds are not too accurate. It appears, however, that the *A* factor for the addition to *trans*-2-butene is slightly higher than that found in the addition to the *cis* isomer. The cause of this difference is obscure.

The case of di-*t*-butylethylenes is extremely interesting. However, much more work has to be done on these compounds before the final conclusions can be arrived at. The values quoted in Table I should be considered only as preliminary, given here for the sake of completeness of the survey. It is hoped that the studies of these compounds will be resumed when an additional supply of these olefins will be available.

Finally, we wish to discuss the direction of approach of a methyl radical to a C=C double bond. Although this discussion is highly speculative, nevertheless it might be of interest since it exemplifies the way of solving such a problem.

Essentially two extreme modes for the approach of a radical to a double bond should be considered. Either the radical approaches in a direction perpendicular to the nodal plane of the C=C double bond, or it approaches along the C=C axis. This kinetic representation of the problem can be translated into a static representation, namely, is the configuration of the transition state represented by a model in which the methyl radical is located above the nodal plane or along the C=C axis?

It is plausible to assume that the magnitude of the *A* factor measures the number of permissible configurations in the transition state. If the approach is sterically hindered, then the *A* factor would decrease. Our data indicate that the *A* factors for the addition to *cis*- and *trans*-stilbenes are approximately the same, the *A* factor for the addition to the *cis* isomer being even slightly higher than that for the addition to the *trans* isomer. Inspection of the models suggests strongly that the *A* factor for the addition to *cis*-stilbene should be considerably smaller than that for the addition to the *trans* isomer if the radical approaches in the direction perpendicular to the nodal plane. Hence, it appears that the preferential approach is along the C=C axis. A similar conclusion can be drawn from the consideration of the reaction involving diethyl maleate and diethyl fumarate. The models of these molecules show that the axial approach to a *planar* diethyl fumarate is considerably hindered by the O atoms, while this approach to a non-planar maleate is more accessible. On the other hand, the approach perpendicular to the nodal plane would be hindered in the non-planar maleate. The data indicate that the *A* factor for diethyl fumarate is exceedingly low, while for diethyl maleate it is considerably higher and, hence, they point out again the approach along the C=C axis as the most probable.[16]

If we accept this point of view, we are able to comprehend the blocking effects of methyl groups and chlorine atoms. These effects were discussed previously for a series of quinones.[17] They are demonstrated again in this study for the series of maleic anhydride and its chloro- and dichloro derivatives. As was pointed out in ref. 10, chlorine atoms attached to a C=C double bond activate it. However, if the double bond is fully substituted by bulky substituents then the "blocking" effect shows itself fully and such a compound is found to be very inert in the addition reaction. This pattern is reflected fully in the reactivities of the maleic anhydride and its chloro and dichloro derivatives (see Table I).

Acknowledgment.—This research was supported by a grant from the National Science Foundation.

[16] It is advisable to remind the reader that the latter data were obtained in a polar solvent, and therefore should be considered with some reservation.

[17] A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 4468 (1955).

SYRACUSE 10, N. Y., AND MILWAUKEE 12, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Some Chemical Reactions of Trifluoromethyl Hypofluorite[1]

BY ROGER S. PORTER[2] AND GEORGE H. CADY

RECEIVED MAY 4, 1957

Mercury and lithium react with trifluoromethyl hypofluorite at room temperature to give carbonyl fluoride and the fluorides of the metals. Nickel, pretreated with fluorine, is not appreciably attacked by trifluoromethyl hypofluorite below 470°. Above this temperature nickel is attacked and the reactive gas appears to be F_2 rather than CF_3OF. Trifluoromethyl hypofluorite reacts with lithium carbonate at room temperature to give carbon dioxide, oxygen and lithium fluoride. Perfluorocyclopentene (C_5F_8) adds trifluoromethyl hypofluorite across the double bond at 80° to form perfluoromethoxycyclopentane. Some physical properties of this compound have been studied. Trifluoromethyl hypofluorite and tetrafluoroethylene have been allowed to react under two sets of conditions; one produced carbon monoxide and carbon tetrafluoride, the other formed polymeric materials.

Although alcohols are fundamental to conventional organic chemistry, they have not yet been prepared in which the alkyl group is completely fluorinated. Conversely, the –OF group is stable in some highly fluorinated compounds; yet it is entirely unknown in hydrocarbon derivatives. In the fluorocarbon domain this gives –OF distinction as a functional group, and adds interest to the reactions of CF_3OF.

Experimental

Materials.—Trifluoromethyl hypofluorite was prepared by allowing carbon monoxide to react with an excess of fluorine.[3]

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[1] From the Ph.D. thesis of R. S. Porter, University of Washington, 1956. Presented at the Minneapolis Meeting of the American Chemical Society, Sept., 1955.

[2] California Research Corp., Richmond, California.

[3] K. B. Kellogg and G. R. Cady, THIS JOURNAL, **70**, 3986 (1948).