

N-Benzyl-*N*-methylchloramine (IIC) was prepared by the method of Coleman.¹⁶ The product was a pale yellow oil which had an n.m.r. spectrum consistent with the pure chloramine.

(16) G. H. Coleman, *J. Am. Chem. Soc.*, **55**, 3001 (1933).

N-Benzyl-*N*-methylhydroxylamine (IIB) was obtained as colorless crystals, m.p. 39.5–40.5° (lit.¹⁷ m.p. 41–42°), by alkylation of *N*-methylhydroxylamine (Aldrich Chemical Co.) with benzyl chloride.

(17) J. Meisenheimer and H. Denner, *Ber.*, **65**, 1799 (1932).

Spin-Echo Nuclear Magnetic Resonance Studies of Chemical Exchange. VI. Rearrangement of Bullvalene and of Its Silver Nitrate Complex¹

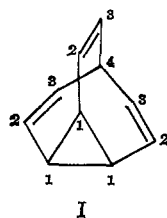
Adam Allerhand and H. S. Gutowsky²

Contribution from Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. Received May 17, 1965

The degenerate Cope rearrangement of bullvalene has been studied from 25 to 123°, in a tetrachloroethylene solution, by means of a spin-echo n.m.r. method, at 26.85 Mc./sec. In effect, the inhomogeneity broadening of the n.m.r. absorption is avoided in the spin-echo experiments so that exchange rates could be measured which were faster by a tenfold factor than the upper limit in previous high-resolution work. More precise values were obtained for the frequency factor, 0.8×10^{13} sec.⁻¹, and for the activation energy, 12.8 ± 0.1 kcal./mole. Bullvalene was found to form several complexes with AgNO₃ in D₂O and in CH₃CN solution and with AgBF₄ in CH₂ClCH₂Cl. The rearrangement rates were reduced in these solutions. A 3:1 Ag⁺ to bullvalene system, 0.32 g. in 7.15 M AgNO₃ in D₂O, was studied in some detail. For it, the apparent activation energy for the rearrangement is 15.1 ± 0.8 kcal./mole.

I. Introduction

Since the discovery by Doering and Roth³ of a rapid degenerate Cope rearrangement in bicyclo[5.1.0]octa-2,5-diene, by means of n.m.r. spectroscopy, the generality of the phenomenon has been confirmed.^{4,5} The case of bullvalene (I) is particularly interesting, since all of the four types of protons eventually par-



ticipate in the exchange, so that at elevated temperatures the compound should show a single proton n.m.r. line, as was predicted by Doering and Roth.³ This

(1) This research was supported in part by the U. S. Office of Naval Research, by the National Science Foundation, and by the National Institutes of Health.

(2) Author to whom inquiries should be addressed.

(3) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(4) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(5) J. B. Lambert, *ibid.*, 1901 (1963).

has been confirmed by Saunders, who investigated the rate of rearrangement as a function of temperature.⁴

Our interest in this compound is twofold. It affords a means of extending the spin-echo methods for n.m.r. rate determinations⁶⁻⁹ to chemical exchange which is more complex than in the two-site systems studied previously. In addition, the preparation and n.m.r. study of transition metal complexes of bullvalene could throw light on the nature of such olefinic complexes in general.¹⁰ The transition metal-olefin bond can be studied indirectly through its effect on the rate of the degenerate Cope rearrangement in bullvalene and perhaps something can be learned about the nature of the rearrangement as well. Indeed, we have found that bullvalene readily forms complexes with silver nitrate and silver fluoroborate,¹¹ and that the rate of the degenerate Cope rearrangement is slowed down considerably (in solution) by the presence of the silver cation. The data available at present are insufficient to characterize both the mechanism for the "slowdown" and the equilibrium constant for the complex formation. However, the results obtained thus far and the prospects are sufficiently promising to report at this time.

II. Chemistry of Bullvalene. Silver Cation Complex Formation

When a solution of bullvalene in CH₂ClCH₂Cl was added to a solution of anhydrous AgBF₄ in the same solvent, a white precipitate formed immediately and was collected by filtration. However, upon recrystallization of this precipitate, two different bullvalene complexes were isolated, depending on the solvent and method of recrystallization (see Section IV). One of these was 2C₁₀H₁₀·AgBF₄. Silver fluoroborate complexes of simple olefins with this 2:1 stoichiometric ratio have been reported recently.¹² Our 2:1 com-

(6) Part I: A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964), and prior work cited therein.

(7) Part II: A. Allerhand and H. S. Gutowsky, *ibid.*, **42**, 1587 (1965).

(8) Part III: A. Allerhand, Fu-ming Chen, and H. S. Gutowsky, *ibid.*, **42**, 3040 (1965).

(9) Part IV: A. Allerhand and H. S. Gutowsky, *ibid.*, **43**, 4203 (1965).

(10) For a review of olefin-transition metal complexes see M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(11) We wish to thank Professor J. C. Martin for suggesting the preparation and n.m.r. study of bullvalene-AgBF₄ complexes.

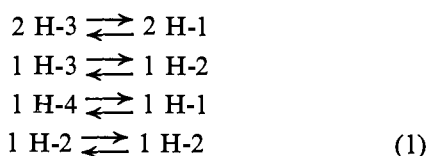
plex was found to be quite stable, and it did not become dark on standing. A complex of *approximate* composition $C_{10}H_{10} \cdot AgBF_4$ also was isolated; it was obtained in a well crystallized form, but microanalyses indicated it was not a simple, pure complex. Moreover, the material became dark upon standing. A similar problem was encountered in the isolation of silver nitrate complexes with high silver content (see section IV). These solids also became dark grey on standing, even when moderately well protected from light, and they were affected by moisture as well.

One of the problems encountered in our n.m.r. studies of these complexes is their scant solubility in most common solvents. Our first successful attempt in this direction was the preparation of a bullvalene solution in aqueous (D_2O) silver nitrate. Bullvalene is of course insoluble in water, but it dissolved readily when the solid compound was added to 7.15 *M* $AgNO_3$ in D_2O . The solubility was about 0.32 g. of bullvalene in 1 ml. of solvent at room temperature, which corresponds to a ratio of just under three Ag^+ for each hydrocarbon molecule. This somewhat viscous solution was quite stable for several weeks in a sealed, degassed glass tube, but then most of the dissolved material crystallized as a complex, which implies that the original solution was supersaturated. All of our n.m.r. experiments in a D_2O medium were carried out on the supersaturated solution.

Subsequent attempts to prepare similar solutions required heating of the mixture to dissolve the bullvalene, and crystallization of the complex occurred readily on cooling, leaving a saturated solution which was too dilute for n.m.r. Thus, D_2O does not appear to be a good medium for systematic n.m.r. studies of bullvalene complexes of this type. In the latter phase of our work thus far, it was found that complexes of bullvalene with $AgBF_4$ and $AgNO_3$ are readily soluble in acetonitrile. Silver nitrate itself is very soluble in acetonitrile¹³ and the ratio of bullvalene to $AgNO_3$ can be varied widely in it. We have carried out one preliminary n.m.r. rate study in this solvent as described in the next section. Part of the bullvalene spectrum is obscured by the intense solvent absorption, but this could be avoided by using the deuterated material, CD_3CN .

III. N.m.r. Rate Determinations in Bullvalene and Its Silver Complexes

High-Resolution Results. The rate of the degenerate Cope rearrangement in bullvalene has been determined by Saunders⁴ in the temperature range 10–83° from the high-resolution line shapes. There are three possible 1,5-hexadiene systems in I in which the rearrangement can take place.⁸ During each rearrangement, the following interchanges occur among the four types of protons. The last of these equations means



(12) J. S. McIntyre and H. W. Quinn, *Can. J. Chem.*, to be published. We wish to thank them for making their results available to us prior to publication.

(13) W. F. Linke, "Solubilities of Inorganic and Metal-Organic Compounds," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p. 120.

that two of the H-2 hydrogens go to equivalent sites but interchange relative positions in the molecule. The two kinds of olefinic hydrogen H-2 and H-3 have chemical shifts^{4,14} close to τ 4.4, and the two kinds of aliphatic hydrogen H-1 and H-4 close to 7.8.

Two simplifying assumptions were made in the previous analysis.⁴ One is that the small chemical shifts between H-2 and H-3 and between H-1 and H-4 are negligible; this is reasonable because of the large chemical shift (τ 3.4) between the olefinic and aliphatic protons. The other is that the effects of the H–H couplings can be neglected if the exchange rate in sec^{-1} is much larger than the coupling constants in c.p.s., which has theoretical and also experimental support.⁹ With these assumptions, the steady-state line shape can be calculated readily for any value of the rate of molecular rearrangement k . The matrix notation of Sack¹⁵ is entirely equivalent to the system of linear equations resulting from the steady-state solutions of the Bloch equations modified to include exchange effects^{16,17} for this case (a system of four equations if written in complex form) except that the Sack matrix notation omits T_2^0 , the natural "line-width parameter in the absence of exchange."^{4,15} Both solutions assume that negligible saturation is produced by the radiofrequency field.

Although most of our rate determinations were by means of spin-echo methods, a few high-resolution observations were made with samples at 33°, using a proton resonance frequency of 60 Mc./sec. Exchange rates were obtained by visual comparison of the observed spectra with theoretical spectra calculated from the line-shape equations⁴ with the use of a simple Fortran program for an IBM 7094 computer.¹⁸ For more extensive studies, a computer fit of the observed spectra could be made, as described previously.¹⁹ The high-resolution measurements were carried out on three systems: (A) 0.195 g. of bullvalene dissolved in 1 ml. of tetrachloroethylene, (B) 0.20 g. of bullvalene in 1 ml. of 5.4 *M* $AgNO_3$ in CH_3CN , and (C) 0.32 g. of bullvalene in 1 ml. of 7.15 *M* $AgNO_3$ in D_2O , which is the supersaturated solution described in Sections II and IV.

The effect of the different environments on the bullvalene spectrum is shown clearly in Figure 1. The highest rate of Cope rearrangement occurs in the absence of Ag^+ ions. It should be noted at this point that rates for uncomplexed bullvalene in acetone- d_6 were essentially identical with those in tetrachloroethylene (see below) and that our rates for bullvalene are practically identical with those reported previously,⁴ where the solvent used was not indicated. The presence of $AgNO_3$ reduces the exchange rate by as much as a factor of 10. The rates for the silver complex are somewhat different in CH_3CN and D_2O solutions. If the degenerate Cope rearrangement does not occur or if it is slowed down considerably in the silver complex with respect to free bullvalene, then it is possible that

(14) G. Schroder, *Angew. Chem. Intern. Ed. Engl.*, 2, 481 (1963), reported values of τ 4.3 and 7.9, respectively.

(15) R. A. Sack, *Mol. Phys.*, 1, 163 (1958).

(16) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, 88, 1070 (1952).

(17) H. M. McConnell, *J. Chem. Phys.*, 28, 430 (1958).

(18) We wish to thank the Department of Computer Science for their services in processing our calculations.

(19) J. Jonáš, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.* 42, 3396 (1965).

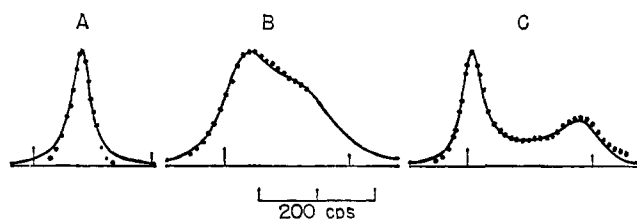


Figure 1. Proton spectra of bullvalene (I) and of its silver nitrate complex, at 33° and 60 Mc/sec. The points represent the observed, high-resolution spectra and the solid lines, the calculated. The vertical lines give the chemical shifts of olefinic (left) and aliphatic protons (right) in the absence of exchange. The systems are: (A) 0.195 g. of I in 1 ml. of $\text{CCl}_2=\text{CCl}_2$; (B) 0.2 g. of I in 1 ml. of 5.4 M AgNO_3 in CH_3CN ; and (C) 0.32 g. of I in 1 ml. of 7.15 M AgNO_3 in D_2O . In (B), part of the spectrum was obscured by solvent absorption. The exchange rates obtained for the three cases are $k = 6200, 1800, \text{ and } 700 \text{ sec.}^{-1}$, respectively.

the different exchange rates in systems B and C may reflect differences in the ratio of free bullvalene to the complex. This could arise from greater complexing ability of CH_3CN than D_2O toward AgNO_3 , and also from the smaller total AgNO_3 and bullvalene concentrations in system B. Concentration dependence studies, with CD_3CN as solvent, should shed some light on this point.

The high-field part of the spectrum in Figure 1 (C) was very sensitive to the value chosen for the chemical shift. In fact, when a value of 3.4 p.p.m.⁴ was used, the best-fit spectrum differed from the experimental one considerably more than if a higher value was used. Because of this a value of 3.6 p.p.m. was assumed throughout this work for bullvalene in the presence of AgNO_3 , both in D_2O and CH_3CN solutions, while the value of 3.4 p.p.m., reported by Saunders⁴ was used for uncomplexed bullvalene. It is not certain that the chemical shift between aliphatic and olefinic protons in bullvalene increases on complex formation, since a value of 3.6 p.p.m. has also been reported¹⁴ for uncomplexed bullvalene. We have used the 3.4-p.p.m. value for better comparison with the rates given by Saunders.⁴ The larger chemical shift would give values of the rate larger by about 10%, so that the discrepancy, although interesting in itself, has little effect on the rates calculated for the rearrangement.

Spin-Echo Results. Spin-echo n.m.r. methods have been developed and employed⁶⁻⁹ to extend the range of measurable exchange rates beyond those possible with high-resolution techniques. The experiment consists of determining the apparent decay constant $1/T_2$, in sec.^{-1} , for the amplitudes of successive echoes in a Carr-Purcell train as a function of the radiofrequency pulse repetition rate $1/t_{cp}$, where t_{cp} is the time between echoes. Coupled⁹ and uncoupled^{6,7} systems have been treated in some detail and for the latter analytical expressions^{7,20} have been derived which give $1/T_2$ as a function of $1/t_{cp}$, of the chemical shift $\delta\omega$, the natural line-width parameter $1/T_2^0$, and of the exchange rate $1/2\tau$. In practice, the details of determining a two-site exchange rate from $1/T_2$ vs. $1/t_{cp}$ data depend upon how much of the function is experimentally accessible,^{7,8,21} but the procedures are simple enough.

(20) M. Bloom, L. W. Reeves, and E. J. Wells, *J. Chem. Phys.*, **42**, 1615 (1965).

(21) Z. Luz and S. Meiboom, *ibid.*, **39**, 366 (1963).

Bullvalene presents complexities of three kinds. The exchanging protons are coupled, there are multiple sites, and the intramolecular exchange among these sites involves the several correlated motions summarized by eq. 1. We have not been able to derive analytical expressions describing these complexities in general. In principle, the system can be treated by numerical methods in conjunction with a density matrix formulation, as was used for the coupled AB system in the case of slow exchange.⁹ However, a simpler, semiempirical approach can be based on the finding⁹ that, for faster rates in a coupled AB system undergoing intramolecular exchange, the coupling produces negligible effects on a spin-echo train provided that $(1/2\tau) \gtrsim 6\pi J_{AB}$, where J_{AB} is in c.p.s. Then, in the limit of large pulse separation and fast exchange, *i.e.*, $1/2\tau \gg \delta\omega$, the decay constant $1/T_2^m$ of the echo train is described by eq. 2 where

$$(1/T_2^m) = (1/T_2^0) + P_a P_b (\delta\omega)^2 \tau \quad (2)$$

P indicates the relative populations of the two sites. Analogous results have been obtained for multiple site exchange,²¹ but only for random exchange and not for correlated motions such as occur in bullvalene.

However, bullvalene is a "degenerate" two-site system, so we would expect it to be described by eq. 3

$$(1/T_2^m) = (1/T_2^0) + C(\delta\omega)^2 k^{-1} \quad (3)$$

which is the same mathematical form as eq. 2 but is in terms of the rate constant k and an as yet undetermined proportionality constant C . This constant can be evaluated *via* line-shape calculations. The closed expressions for two-site⁷ and random, multiple-site²¹ exchange show that for fast exchange with respect to the chemical shift, and for long pulse separations with respect to exchange life-time, the decay of the echo train is related to the corresponding steady-state line width W through eq. 4 where W is the full width in c.p.s.

$$W_{ex} = W - W_0 = (1/\pi T_2^m) - (1/\pi T_2^0) \quad (4)$$

at half-peak intensity, excluding any instrumental broadening of the line, and W_{ex} is the exchange contribution. This result is not as trivial as it might seem. The decay of a Carr-Purcell echo train, unlike a single induction decay or echo, is not, in general, the Fourier transform of the steady-state line shape. Equations 3 and 4 do not apply to slow exchange or to small pulse separations.

Theoretical values of W_{ex} were calculated for appropriate values of $\delta\omega$ and k with the line-shape program mentioned in the preceding section. The resultant plot of $\log k$ vs. $\log W_{ex}$ is a straight line for exchange rates greater than $8 \times 10^4 \text{ sec.}^{-1}$, for $\delta\nu = 91.3 \text{ c.p.s.}$, with a slope corresponding to $C = 0.455$ in eq. 3. The plot begins to curve for slower rates; for example, C is 0.5 at $k = 1.5 \times 10^4 \text{ sec.}^{-1}$. This change in C probably is due to the approximations of eq. 3 rather than those of eq. 4. At slower exchange rates than those for which eq. 2 and 3 apply, *i.e.*, for $(1/2\tau) \gtrsim \delta\omega$, a more accurate expression for the equally populated, two-site case than eq. 2 is⁸ eq. 5, which is the

$$(1/T_2^m) = (1/T_2^0) + (1/2\tau) - 0.5[(1/\tau)^2 - (\delta\omega)^2]^{1/2} \quad (5)$$

approximate form of the graph. In any case, the graph was used in combination with eq. 4 to determine exchange rates from the spin-echo data.

The values of $1/T_2^m$ were measured for three solutions over a range of temperatures. In addition $1/T_1$ was measured so that corrections for the natural line width could be made *via* eq. 4 by assuming that $1/T_1 = 1/T_2^0$, but its effect was small even at the highest temperatures.²² In the calculation of W_{ex} , and thereby in the determination of k , an aliphatic-olefinic chemical shift of 3.4 p.p.m. was used for bullvalene and 3.6 p.p.m. for its silver complexes. The results are summarized in Table I. Spin-echo studies were not made

Table I. The Rate of the Degenerate Cope Rearrangement of Bullvalene and of Its Silver Nitrate Complex in Solution^a

Temp., °C.	$(1/T_2^m)$, sec. ⁻¹	$(1/T_1)$, sec. ⁻¹	k , sec. ⁻¹
Bullvalene in $CCl_2=CCl_2^b$			
25	50.0	7.9×10^{-2}	3.2×10^3
33	29.7	7.3×10^{-2}	$5.3 (6.2)^c$
41	17.5	6.5×10^{-2}	8.8×10^3
50	10.3	5.6×10^{-2}	1.5×10^4
61.5	4.76	5.1×10^{-2}	3.3×10^4
67.5	3.58	4.7×10^{-2}	4.3×10^4
76	2.13	4.6×10^{-2}	7.4×10^4
80	1.72	4.4×10^{-2}	9.2×10^4
88	1.18	4.2×10^{-2}	1.36×10^5
100	0.67	3.8×10^{-2}	2.45×10^5
112	0.42	3.5×10^{-2}	4.0×10^5
123	0.28	3.3×10^{-2}	6.2×10^5
Bullvalene in acetone- d_6^d			
23	44.4	6.5×10^{-2}	3.6×10^3
39.5	17.6	5.5×10^{-2}	8.8×10^3
49	9.1	5.0×10^{-2}	1.7×10^4
60	5.0	4.6×10^{-2}	3.2×10^4
Bullvalene and $AgNO_3$ in D_2O^e			
50	56.2	1.93	3.3×10^3
61	31.3	1.51	5.8×10^3
70	17.1	1.24	1.06×10^4
81	10.2	1.05	1.9×10^4
88	6.1	0.96	3.4×10^4

^a Unless otherwise stated, the rates were determined from observations of the Carr-Purcell echo train, at 26.85 Mc./sec. The null method was used to measure $1/T_1$; the quantity $1/T_2^m$ is defined in the text. ^b 0.195 g. of bullvalene in 1 ml. of solvent. ^c 60 Mc./sec. high-resolution measurement. ^d 0.215 g. of bullvalene in 1 ml. of solvent. ^e Supersaturated solution; 0.32 g. of bullvalene in 1 ml. of 7.15 M $AgNO_3$ in D_2O .

with CH_3CN as solvent because of interference from the solvent protons, but studies with CD_3CN are feasible and should prove interesting. Our measurements of the bullvalene- $AgNO_3$ - D_2O system were not extended beyond 88° because of sample decomposition.

Our results for bullvalene itself are practically identical with those obtained by Saunders⁴ in the temperature range common to both studies, as may be seen in Figure 2. There is a small discrepancy at the higher values, which can be attributed to neglect of the "line width in the absence of exchange" in the high-resolution studies. In the latter, unlike the spin-echo data, this contribution should include the inhomogeneity broadening.⁸ If we assume this to be about 0.5 c.p.s., the resultant corrected rate for the highest temperature in Saunderson's work coincides with ours.

Inspection of Figure 2 reveals a significant advantage of using spin echoes to determine exchange rates;

(22) The 20-fold shorter T_1 values of the D_2O solution compared with the acetone and $CCl_2=CCl_2$ solutions are due probably to the somewhat viscous nature of the former.

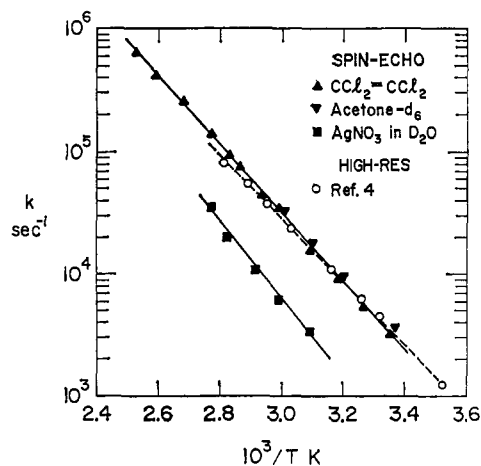


Figure 2. Arrhenius plots of the bullvalene rearrangement rate for several solutions, as determined by proton magnetic resonance methods.

accurate measurements can be made over a substantially larger range of rates.⁸ Our measurements for bullvalene extend to 6.5×10^5 sec.⁻¹, which is tenfold faster than the high-resolution limit. Furthermore, our operating frequency was only 26.85 Mc./sec. and eq. 2 shows that the exchange contribution to $1/T_2^m$ is proportional to $(\delta\omega)^2$ so the range could be extended eightfold further by making the spin-echo measurements at the same frequency, 60 Mc./sec., as the high resolution. This advantage of spin-echo experiments is because they avoid the instrumental broadening of the lines, which limits the high-resolution methods.⁷⁻⁹ On the other hand, extension of the spin-echo studies to slower rates would be difficult for bullvalene because of the coupling between different types of protons and the multiple sites.

Activation parameters determined in the several studies of the rearrangement are summarized in Table II. The high-resolution and spin-echo results for bullvalene itself agree within their respective error, but some systematic error may be present because of the proportionality between the frequency factor A and the activation energy E_a in the two studies.⁸ The activation energy of 15.1 ± 0.8 kcal./mole for the rearrangement in the presence of $AgNO_3$ is sufficiently larger than the 12.8 ± 0.1 kcal./mole value for bullvalene itself that the difference most probably is real.

The difference could be explained by assuming that the mechanism for rearrangement is *via* the uncomplexed bullvalene, since the dissociation constant for the silver complex is expected to increase with temperature. However, the possibility of rearrangement in the complex itself, with a higher activation energy and a slower rate than in free bullvalene, cannot be excluded. Moreover, both mechanisms might occur. The situation could be further complicated by equilibria among several complexes with various numbers of attached silver ions. Therefore, concentration-dependence studies of the exchange are desirable as are studies of the complexes by other physical methods. As to the rearrangement of bullvalene itself, it would be of interest to determine what effect, if any, partial substitution by deuterium would have on the exchange rate of the remaining protons. The absence of any appreciable isotope effect would indicate that the rate of the rear-

Table II. Activation Parameters for the Degenerate Cope Rearrangement of Bullvalene and of Its Silver Nitrate Complex in Solution

Solvent	Method (Mc./sec.)	Temp. range, °C.	A , sec. ⁻¹	E_a , kcal.	Ref.
Not cited	High res. (60.00)	10-83	0.2×10^{13}	11.8 ± 1.0	4
CCl ₂ =CCl ₂	Spin-echo (26.85)	25-123	0.8×10^{13}	12.8 ± 0.1^a	This work
AgNO ₃ -H ₂ O ^b	Spin-echo (26.85)	50-88 ^c	4.9×10^{13}	$15.1 \pm 0.8^{a,c}$	This work

^a The experimental error given is the standard deviation from the least-squares fit of the data. ^b 0.32 g. of bullvalene in 7.15 M AgNO₃ in D₂O. ^c A high-resolution measurement at 60 Mc./sec. and 33° was also carried out, and the resultant rate was included in the least-squares determination of A and E_a .

rangement is governed by the motions of the carbon atoms, as seems most likely.

IV. Experimental

Reagents. All of the following substances were used without further purification: spectral grade tetrachloroethylene and acetonitrile, 99.8% D₂O (General Dynamics), 99.5% acetone-*d*₆ (Merck Sharp and Dohme of Canada Ltd.), anhydrous silver fluoroborate (Ozark Mahoning Co.), and silver nitrate (ACS grade, Schaar and Co.). The sample of bullvalene was from G. Schroder¹⁴ via Earl Whipple, both of whom we wish to thank for their interest and assistance.

N.m.r. Measurements. Spin-echo measurements were carried out as described previously.⁴ The temperatures used in the spin-echo experiments were very stable and could be determined to within $\pm 0.5^\circ$ by a copper-constantan thermocouple. High-resolution measurements were carried out on a Varian A-60 spectrometer with the "room-temperature" probe. The temperature was measured with a methanol sample and is believed to be accurate to $\pm 1.5^\circ$. In both types of experiment at least 15 min. were allowed for the sample to attain thermal equilibrium before the measurement.

Preparation of Solid Bullvalene Complexes. This part of our investigation must be considered very preliminary (see section II). In the initial experiment a 7.15 M AgNO₃ solution in D₂O was prepared. Solid bullvalene was found to dissolve in this solution, to the extent of about 0.32 g./ml. of solvent. No heating was required. This solution was used for our n.m.r. measurements, but part of it was set aside for chemical tests before degassing and sealing the rest of the sample in a Pyrex tube. When some additional D₂O was

added to the test sample crystallization occurred rapidly. The solid was isolated and dried. It was insoluble in cold or warm tetrachloroethylene, but it was somewhat soluble in water. It did not melt (in an open melting-point tube) but started decomposing at about 140°. (Bullvalene has m.p. 96°.) Elemental analysis indicated an approximate composition C₁₀H₁₀·2AgNO₃. H and N analyses were within 0.1 and 0.2% of theoretical, respectively, but C was 4% too low. The compound was hygroscopic and darkened on standing.

Preparation of Bullvalene-Silver Fluoroborate Complexes. Bullvalene (0.26 g.) in 5 ml. of CH₂ClCH₂Cl was added to 2.71 g. of AgBF₄ in the same solvent. A white precipitate formed immediately. The solid was filtered and recrystallized from 20 ml. of isopropyl alcohol. After standing overnight in a refrigerated desiccator, about 0.3 g. of solid was isolated. The dried compound decomposed without melting at about 150° (somewhat violently, in open tube). It was soluble in acetone and methanol and very soluble in acetonitrile. Elemental analysis indicated the composition 2C₁₀H₁₀·AgBF₄.

Anal. Calcd.: C, 52.78; H, 4.43; Ag, 23.70. Found: C, 52.50; H, 4.37; Ag, 23.82 (approximate, residue).

This compound did not darken with time and did not appear to be hygroscopic. It should be noted that by changing the recrystallization conditions (dichloroethylene and acetone mixture instead of isopropyl alcohol) a complex with a higher Ag ratio was prepared. Elemental analysis showed an approximate 1:1 composition, but as with the nitrate the carbon analysis was too low (by 2.5%), and the complex darkened rapidly. This type of behavior on recrystallization is not uncommon for silver-olefin complexes.¹⁰