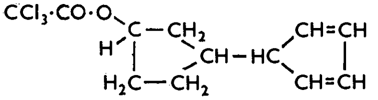
375. *Kinetics and Mechanism of the Formation of a Novel Bicyclopentyl Derivative: Rôle of Carbonium Ions in the Reaction between Cyclopentadiene and Trichloracetic Acid.*

By C. F. BLAKELY and ALBERT WASSERMANN.

A vapour-pressure technique has been developed to study the kinetics of the conversion of cyclopentadiene and trichloroacetic acid into 3-(cyclopenta-2,4-dienyl)-cyclopentyl trichloroacetate, in non-polar and polar solvents, at different temperatures, without and with oxygen, and in the presence of added substances. The observations are explained by a mechanism involving proton-transfer with formation of carbonium-ion intermediates. This accounts for the structure of the novel bicyclopentyl derivative and for the fact that it is formed only if the trichloroacetic acid concentration is high.

IN the preceding paper[1] the conversion of trichloroacetic acid and cyclopentadiene into 3-(cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate (I) is described. In this product which is formed only if the trichloroacetic acid concentration is relatively high, the two five-membered rings are united by a single carbon–carbon bond. In the Diels–Alder dimerisation of cyclopentadiene, on the other hand, which occurs either without acid[2] or at low acid concentration,[3] the two reactants are linked together by two bonds. It is the purpose of this investigation to establish the mechanism of the formation of ester (I) and to explain why the stoicheiometry depends on the acid concentration.



(I)

EXPERIMENTAL

Trichloroacetic acid in carbon tetrachloride was introduced into a round-bottomed flask, fitted with a tap and ground joint, by which it could be connected with a vacuum-line; the solvent was slowly distilled off, thereby affording the acid as a film, which was dried at ~30°/10^{-3} mm. Redistilled dry solvent and cyclopentadiene [the latter dried over Na_2SO_4—$Mg(ClO_4)_2$] were freed from air by cooling, evacuation to 10^{-3} mm., and thawing *in vacuo*, these operations being repeated four times. The acid film in the evacuated vessel was cooled and air-free solvent and cyclopentadiene were added by bulb-to-bulb distillation *in vacuo*, in such a manner that the cooled reaction vessel contained solid layers of acid and cyclopentadiene, separated by solid solvent. Taps and ground joints were coated with sugar grease.[4] The reaction vessel was attached to a mercury manometer, as shown in Fig. 1, and reaction was started by thawing and rapid mixing. The concentrations were calculated from the known weights of the components. The size and shape of the vessels was such that they could be fitted on an analytical balance. For conversion into molarites, specific gravities of appropriate solutions were measured (solutions used for these experiments were not freed from air). The temperature of the water-thermostat, into which manometer and reaction vessel were introduced, was constant within ±0·01°. The brass plate shown in Fig. 1 was fitted into the thermostat in a manner safeguarding its vertical position and permitting shaking, so that equilibrium between liquid and gas phase was established. Readings of illuminated mercury levels were made through a glass window of the thermostat with the help of a lens fitted with cross-wires. The mercury was frequently tapped to prevent sticking. The reproducibility of readings was ±0·1 mm. The sugar grease was protected from water by coating of the outside of taps and ground joints with Vaseline.

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[1] Blakely, Gillespie, Roubinek, Wassermann, and White, preceding paper.
[2] Kauffmann and Wassermann, *J.*, 1939, 870.
[3] Wassermann, *J.*, 1942, 618; Rubin, Steiner, and Wassermann, *J.*, 1949, 3046.
[4] Meloche and Frederick, *J. Amer. Chem. Soc.*, 1932, **54**, 3264.

If P_0, P_t, and P_∞ are the vapour pressures of the reaction mixture, at zero time, time t, and at the end of the reaction, then x, the concentration of cyclopentadiene consumed at time t, is given by

$$x = b[(P_0 - P_t)/(P_0 - P_\infty)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where b is the initial concentration of cyclopentadiene. In most runs P_0 was determined by back-extrapolation of P_t to zero time, the time interval between thawing of the reaction mixture and zero time being measured with cyclopentadiene solution free from acid. When the acid concentration and the temperature were not too high, then P_0 could be directly observed and agreed with $P_0' - \Delta P$, where P_0' is the vapour pressure of an acid-free cyclopentadiene solution of the appropriate concentration and ΔP is the experimentally determined difference between the vapour pressure of the solvent and that of the trichloroacetic acid solution. If the rate of reaction was sufficiently high, then P_∞ was taken to be the steady-state vapour pressure at the end of reaction. In most experiments, however, the approach to the steady state was so slow that P_∞ was calculated from the vapour pressure of trichloroacetic acid solutions containing the product of the reaction. It was established that the partial vapour pressure of cyclopentadiene is a linear function of its concentration. The validity of expression (1) was confirmed, furthermore, by calculating x from the results of colorimetric measurements.[5] The results of experiments carried out by the two techniques agreed to within ±2%. In experiments with molecular oxygen the reaction mixture was prepared *in vacuo*, as described. Vessel (1) (Fig. 1) containing the frozen components was connected with them anometer, tap (a) being closed. Tap (b) was opened, and the manometer was evacuated and filled with oxygen from a reservoir. Tap (b) was closed, (a) was opened, and, after equilibration with the thawed solution, the oxygen concentration in solution could be calculated from manometer readings, temperature, and the dimension of the apparatus. In these experiments x was calculated from the results of colorimetric measurements.[5]

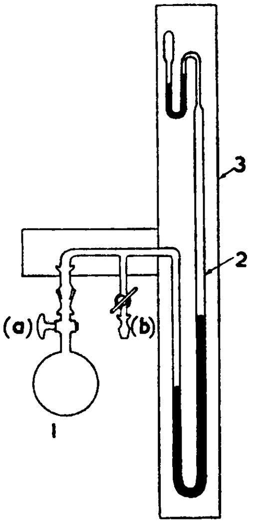

FIG. 1. *Apparatus*: (1) *Reaction vessel; capacity about* 100 *ml., containing* 20—40 *ml. of solution.* (2) *Mercury manometer.* (3) *Polished brass plate on which manometer was fixed*; *two* 80 cm. *scales* (*not shown*), *divided in* 0·1 *cm., were etched on the plate, at positions adjoining the two manometer arms. Tap* (a) *remained closed, while the manometer was evacuated through* (b). *At this stage the reaction mixture in vessel* (1) *was still frozen. After tap* (b) *had been closed and tap* (a) *opened, the whole apparatus was immersed in the thermostat* (*see text*).

RESULTS

In each solvent and at each temperature, preliminary experiments, such as those described before,[1] were carried out to establish that, under the specified concentration conditions, 3-(cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate (I) rather than *endo*-dicyclopentadiene is the main product. The rate of formation of ester (I) is given by:

$$dx_4dt = k(a - x/2)^2(b - x)$$

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[5] Wassermann, *J.*, 1936, 1033.

which on integration gives:

$$k = \frac{1}{t}\left(\frac{9{\cdot}21}{(b-2a)^2}\right)\log_{10}\left\{\left(\frac{1-x/2a}{1-x/b}\right) - \frac{2}{a(b-2a)}\left[\frac{x/2a}{(1-x/2a)}\right]\right\} \quad . \quad . \quad (2)$$

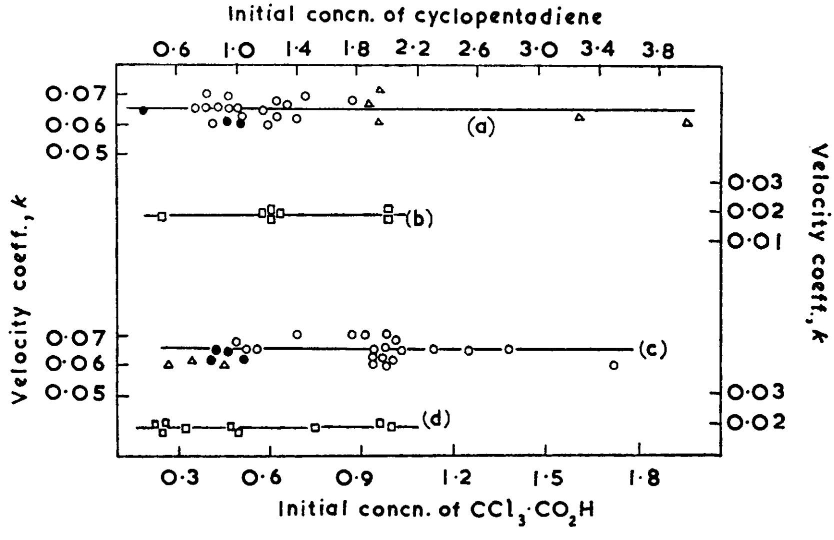
where a and b are the initial concentrations of acid and cyclopentadiene. In most runs the k values increased or decreased with increasing conversion, which is due to the influence of a

TABLE 1. *Rate of reaction between cyclopentadiene and trichloroacetic acid.*

Results of typical experiments. Solvent C_6H_6, 20·0° in (A) and (B); solvent CCl_4, 25·1° in (C). Initial concn. (mole/l.) of cyclopentadiene: 0·717 (A); 0·955 (B); 0·984 (C). Initial concn. (mole/l.) of $CCl_3{\cdot}CO_2H$: 0·988 (A); 0·354 (B); 0·978 (C). % Conversion: 13·6—98·5 (A); 4·3—31·3 (B); 3·8—65·9 (C). Extrapolated and mean k values (l.^{2} mole^{-2} min.$^{-1}$): 0·066 (A); 0·062 (B); 0·020 (C). t (time), X, and k are given in min., mole l.$^{-1}$, and l.^{2} mole^{-2} min.$^{-1}$, respectively.

A			B			C		
t	*X*	*k*	*t*	*X*	*k*	*t*	*X*	*k*
2	0·0909	0·073	6	0·0409	0·062	2	0·0376	0·021
3	0·143	0·082	9	0·0595	0·062	5	0·0888	0·021
4	0·182	0·083	17	0·0966	0·058	6	0·109	0·022
5	0·210	0·083	21	0·115	0·059	8	0·120	0·018
6	0·266	0·093	33	0·141	0·049	10	0·161	0·020
7	0·287	0·089	57	0·208	0·049	12	0·181	0·020
10	0·367	0·093	102	0·282	0·047	14	0·198	0·019
14	0·437	0·092	118	0·301	0·046	17	0·243	0·020
18	0·493	0·093				20	0·273	0·020
21	0·511	0·087				25	0·311	0·019
24	0·542	0·093				30	0·359	0·020
						41	0·454	0·021
						57	0·557	0·022
						76	0·649	0·024

FIG. 2. *Rate of reaction between cyclopentadiene and trichloroacetic acid in benzene and carbon tetrachloride. Influence of initial concentration.*



Ordinates: velocity coefficient, k (in l.^{2} mole^{-2} min.$^{-1}$). Upper abscissa: initial concn. (mole l.$^{-1}$) of cyclopentadiene. Lower abscissa: initial concn. of trichloroacetic acid.

Graphs (a) *and* (b) *relate to upper abscissa; graphs* (c) *and* (d) *relate to lower abscissa.*

Symbols △, ●, ○ relate to left ordinate; benzene solution, 20·0°.
Symbol □ relates to right ordinate; carbon tetrachloride, 25·1°.

In the experiments designated by ● and □, k did not significantly vary in each run; in the experiments designed by △ and ○, k decreased or increased with time, the value in the Figure being obtained by back-extrapolation to zero conversion.

For % conversion, and trend of k values, in each run, see Tables 12, 13, *and* 15 *of Blakeley's Ph.D. Thesis* (*London,* 1957).

consecutive reaction,[6] or of the product which acts as retarder (see Table 3). When there was a trend of the velocity coefficients, back-extrapolation to zero conversion was carried out. For carbon tetrachloride solutions below 35°, the k values showed no significant trend. There was no indication that under the conditions of these experiments decomposition of ester (I) into trichloroacetic acid and cyclopentadiene is significant. The accuracy of the velocity coefficients in the following Tables and Figures is $\pm 5\%$ if there was no trend, $\pm 10\%$ if a back-extrapolation had to be carried out, and about $\pm 15\%$ in a few runs at relatively high temperatures or concentrations where the initial vapour pressures of the solution could not be directly determined but had to be estimated by extrapolation or interpolation. The results of three typical experiments are in Table 1 and the dependence of the extrapolated or mean velocity coefficients on the initial concentrations (test of rate equation 2) is shown in Fig. 2. The influence of temperature was established by experiments at four temperatures between 20° and 45°, the Arrhenius rate equation, $k = A \exp(-E/\boldsymbol{R}T)$, being obeyed. The numerical value of the two parameters (A, in $\text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}$, and E in cals. mole^{-1}) are as follows:

$$\left.\begin{array}{ll} C_6H_6: & \log_{10} A = 4{\cdot}3 \pm 0{\cdot}4;\ E = 9900 \pm 500 \\ CCl_4: & \log_{10} A = 4{\cdot}4 \pm 0{\cdot}4;\ E = 9700 \pm 500 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

Sixteen experiments were carried out, which showed that molecular oxygen does not influence the rate of formation of ester (I), the ratio moles of cyclopentadiene/moles of oxygen in the reaction mixture, at zero time, being varied from 68 to $>10^5$. Table 2 shows that the polar

TABLE 2. *Rate of reaction between cyclopentadiene and trichloroacetic acid in benzene–nitrobenzene and nitromethane.* Initial concns. (mole l.^{-1}) of cyclopentadiene and trichloroacetic acid between 0·849 and 1·126; 20·0°.

Solvent	C_6H_6–$PhNO_2$					$MeNO_2$
Concn. of $PhNO_2$	0·00	0·805	1·292	2·295	3·650	—
k ($\text{l.}^2\ \text{mole}^{-2}\ \text{min.}^{-1}$)	0·07	0·1	0·2	0·3	0·6	0·3

TABLE 3. *Rate of reaction between cyclopentadiene and trichloroacetic acid in the presence of added substances.*

	Initial concn. (mole l.^{-1})				
Addendum	C_5H_6	$CCl_3{\cdot}CO_2H$	Addendum	k ($\text{l.}^2\ \text{mole}^{-2}\ \text{min.}^{-1}$)	Retardation (%)
		At 20° *in* C_6H_6.			
H_2O	0·880	0·941	2·74[a]		90
,, ...	1·03	0·971	0·973		90
,, ...	0·933	1·00	0·623		70
,, ...	0·975	0·971	0·282		30
MeOH	0·949	0·954	0·877		90
,, ...	0·885	0·980	0·541		70
,, ...	0·926	0·963	0·398		60
,, ...	0·825	0·964	0·130		20
Dioxan	0·945	0·964	0·995		90
,, ...	0·905	0·953	0·398		90
$COMe_2$	0·912	0·982	0·904		90
,, ...	0·963	0·962	0·421		60
$CHCl_3$	0·907	0·998	0·934	0·09[b]	—
Bz_2O_2	0·991	0·917	0·249		30
Cyclopentadiene polymer[c]...	0·950	0·999	0·006	0·08	—
8 g. glass powder[d]	1·10	0·980	—	0·09	—
Glass tubes[e]	0·852	0·993	—	0·08	
		At 25° *in* CCl_4.			
Ester (I)	1·31	0·506	0·845		75

[a] This molarity is computed on the assumption that all the added water is dissolved; in fact, only partial dissolution occurred. [b] In an experiment in chloroform solution at 20° (initial concn. of cyclopentadiene and trichloroacetic acid, respectively, 0·924 and 0·976 mole l.^{-1}), k was 0·03 $\text{l.}^2\ \text{mole}^{-2}\ \text{min.}^{-1}$. [c] Prepared by stannic chloride-catalysis in chloroform solution; average molecular weight 5×10^4. [d] Total volume of reaction mixture 11·0 c.c. [e] The length and diameter of the tubes were adjusted in such a way that the surface–volume ratio was twice as great as in the tests without added glass.

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[6] Murphy, Roubinek, and Wassermann, *J.*, 1931, 1964.

aprotic solvents nitrobenzene and nitromethane increase the rate of reaction. The influence of other added substances is shown in Table **3**: water, various " basic " solvents, benzoyl peroxide, or the product of the reaction act as retarders, while addition of glass or of a cyclopentadiene polymer made by stannic chloride-catalysis had no significant influence. The percentage retardation in Table 3 was calculated from $100(k - k_r)/k$ where k and k_r are velocity coefficients without and with retarders. For the present purpose both velocity coefficients were calculated from eqn. (2), k_r being the mean of the observed values relating to 20% and 40% conversion.

It could be suggested that the primary product of the reaction between cyclopentadiene and trichloroacetic acid is dicyclopentadiene which is converted into ester (I) in a consecutive reaction if the acid concentration is sufficiently high. This possibility is ruled out by unpublished experiments, which show that the reaction between dicyclopentadiene and trichloroacetic acid produces, not ester (I), but the trichloroacetic acid ester of *exo*-dihydrohydroxydicyclopentadiene, the ratio of the rate of formation of ester (I) and of this ester being about 10^4. The dicyclopentadiene alcohol is known from previous work; [7] it is different from the alcohol obtained from our ester and described in the preceding paper.[1]

DISCUSSION

Stoicheiometry and Mechanism.—The observed rate equations of the trichloroacetic acid-catalysed dimerisation of cyclopentadiene [3] and of the formation of ester (I) are

$$\mathrm{d[Dimer]}/\mathrm{d}t = k_d[C_5H_6][CCl_3{\cdot}CO_2H] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathrm{d[Ester\ (I)]}/\mathrm{d}t = k[C_5H_6][CCl_3{\cdot}CO_2H]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If experiments in carbon tetrachloride at 25° are carried out with 0·0050M- and 1·0M-trichloroacetic acid it follows from the specified numerical values of k_d and k that the ratios $\mathrm{d[Dimer]}/\mathrm{d}t/\mathrm{d[Ester\ (I)]}/\mathrm{d}t = k_d/k[CCl_3{\cdot}CO_2H]$ are respectively $4{\cdot}4 \pm 0{\cdot}8$ and $0{\cdot}022 \pm 0{\cdot}004$. It is understandable, therefore, why the preparative isolation of ester (I) is only possible if the trichloroacetic acid concentration is sufficiently high.[1]

Rate equations (4) and (5) are consistent with the following reactions:

$$M + HB \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

$$i + M \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} i' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

$$i' \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \textit{endo}\text{-dicyclopentadiene (dimer)} + HB \quad . \quad (III)$$

$$i' + HB \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} i'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

$$i'' \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} \text{Ester (I)} + HB \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

where M is cyclopentadiene, HB is trichloroacetic acid (the base B being the trichloroacetate ion), i and i′ are singly charged ion pairs, $C_5H_7^{+}\cdots B^{-}$ and $C_{10}H_{13}^{+}\cdots B^{-}$, and i″ is a doubly charged ion pair $C_{10}H_{14}^{2+}\cdots 2B^{-}$. The structure $C_{10}H_{13}^{+}\cdots\overset{\frown}{\overset{-}{B}\,HB}$, rather than $C_{10}H_{14}^{2+}\cdots 2B^{-}$, could perhaps be suggested for i″; the doubly charged ion pair formula is however preferred, because it fulfils the structural requirements to be discussed below, but the kinetic feature of this reaction can be accounted for by both types of intermediate. The cations and anions of these ion pairs must be held firmly together, if the dielectric constant of the solvent is low. Application of the stationary-state approximation leads, as in similar problems, to a complicated rate equation, which can be reconciled with the

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[7] Bruson and Riener, *J. Amer. Chem. Soc.*, 1945, **67**, 725; Bartlett and Schneider, *ibid.*, 1946, **68**, 6.

experimental expressions, if arbitrary assumptions are made. These are in the present case * as follows

$$\left.\begin{aligned} k_1[\mathrm{M}][\mathrm{HB}] &\gg k_2'[i'] \\ k_2[\mathrm{i}][\mathrm{M}] &\gg \{k_4'[i''] + k_3'[\mathrm{Dimer}]\} \\ k_3 &\gg k_2' \text{ or } k_4[\mathrm{HB}] \\ k_4[\mathrm{i}'] &\gg k_5'[\text{Ester (I)}] \\ k_2[\mathrm{M}] &\gg k_1' \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

Assumptions (6) are justified because they lead to the experimental rate equations (4) and (5) with $k_d = k_1$ and

$$k = k_1k_4k_5/(k_4' + k_5)k_3 \quad \ldots\ldots\ldots \quad (7)$$

Furthermore, k, according to eqn. (7), is compatible with the observed A factors and the influence of solvent polarity, as shown below.

Kinetic A Factors.—If each velocity coefficient of eqn. (7) is expressed by the appropriate product of non-exponential and exponential factors, the over-all A values (3 above) are given by $A_1A_4A_5/(A'_4 + A_5)A_3$, where A_1 and A_4 relate to the bimolecular formation of the ion pairs in eqn. (I) and (IV), while A_3, A_5, and A'_4 relate to (III), (V), and the reverse reaction (IV). If these were " normal " unimolecular processes, A_3, A'_4, and A_5 should be about 10^{13} sec.$^{-1}$, whence it follows from (3) that $A_1 \times A_4 \approx 10^{17}$ l.^{2} mole^{-2} sec.$^{-2}$. A_1 is about 10^{-1} l. mole^{-1} sec.$^{-1}$ (see ref. 3), so that $A_4 \approx 10^{18}$ l. mole^{-1} sec.$^{-1}$, which is much too large, for the following reason: (IV) involves a charge separation, and therefore an increased solvation of the transition state, which is assumed to be similar to i$''$; this, in turn, should give rise to a negative entropy of activation and to a non-exponential A factor smaller than 10^{11} l. mole^{-1} sec.$^{-1}$. It is concluded that $A_5 \gg A'_4$ and $A_3 \gg 10^{13}$, so that $A_4 \ll 10^{18}$. The first inequality can be related to desolvation of the transition state in (V), owing to the collapse of the ion pair, it being assumed as before that transition and final states are similar. The " release " of solvent molecules will increase the entropy of activation and thus A_5 will be relatively large. The second inequality cannot be explained by solvation effects, but is explained by a low configurational entropy of the transition state in (III), which may over-compensate an opposing influence of " desolvation." If the transition state in (III) is similar to *endo*-dicyclopentadiene, a low configurational entropy is to be expected, because the intermediate i$'$, the structure of which will be discussed below, cannot be so " stiff " as dicyclopentadiene, in which a number of low vibrational modes are prevented by the two bonds which unite the five-membered rings.

Influence of Polarity of Solvent.—According to Bruson *et al.*,[7] the over-all activation energy, E, of the formation of ester (I) is given by $E = (E_2 + E_4 + E_5) - [(E_4' \text{ or } E_5) + E_3]$, where the subscripts have the same significance as above. E_1 and E_4 relate to eqn. (I) and (IV), in which a charge separation occurs, while E_3, E_4', and E_5 are the activation energies of (III), of the reverse reaction (IV) and of (V), in which either electrically neutral species are formed from the ion pairs i$'$ and i$''$ or a doubly charged ion pair is transformed into a singly charged ion. Reactions (I) and (IV) should be facilitated if the solvent is made more polar, while in the other reactions the situation is reversed. If we assume that in all cases the transition and the final state are similar, it can be expected that E_2 and E_4 will decrease with increasing polarity of the solvent, while the trend of E_3, E_4', and E_5 will be in the opposite direction. The influence of the activation energy is probably more important than opposing effects, owing to the entropy of activation, and it would follow, therefore, that an increase in the polarity of the solvent should increase k_1 and k_4 and decrease k_3, k_4', and k_5. The figures in Table 3 show that the over-all rate constant, k, increases with increasing polarity of the solvent. This is consistent with

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* A search for a set of assumptions different from (6) was not successful.

the suggested mechanism if the trend of $k_1k_4/(k_4' + k_5)k_3$ rather than that of k_5 is decisive.

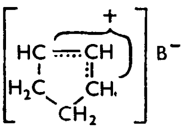
Retarders.—Added proton acceptors should compete with cyclopentadiene in reaction (I) for the proton derived from the acid, and retardation of the over-all reaction should result. The figures in Table 3 show that a number of basic solvents and ester (I), the product of the reaction, act as retarders. Rate equations for the formation of ester (I) or dicyclopentadiene, in the presence of retarders have been developed, but kinetic tests have not been carried out.

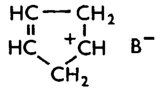
Proton Transfer to endo-*Dicyclopentadiene.*—It has been shown that the interaction of *endo*-dicyclopentadiene and trichloroacetic acid leads predominantly to trichloroacetate (Y) of *exo*-dihydrohydroxydicyclopentadiene, rather than to ester (I). Thus the velocity coefficient k_6 of the reaction:

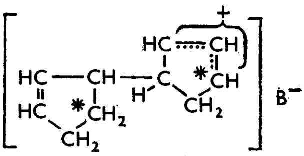
$$\textit{endo}\text{-Dicyclopentadiene} + CCl_3{\cdot}CO_2H \xrightarrow{k_6} \text{ester (Y)} \qquad . \quad . \quad (VI)$$

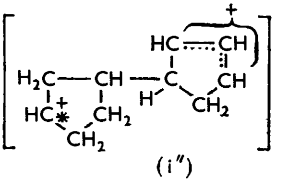
is probably large compared with k_3'. Addition of trichloroacetic acid to *endo*-dicyclopentadiene must lead to the intermediate i′ of reaction (III), according to the principle of microscopic reversibility: this, however, is without kinetic consequence because of the competitive reaction (VI), which occurs probably through an ion pair $C_{10}H_{13}^+ \cdots B^-$ of a structure different from that of intermediate i′.

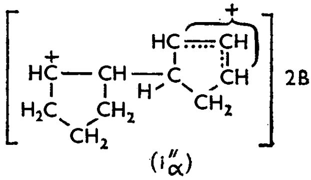
Structural Considerations.—Addition of a proton to cyclopentadiene leads to two ion pairs $C_5H_7^+ \cdots B^-$, designated by i and i_α. It is assumed that i is preferentially formed, owing to resonance stabilisation. In reaction (II), i combines with cyclopentadiene, thereby forming the species $C_{10}H_{13}^+ \cdots B^-$, which can exist in the form of three structural isomers, one of which is i′. This is the only one which can be converted into *endo*-dicyclopentadiene by formation of a bond between the carbons marked by asterisks and removal of acid, without other rearrangements. The same ion pair, i′, is assumed to participate in reaction (IV), in which the doubly charged ion pair $C_{10}H_{14}^{2+} \cdots 2B^-$ is formed. Five structural isomers of this are possible, but only in two of them, i″ and i''_α, is there resonance-stabilisation of the kind occurring in i′, and for this reason the formation of isomers other than i″ and i''_α is not taken into account here. An inspection of models of i″ and i''_α shows that in the former intermediate the maximum distance between the two positively charged carbon atoms is larger; it is assumed, therefore, that i″ is more stable and is preferentially formed. This species can be simply converted into the observed product of the reaction, 3-(cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate, by removal of one acid molecule, HB, and by combination of the remaining trichloroacetate counter-ion, B^-, with the carbon atom indicated by an asterisk. A similar reaction would convert the isomeric intermediate, i''_α, into the ester of 2-(cyclopenta-2,4-dienyl)cyclopentanol,


(i)


(i_α)


(i′)


(i″)


(i''_α)

which is not formed under the specified conditions.[1] Thus the suggested mechanism accounts, not only for the formula [1] of the product, but also for the predominant formation of one of the possible structural isomers of the new bicyclopentyl derivatives.

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