

[CONTRIBUTION FROM THE UNION CARBIDE RESEARCH INSTITUTE, UNION CARBIDE CORPORATION, TARRYTOWN, N. Y.]

Chlorination Studies of Unsaturated Materials in Nonpolar Media. I. Solvent Effects on Radical Addition of Chlorine to Chloroethylenes

BY M. L. POUTSMA AND R. L. HINMAN

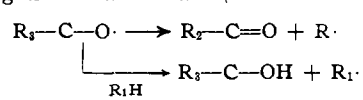
RECEIVED APRIL 25, 1964

The relative rates of addition of chlorine atom to 1,1-dichloroethylene, *cis*- and *trans*-1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene in noncomplexing solvents have been measured both directly by competitive photochlorination of pairs of olefins and indirectly by comparison of addition to each olefin in competition with hydrogen abstraction from cyclohexane. The selectivity of chlorine atom with respect to such radical addition has been found to be substantially increased by the presence of the complexing solvents benzene and carbon disulfide. Solvent dependence has also been demonstrated for the competition between addition to the olefins and hydrogen abstraction from cyclohexane; attempts to extend such solvent effects to competitive addition and abstraction behavior of the trichloromethyl radical were unsuccessful.

Introduction

The reactivity of certain free radicals is markedly affected by the nature of the solvent in which they are allowed to react. Current explanations^{1,2} of these effects involve formation of a complex between the electrophilic radical and the electron-rich solvents such as aromatic hydrocarbons or carbon disulfide; the presence of this solvent molecule modifies the nature not only of the ground state of the radical but also of the transition states of any reactions that the complexed radical undergoes.³

The first examples of such solvent effects were found in studies of the relative rates of abstraction of tertiary and primary hydrogen atoms from 2,3-dimethylbutane by chlorine atom during photochlorination.^{1,2} The enhancement in abstraction selectivity of chlorine atom by aromatic solvents has now been demonstrated for a variety of substrates.^{4,5} Smaller, although similar, solvent effects have also been demonstrated for competitive hydrogen abstraction reactions of the *t*-butoxy radical.^{3,6,7} More dramatic changes have been observed with alkoxy radicals for the competition between hydrogen abstraction and β -scission



The unimolecular cleavage process is strongly favored over the bimolecular abstraction process by the usual complexing solvents^{3,8} as well as by a number of olefinic materials.⁹

Although solvent effects on radical reactions have thus been demonstrated for hydrogen abstraction and β -scission processes, no comparable data are available for radical addition reactions.¹⁰ It was the purpose of this study to determine if similar solvent dependence could be realized in a simple free-radical addition reaction. Chlorine atom was chosen for initial study since solvent effects on its abstraction reactions are

- (1) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).
- (2) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).
- (3) C. Walling and P. Wagner, *ibid.*, **85**, 2333 (1963).
- (4) G. A. Russell, *ibid.*, **80**, 4997 (1958).
- (5) G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85**, 2976 (1963).
- (6) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960).
- (7) E. L. Patmore and R. J. Gritter, *J. Org. Chem.*, **27**, 4196 (1962).
- (8) G. A. Russell, *ibid.*, **24**, 300 (1959).
- (9) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

(10) We are referring to solvent effects which are dependent on the chemical nature of the solvent. These are different in character from the results of Dixon and Szwarc¹¹ who found that the ratio of addition to abstraction observed for reaction of the trifluoromethyl radical with olefins was lower in the gas phase than in the liquid phase.

- (11) P. S. Dixon and M. Szwarc, *Trans. Faraday Soc.*, **59**, 112 (1963).

large and well characterized and since it is easily generated under mild conditions by photolysis of chlorine.

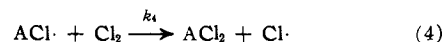
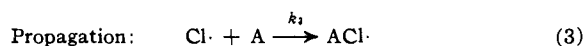
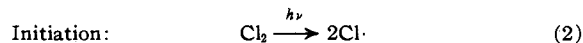
Results

Choice of System.—Photochlorination of alkylethylenes would be undesirable for study of solvent effects on chlorine atom addition for at least two reasons: (1) it is difficult, if not impossible, for many olefins to isolate the radical reaction from a competing polar reaction,^{12a} and (2) radical chlorination leads to abstraction as well as addition products.^{12b} However, it appeared likely that photochlorination of chloroethylenes would be suitable since the polar reactions should be retarded by electronegative substituents. This prediction was confirmed when it was found that solutions of chlorine in 1,1-dichloroethylene (I), *cis*- (II) and *trans*-1,2-dichloroethylene (III), trichloroethylene (IV), and tetrachloroethylene (V) were stable for extended periods in the dark at 25° but were rapidly decolorized by illumination.

Photochlorination of several chloroethylenes has been extensively studied in the gas phase. Early data of Schumacher and co-workers showed that, at 40–115° and above a certain limiting pressure (20–150 mm.) characteristic of each olefin, the addition reaction followed rate law 1 for vinyl chloride,¹³ *cis*- and *trans*-1,2-dichloroethylene,^{14,15} trichloroethylene,¹⁵ and tetrachloroethylene¹⁶; that is, the rate is proportional to the half power of the absorbed illumination

$$-d(\text{Cl}_2)/dt = k_0(I_{\text{abs}})^{1/2}(\text{Cl}_2) \quad (1)$$

and to the first power of the chlorine concentration but is independent of the olefin concentration. This observed rate law¹⁷ is consistent with elementary steps 2, 3, and 4 followed by termination only through step 5 of the following chain where A represents the chloroethylene.



(12) (a) M. L. Poutsma, *J. Am. Chem. Soc.*, **85**, 3511 (1963); (b) M. L. Poutsma, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, p. 30N.

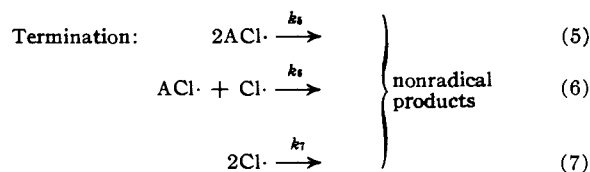
(13) R. Schmitz and H. J. Schumacher, *Z. physik. Chem.*, **B55**, 72 (1942);

(14) K. L. Müller and H. J. Schumacher, *ibid.*, **B55**, 285 (1937).

(15) K. L. Müller and H. J. Schumacher, *ibid.*, **B55**, 455 (1937).

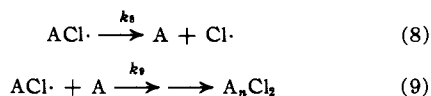
(16) C. Schott and H. J. Schumacher, *ibid.*, **B49**, 107 (1941).

(17) This result also suggests that reversal of addition (step 8) is unimportant since it would tend to raise the steady-state concentration of chlorine atoms and thus favor at least partial operation of termination step 6.



More recent studies¹⁸⁻²⁴ of these systems over wider ranges of temperature and concentration by use of both steady and intermittent initiation methods (see the Discussion section for a further description) have confirmed this over-all rate behavior for temperatures below 150°.

For such a simple chain, the relative rate constants for addition of chlorine atom to olefins A and A' (k_3 and k_3') could be determined by photochlorination of mixtures of A and A' and measurement of relative rates either of disappearance of A and A' or (at low conversion) of appearance of ACl_2 and $\text{A}'\text{Cl}_2$. However, the importance of two possible complicating factors in the liquid phase would need to be evaluated first: (1) reversal of addition (step 8), and (2) telomerization of the olefin (step 9).



Therefore, each of these factors was subjected to experimental test.

Reversal of addition should lead to geometrical isomerization of starting olefin. No such isomerization of recovered starting material could be detected in any of the liquid-phase chlorinations involving the *cis-trans* pair II and III even at the lowest chlorine concentrations employed. Although such direct evidence cannot be obtained for olefins I, IV, and V, indirect evidence from studies of photochlorination of mixtures of each olefin with cyclohexane (*vide infra*) supported the absence of reversal of addition for these olefins as well.

The presence of telomerization would be indicated by less than quantitative yields of 1:1 addition product. Therefore, the yield of 1:1 product was directly determined by addition of a known amount of standardized chlorine solution in carbon tetrachloride to each of the olefins I-V, initiation of reaction by illumination under nitrogen, and determination of the amount of 1:1 product formed by g.l.c. with the aid of an internal standard. Results are shown in Table I. Only for 1,1-dichloroethylene at high initial olefin:chlorine ratios (30-40) did the yield fall significantly below 100%; this dependence was essentially removed by lowering the initial ratio to 8. Such a dependence of extent of telomerization on the olefin:chlorine ratio is the expected result for competition between steps 4 and 9. Therefore all direct competitive chlorinations of pairs of olefins were conducted at initial

(18) J. Adam, P. Goldfinger, and P. A. Gosselain, *Bull. soc. chim. Belges*, **65**, 549 (1956).

(19) F. S. Dainton, D. A. Lomax, and M. Weston, *Trans. Faraday Soc.*, **53**, 460 (1957).

(20) S. Dusoleil, P. Goldfinger, A. M. Mahieu-Van der Auwera, G. Martens, and D. Van der Auwera, *ibid.*, **57**, 2197 (1961).

(21) P. Goldfinger, G. Huybrechts, and G. Martens, *ibid.*, **57**, 2210 (1961).

(22) P. Goldfinger and G. Martens, *ibid.*, **57**, 2220 (1961).

(23) F. S. Dainton, D. A. Lomax, and M. Weston, *ibid.*, **58**, 308 (1962).

(24) G. Huybrechts, L. Meyers, and G. Verbeke, *ibid.*, **58**, 1128 (1962).

TABLE I

YIELD OF 1:1 ADDITION PRODUCTS FROM LIQUID-PHASE PHOTOCHEMICAL CHLORINATION OF CHLOROETHYLENES AT 25°

Olefin, ethylene	(Olefin) ₀ /(Cl) ₀	Yield, %
1,1-Dichloro- (I)	37	89, 88
1,1-Dichloro- (I)	8	98, 96
<i>cis</i> -1,2-Dichloro- (II)	40	97, 97
<i>trans</i> -1,2-Dichloro- (III)	39	98, 94
Trichloro- (IV)	32	106, 104
Tetrachloro- (V)	29	100, 100

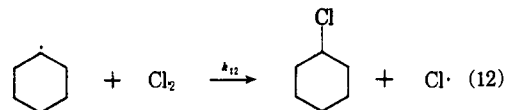
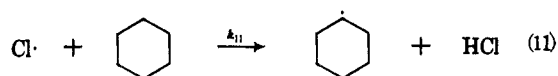
olefin:chlorine ratios of less than 4 to eliminate complications owing to telomerization.

Relative Rate Constants for Addition.—The relative rate constants for addition of chlorine atom to olefins I-V were determined by competitive chlorination of each olefin with *trans*-1,2-dichloroethylene as standard. Reactions of mixtures of the two olefins, carbon tetrachloride (internal standard for g.l.c. analysis), and chlorine in varying proportions in 1,1,2-trichlorotrifluoroethane as solvent in sealed tubes at 25° under a nitrogen atmosphere were initiated by means of illumination. Initial and final olefin concentrations were determined by g.l.c. and the ratio of rate constants determined from eq. 10 where k_3' is the specific rate of

$$\frac{k_3'}{k_3} = \frac{\log(A'_0) - \log(A'_f)}{\log(A_0) - \log(A_f)} \quad (10)$$

chlorine atom addition to olefin A', k_3 that to *trans*-1,2-dichloroethylene (A), and 0 and f refer to initial and final concentrations. Representative values from some 75 runs are given in Table II. The relative rate constants are insensitive to significant changes of absolute concentration of the olefins, of ratio of the olefins, of extent of conversion (determined by the initial chlorine concentration), and of amount of noncomplexing solvent present. The results for tetrachloroethylene show some scatter but no systematic variations are apparent.

The relative rate constants for addition were also determined in an indirect fashion by competitive photochlorination of each of the olefins I-V with cyclohexane. In this case steps 3 and 4 compete with steps 11 and



12. Mixtures of olefin and cyclohexane were treated with a limited amount of chlorine in the dark under nitrogen at 25° and reaction was initiated by illumination. Analysis of the products by g.l.c. gave the necessary quantities to solve eq. 13²⁵ where P_1 is the chlorine addition product of the chloroethylene, P_2 is chlorocyclohexane, F is a statistical factor de-

$$\frac{k_3}{k_{11}} = \frac{(P_1) (\text{cyclohexane})_0}{(P_2) (\text{olefin})_0} (F) \quad (13)$$

defined below, and 0 refers to initial concentrations. Results are summarized in Table III; as a matter of

(25) This is a good approximation at low conversion (<10% in all cases) for the logarithmic expression analogous to eq. 10.

TABLE II
RELATIVE RATE CONSTANTS FOR CHLORINE ATOM ADDITION TO CHLOROETHYLENES IN NONCOMPLEXING SOLVENTS AT 25°^a

Olefin, ethylene	Initial mole fraction					k_3/k_2	
	Olefin	III	CCl ₄	C ₂ F ₂ Cl ₂	Chlorine		
1,1-Dichloro- (I)	0.06	0.28	0.09	0.36	0.21	1.34	(1) ^b
	.09	.09	.07	.70	.065	1.26 ± 0.07 ^c	(3)
	.19	.19	.15	.37	.09	1.28 ± .01	(3)
	.23	.23	.19	.12	.22	1.31 ± .02	(2)
	.39	.08	.19	0	.34	1.20	(1)
<i>cis</i> -1,2-Dichloro- (II)	.09	.09	.07	0.68	.06	1.09 ± 0.03	(2)
	.18	.19	.14	.35	.14	1.20 ± .01	(2)
	.27	.26	.21	.13	.13	1.14 ± .01	(2)
Trichloro- (IV)	.02	.22	.10	.55	.12	0.74 ± .07	(4)
	.075	.09	.07	.68	.08	.76 ± .02	(2)
	.10	.13	.10	.55	.12	.76 ± .03	(2)
	.11	.13	.11	.60	.05	.72 ± .01	(2)
	.19	.02	.10	.54	.15	.75	(1)
	.21	.03	.11	.60	.05	.69 ± 0.01	(3)
	.24	.28	.23	.14	.11	.72 ± .02	(2)
	.01	.015	.01	.95	.015	.54 ± .01	(2)
Tetrachloro- (V)	.02	.22	.10	.55	.12	.42 ± .02	(4)
	.06	.34	.13	.37	.10	.32 ± .05	(2)
	.095	.13	.10	.56	.11	.44 ± .01	(2)
	.095	.50	.20	0	.21	.27 ± .02	(2)
	.19	.03	.11	0.62	.05	.34 ± .03	(4)
	.20	.27	.22	.23	.08	.26 ± .01	(2)
	.25	.09	.13	.38	.15	.42 ± .01	(2)
	.26	.35	.24	0	.15	.36 ± .04	(3)
	.45	.15	.25	0	.15	.40 ± .04	(2)

^a Referred to $k_2 = 1.00$ for *trans*-1,2-dichloroethylene. ^b Number of runs. ^c Average deviation.

usage, we define k_3 as the specific rate of addition of chlorine atom to the olefin as a whole, k_3 being the sum of k_{3a} and k_{3b} which are the specific rates of addition to either terminus of the double bond; and we define k_{11} as the specific rate of abstraction of a single cyclohexyl hydrogen atom; therefore, F in eq. 13 has a value of 12. (This approach averages any differences in rates of abstraction of axial and equatorial hydrogen atoms.) Since the response of the g.l.c. detector to hexachloroethane was somewhat erratic and nonlinear with concentration, the results for tetrachloroethylene are only approximate. Also, since this indirect method demands that the initial olefin:chlorine ratio be kept high to avoid polychlorination, the values for 1,1-dichloroethylene are lower limits since the yield of 1:1 product may have been low owing to telomerization (cf. Table I).

In these runs, as in the direct comparison, no geometrical isomerization was observed for the 1,2-dichloroethylenes. Also, the failure of k_3/k_{11} to vary in any regular fashion with olefin and/or chlorine concentration suggests that the major portion of reaction in all cases proceeds through steps 3 and 4 rather than 8 or 9.²⁶

The relative rate constants for addition derived from the direct and indirect methods are in essential agreement, as shown in Table IV, if one considers the experimental uncertainties and small changes in medium involved in such comparisons.

Solvent Effects.—The effects of complexing solvents on relative rate constants for chlorine atom addition to each olefin were determined by the direct competition

(26) This invariance with olefin concentration also shows that the chloroethylenes themselves are not exerting any significant solvent effect on the k_3/k_{11} ratio. The failure of olefin IV to affect the tertiary:primary abstraction ratio from photochlorination of 2,3-dimethylbutane was demonstrated by Russell¹; similar results have been obtained in the present study for olefins I and III.

method; all solutions were made up in a ratio of olefin:III:carbon tetrachloride:solvent of 1:1:1: x by volume. Results are summarized in Table V for reactions in 20, 50, and 80% benzene and carbon disulfide (by volume), compared to 1,1,2-trichlorotrifluoroethane as a reference solvent. Solvent effects were also determined by the indirect method; mixtures of olefin, cyclohexane, and solvent were chlorinated to low conversion and k_3/k_{11} determined as before (Table VI). In this indirect method, the need to avoid polychlorination required that the initial olefin:chlorine ratios be rather high; therefore, the values for I are again lower limits due to possible telomerization. The magnitude of the solvent effect as measured by the two methods is compared in Table VII. Except for I, agreement is good if one considers the large solvent effects on individual k_3/k_{11} values.

Attempted Demonstration of Solvent Effects on Trichloromethyl Radical.—From the radical reaction between bromotrichloromethane and olefins, Huyser²⁷ has determined the ratio of rate constants for addition, k_a , to allylic hydrogen atom abstraction, k_t , for reaction of a series of olefins with trichloromethyl radical. Since, with reasonably long chains, each act of addition consumes one molecule of bromotrichloromethane and each act of abstraction consumes one molecule of bromotrichloromethane and produces one molecule of chloroform, the ratio k_a/k_t is simply determined from eq. 14. The reactions were carried out with a fourfold excess of olefin to avoid complications of secondary products and were initiated photochemically. Typical values of Huyser for k_a/k_t at 77.8° are: 1-octene, 43; cyclopentene, 5.4; and cyclohexene, 1.20. With this background material at hand, the interaction of trichloromethyl radical with these three olefins has been studied in a number of aromatic solvents. The results

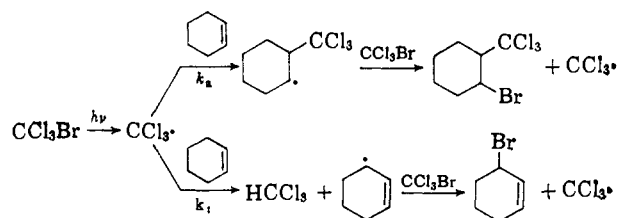
(27) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

TABLE III

Olefin, ethylene	RELATIVE RATE CONSTANTS FOR ADDITION OF CHLORINE ATOM TO CHLOROETHYLENES COMPARED TO ABSTRACTION FROM CYCLOHEXANE AT 25.0°			k_1/k_{11}
	(Olefin) ₀ ^a	(Cyclohexane) ₀ ^a	(Chlorine) ₀ ^a	
1,1-Dichloro-	19.3	78.2	2.9	3.3
	38.7	64.3	4.2	3.8
	64.4	46.0	3.8	3.7
	103.0	18.4	3.5	4.1
			Av.	3.7 ^b
<i>cis</i> -1,2-Dichloro-	26.3	73.6	3.8	4.3
	26.3	73.6	4.7	3.8
	65.9	46.0	5.0	3.9
	65.9	46.0	5.0	3.8
	105.1	18.4	3.9	4.0
		Av.	3.95	
<i>trans</i> -1,2-Dichloro-	26.1	73.6	4.6	3.0
	65.2	46.0	3.9	3.3
	65.2	46.0	4.2	3.2
	104.3	18.4	4.7	3.4
			Av.	3.2
Trichloro-	22.2	73.6	4.6	2.6
	22.2	73.8	4.2	1.9
	27.7	69.3	3.5 ^c	1.8 ^c
	48.6	50.8	3.5 ^c	2.0 ^c
	55.4	46.0	3.8	2.4
	55.4	46.0	4.2	2.3
	82.1	23.1	2.5 ^c	2.3 ^c
	88.7	18.4	4.0	2.9
		Av.	2.3	
Tetrachloro-	19.7	73.6	2.5	0.7 ^d
	49.2	46.0	4.2	1.0 ^d
	49.2	46.0	1.8	0.8 ^d
	78.7	18.4	3.2	1.3 ^d
	78.7	18.4	1.6	1.2 ^d
		Av.	1.0 ^d	

^a Initial concentration in millimoles. ^b Lower limit caused by probable occurrence of telomerization; see text. ^c Illumination during run so that average chlorine concentration was considerably lower than in other runs. ^d Approximate due to nonlinear g.l.c. response; see text.

are listed in Table VIII; almost all the ratios are averages of two runs.



$$\frac{\text{total reaction} - \text{abstraction}}{\text{abstraction}} = \frac{\text{addition}}{\text{abstraction}} = \frac{k_a}{k_t} = \frac{\{[\text{CCl}_3\text{Br}]_0 - [\text{CCl}_3\text{Br}]\} - [\text{HCCl}_3]}{[\text{HCCl}_3]} \quad (14)$$

$$[\text{CCl}_3\text{Br}]_0 =$$

init. concn. of $[\text{CCl}_3\text{Br}]$ and $[\text{HCCl}_3]$ = final concn.

Discussion

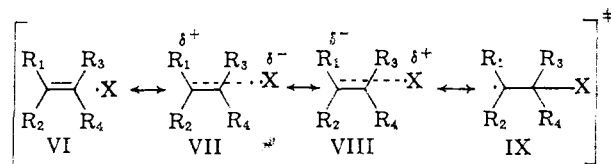
Relative Rates of Chlorine Atom Addition.—The transition state for addition of a radical to an olefin might be represented by the extreme resonance structures VI–IX. Structural factors influencing rates of addition of a radical to a series of structurally related

TABLE IV

Olefin, ethylene	$k_2(\text{direct})^a$	$k_2(\text{indirect})^b$
1,1-Dichloro-	1.26	1.15 ^c
<i>cis</i> -1,2-Dichloro-	1.15	1.23
<i>trans</i> -1,2-Dichloro-	1.00 ^d	1.00 ^d
Trichloro-	0.73	0.72
Tetrachloro-	0.38	0.31 ^e

^a Average of all direct competition runs (partially listed in Table II). ^b Average of all runs shown in Table III. ^c Lower limit; cf. footnote b of Table III. ^d Assigned. ^e Approximate; cf. footnote d of Table III.

olefins have generally been separated into two classes^{28,29}: (1) those determined by the nature of R_1 and R_2 and due to stabilization of the incipient radical and/or to stabilization of charge-separated structures such as VII and VIII, and (2) those determined by the nature of R_3 and R_4 and due to steric interference with the approach of radical X to the olefin and/or to polar repulsive forces between X and the olefin. The relative rate constants for addition of chlorine atom to the series of chloroethylenes I–V are best discussed in terms of rates of addition at a single



olefinic terminus as shown in column 1 of Table IX.³⁰ For the unsymmetrical cases, the assumption has been made that addition to I occurs almost entirely at the unsubstituted end while the majority of addition to IV occurs at the monosubstituted end. Factors of class 1 would predict a rate order $I \sim IV \sim V > II \sim III$ since chloro substituents are known to stabilize a free radical on carbon.³¹ On the other hand, factors of class 2 would predict a rate order $I > II \sim III \sim IV > V$. In fact, addition of a chloro substituent at the carbon atom being attacked decreases the rate by a factor of 2.5 while addition of a chloro substituent at the carbon atom where the radical will ultimately reside increases the rate by a factor of, at best, 1.25. From this observed order (particularly the fact that the rate for IV is much closer to that for II and III than to that for I), it appears that factors of class 2 play the more important role in this series. The comparison of relative rates of chlorine atom addition to olefins I–V and hydrogen abstraction from cyclohexane (Table III) shows that the additions are low activation energy processes,³² in agreement with results from the gas phase.^{18–24} For such low activation-energy processes, it might have been predicted that the transition state would resemble the starting materials³³ and that there

(28) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapters 4, 6, and 7.

(29) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Butterworths, London, 1959, p. 262.

(30) The assumption has been made that, in the transition state for radical addition, the chlorine atom is more closely associated with a specific terminus rather than with the center of the olefinic system.

(31) Reference 28, pp. 50–51.

(32) E_a for reaction of chlorine atom with cyclopentane has been determined in the gas phase to be 0.6 kcal./mole: H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **77**, 2629 (1955).

(33) G. S. Hammond, *ibid.*, **77**, 334 (1955).

TABLE V
RELATIVE RATE CONSTANTS FOR CHLORINE ATOM ADDITION TO CHLOROETHYLENES IN VARIOUS SOLVENTS AT 25° (k_2)

Solvent ^a	Olefins, ethylene				
	1,1-Dichloro- (I)	<i>cis</i> -1,2-Dichloro- (II)	<i>trans</i> -1,2-Di-chloro. (III)	Trichloro- (IV)	Tetrachloro- (V)
C₂F₂Cl₂					
20%	1.31 ± 0.02 ^b (4) ^c	1.14 ± 0.01 (2)	1.00 ^d	0.72 ± 0.02 (2)	0.34 ± 0.05 ^e (8)
50%	1.28 ± .01 (4)	1.20 ± .01 (2)	1.00	.71 ± .01 (2)	.34 ± .07 ^f (6)
80%	1.27 ± .05 (4)	1.09 ± .03 (2)	1.00	.73 ± .04 ^g (12)	.39 ± .05 ^h (12)
C₆H₆					
20%	2.11 ± 0.10 (4)	1.26 ± 0.08 (2)	1.00	0.74 (1)	0.15 ± 0.01 (4)
50%	3.07 ± .13 (4)	1.51 ± .11 (4)	1.00	.70 ± 0.05 (2)	.089 ± 0.006 (4)
80%	3.9 ± .3 (4)	1.49 ± .04 (4)	1.00	.68 ± 0.04 (4)	.077 ± 0.007 (3)
CS₂					
20%	2.92 ± 0.16 (4)	1.46 ± 0.01 (2)	1.00	0.81 ± 0.02 (2)	0.088 ± 0.015 (4)
50%	5.4 ± 0.6 (6)	1.66 ± .06 (4)	1.00	.80 (1)	.061 ± .005 (4)
80%	7.0 ± 1.2 (8)	1.77 ± .05 (4)	1.00	.90 ± 0.01 (2)	.054 ± .010 (3)

^a Volume per cent. ^b Average deviation. ^c Number of runs. ^d Assigned for each row. ^e 0% solvent. ^f 30% solvent. ^g 70% solvent.

TABLE VI
RELATIVE RATE CONSTANTS FOR ADDITION OF CHLORINE ATOM TO CHLOROETHYLENES COMPARED TO ABSTRACTION FROM CYCLOHEXANE IN COMPLEXING SOLVENTS AT 25° (k_2/k_{11})

Solvent ^a	Olefins, ethylene			
	1,1-Dichloro- (I)	<i>cis</i> -1,2-Di-chloro- (II)	<i>trans</i> -1,2-Di-chloro- (III)	Trichloro- (IV)
None ^b	3.7 ^c	3.95	3.2	2.3
C ₆ H ₆ , 50%	15.0 ^c	11.3	7.9	6.7
C ₆ H ₆ , 80%	30 ^c	16.3	11.3	8.8
CS ₂ , 50%	29 ^c	18	13	10.4
CS ₂ , 80%	62 ^c	34	19	16

^a Volume per cent. ^b From Table III. ^c Lower limit due to possible telomerization; see text.

TABLE VII
RELATIVE RATE CONSTANTS FOR CHLORINE ATOM ADDITION TO CHLOROETHYLENES IN COMPLEXING SOLVENTS AT 25° BY TWO METHODS (k_2)

Solvent ^a	Olefins, ethylene			
	1,1-Dichloro- (I)	<i>cis</i> -1,2-Dichloro- (II)	<i>trans</i> -1,2-Di-chloro- (III)	Trichloro- (IV)
C ₆ H ₆ , 50%	3.07, ^b 1.90 ^{c,d}	1.51, ^b 1.43 ^c	1.00 ^e	0.70, ^b 0.85 ^c
C ₆ H ₆ , 80%	3.9, ^b 2.7 ^{c,d}	1.49, ^b 1.44 ^c	1.00 ^e	.68, ^b .78 ^c
CS ₂ , 50%	5.4, ^b 2.2 ^{c,d}	1.46, ^b 1.39 ^c	1.00 ^e	.80, ^b .88 ^c
CS ₂ , 80%	7.0, ^b 3.3 ^{c,d}	1.77, ^b 1.79 ^c	1.00 ^e	.90, ^b .84 ^c

^a Volume per cent. ^b Direct measurement from Table V. ^c Indirect measurement from Table VI. ^d Lower limit due to possible telomerization; see text. ^e Assigned.






TABLE VIII
EFFECT OF SOLVENT ON THE k_a/k_t RATIO FOR REACTION OF TRICHLOROMETHYL RADICAL WITH OLEFINS AT 39.1°

Solvent ^a	k_a/k_t		
	Cyclohexene	Cyclopentene ^b	1-Octene
None	1.85 ^c	6.5 ^c	101
Cyclohexane	1.7	6.2	75
Benzene	1.5	7.3	108
Diphenyl ether	1.9	5.9	116
Anisole	1.9		117
Chlorobenzene	2.0		
Thiophene	2.0		
Carbon disulfide	1.6		
Carbon tetrachloride ^d		6.5	107
<i>t</i> -Butyl alcohol	1.8	7.4	123
Acetone	1.8		
Methanol	1.4		

^a 50% by volume; 4:1 ratio of olefin to bromotrichloromethane. ^b Least reliable since cyclopentene and chloroform overlap somewhat in g.l.c. analysis. ^c From ref. 27. ^d Carbon tetrachloride not consumed in reaction.

would be little contribution of class 1 factors. It does not seem possible, however, to determine from these data alone how much of the retarding effect of added chlorine atoms on the olefinic terminus is caused by a simple "size" effect and how much is owing to the fact that a very electrophilic radical is forced to approach a more electron-deficient center in V than in I (a polar repulsive effect depending on the chemical nature of both the radical and the olefin rather than only on their bulk).

TABLE IX
RELATIVE RATES OF ADDITION OF RADICALS TO SUBSTITUTED ETHYLENES

Olefin	Chlorine atom to chloro-ethylenes ^a	Chlorine atom in 80% CS ₂ to chloro-ethylenes ^a	Polystyryl radical to chloro-ethylenes ^b	Methyl radical to methyl-ethylenes ^c
	1.2	7.0	17	5.2
	2 × 0.6	2 × 0.9	2 × 0.072	2 × 0.25
	2 × 0.5 ^d	2 × 0.5 ^d	2 × 0.5 ^d	2 × 0.5 ^d
	0.7	0.9	1.9	0.8
	2 × 0.2	2 × 0.027	2 × 0.085	...

^a R = Cl; in nonpolar solvents at 25°; present study, Tables IV and V. ^b R = Cl; in styrene-chloroethylene mixtures at 60°; ref. 34a. ^c R = CH₃; in isooctane at 65°; ref. 29. ^d Assigned to each column.

It is interesting to attempt to compare two aspects of the details of the liquid phase results with those in the gas phase. In the first place, the gas-phase activation parameters suggest the reverse order of relative rates from that observed in the liquid phase; the activation energies for addition of chlorine atom to olefins II, IV, and V are given as 0.95, 0.7, and 0 kcal./mole, respectively, with similar pre-exponential factors.^{34b} However, since these determinations were made from different approaches by different groups of workers, each of which suggests a possible error of 1 kcal./mole,^{21,24,35a} it appears impossible to say whether the apparent difference between gas- and liquid-phase

(34) (a) K. W. Doak, *J. Am. Chem. Soc.*, **70**, 1525 (1948); (b) P. B. Ayscough, A. J. Cocker, F. S. Dainton, S. Hirst, and M. Weston, *Proc. Chem. Soc.*, 244 (1961).

(35) (a) P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.*, **58**, 318 (1962); (b) *ibid.*, **58**, 295 (1962).

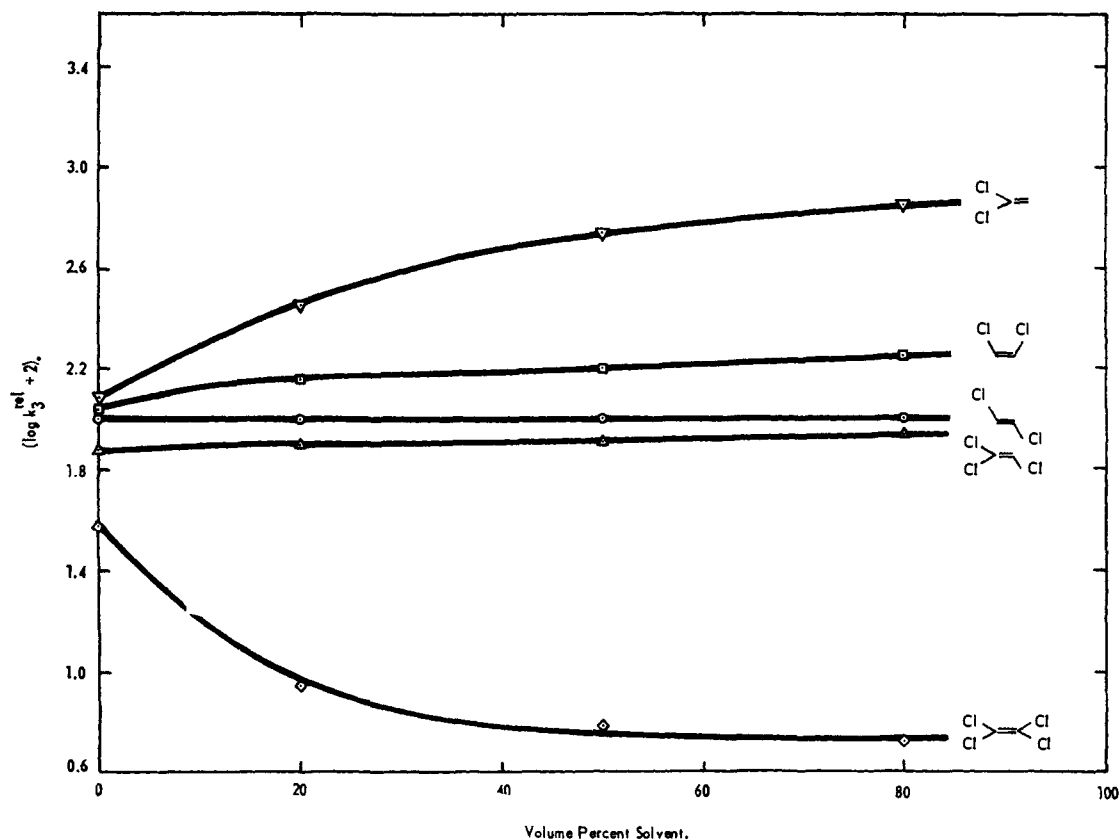


Fig. 1.—Variation of relative rates of chlorine atom addition to polychloroethylenes with per cent carbon disulfide in the medium at 25°: ▽, I; ◻, II; ○, III; △, IV; ◇, V.

results is real. The kinetics of photochlorination in both phases have been determined only for olefin V, very similar over-all rate constants being observed³⁶; however, these results were obtained under conditions which identify the over-all rate constant with $k_4/k_5^{1/2}$ rather than with any function of k_3 , the rate constant for addition. Secondly, the failure to observe reversal of addition in the present liquid-phase studies is consistent with predictions based on the gas-phase activation parameters; the activation energy for chain transfer with chlorine (step 4) is in the range -6 kcal./mole while that for reversal of addition (step 8) is in the range 17–23 kcal./mole.^{22,34b} However, it should be noted that, quite contrary to such predictions, chlorination of II and III in the gas phase has more recently been found to be accompanied by considerable geometrical isomerization of recovered olefin even at 30°. It was postulated^{34b,35,37} that such reversal arose from some decomposition of excited radicals (the actual product of step 3 is vibrationally excited by some 20 kcal./mole) before they could come to thermal equilibrium with the medium. However, such excited radicals should have a much shorter lifetime in the liquid phase, in agreement with our failure to observe isomerization. Unfortunately, this reversal from excited radicals foiled an attempt to measure relative rates of addition in the gas phase.³⁵

Solvent Effects.—The effects of complexing solvents on relative rate constants for addition of chlorine atom to olefins I–V are shown in Table V for results in 20, 50,

and 80% benzene and carbon disulfide compared to 1,1,2-trichlorotrifluoroethane and schematically in Fig. 1 for results in 80% carbon disulfide. The rate spread between I and V has been increased from a factor of 3.5 in the noncomplexing solvent to a factor of 50 in 80% benzene and to a factor of 130 in 80% carbon disulfide. This is a degree of sensitivity similar to that observed by Russell¹ for solvent effects on tertiary *vs.* primary hydrogen abstraction by chlorine atom. A predominant dependence on the degree of substitution at the carbon atom being attacked is noted in that the three olefins having a single chloro substituent at that carbon (II, III, and IV) show similar dependence on solvent while those with zero and two substituents at that carbon (I and V) show a different dependence (*cf.* also column 2 of Table IX).

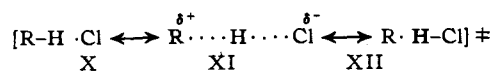
The abstraction behavior of the solvated chlorine atom has been interpreted in terms of attack of a stabilized and hence less electrophilic radical the transition state for which will be further along the reaction coordinate than that for the unsolvated atom. (This implies that the absolute rate of attack even on tertiary hydrogens is much slower for the complexed atom; unfortunately, no absolute rate constants are available.) Such a change should result in greater contribution of any factors which tend to stabilize the incipient radical or charge-separated structures such as XI.^{4,38} Extension of this approach to addition reactions would predict a greater contribution of structure IX (and VII and VIII) compared to VI to the transition state for the solvated chlorine atom. On this basis, olefins

(36) J. A. Leermakers and R. G. Dickinson, *J. Am. Chem. Soc.*, **54**, 4648 (1932); R. G. Dickinson and J. L. Carrico, *ibid.*, **56**, 1473 (1934).

(37) P. B. Ayscough, A. J. Cocker, and F. S. Dainton, *Trans. Faraday Soc.*, **58**, 284 (1962).

(38) G. A. Russell, *Tetrahedron*, **5**, 101 (1960); see also J. M. Tedder, *Quart. Rev. (London)*, **14**, 336 (1960).

bearing the same number of stabilizing chloro substituents on the carbon atom where the radical would ultimately reside (the set I, IV, and V and the set II and III) should show similar sensitivity to solvent. This is not the observed result; several factors may have contributed to the breakdown of the analogy.



For example, the less electrophilic complexed chlorine atom must probably be closer to the olefin at the transition state and at the same time is probably an effectively larger attacking species; this change would enhance the steric effect. Or, changing both the electrophilicity of the attacking species and the geometry of the transition state should change the polar repulsive forces between the attacking radical and olefin. Or, the strength of the bond being formed should affect the rates more and more as the transition state begins more and more to resemble products; there is evidence to suggest that the exothermicity of reaction 3 decreases from 23 to 17 kcal./mole as more and more chloro substituents are placed on olefin A.²²

Examination of Table IX reveals that a similar rate order is observed for: (1) attack of a very electrophilic radical on electron-poor olefins proceeding with a very low activation energy (chlorine atom on chloroethylenes), (2) attack of a resonance-stabilized radical on electron-poor olefins (polystyryl radical on chloroethylenes),^{34a} and (3) attack of a neutral or slightly nucleophilic radical on electron-rich olefins proceeding with a higher activation energy (methyl radical on methylethylenes)²⁹; one might well have expected different rate orders owing to different contributions from the structural factors outlined in the preceding discussion. It seems, therefore, that any decision concerning the relative importance of these factors must await further data, particularly absolute rate constants.

Solvent effects on both chlorine atom addition and abstraction reactions having been demonstrated, the solvent effects on addition:abstraction ratios in the competitive reactions between olefins I-V and cyclohexane are the expected consequence as shown in Table VI. The magnitude of such effects should depend on the type of hydrogen atom chosen as standard; comparison to a tertiary hydrogen atom would be expected to give smaller apparent effects than comparison to a primary hydrogen. The agreement of the relative k_3 values in the complexing solvents as determined by direct competition between the olefins and by indirect competition of each olefin with cyclohexane for olefins II, III, and IV (columns 2-4 of Table VII) is consistent with the description of the systems given herein. Whether the lack of agreement for I is due entirely to telomerization is not certain.

Having observed solvent effects on addition:abstraction ratios for chlorine atom in such intermolecular competitions, one predicts that solvent could be used to control the intramolecular competition which occurs during radical chlorination of simple olefinic hydrocarbons. In fact, we have demonstrated that the ratio of addition to allylic hydrogen abstraction for liquid-phase radical chlorination of cyclohexene^{12a} can be increased from ~ 2 in noncomplexing solvents to >25

in a large excess of carbon disulfide.³⁹ In comparison, solvent has no significant effect on addition:abstraction ratios for the trichloromethyl radical as shown in Table VIII. Association between trichloromethyl radicals and aromatic nuclei has recently been postulated⁴⁰ as a step in the reaction of trichloromethyl radicals with ω -phenylalkenes where an intramolecular shift of the radical from the aromatic ring to the double bond is envisioned. However, even if this less electrophilic radical does indeed complex to a certain extent with aromatic molecules, a solvent effect on an intermolecular competition is not a necessary result. Such complexed radicals either could have reactivity similar to that of uncomplexed radicals or they could be so unreactive that the major portion of reaction proceeds through a minor fraction of uncomplexed radicals. Whatever the exact reason, the lower reactivity of trichloromethyl radical compared to chlorine atom precludes the possibility of using solvent to control addition:abstraction ratios for the former radical.

Experimental

Materials.—1,1-Dichloroethylene (I), *cis*- (II) and *trans*-1,2-dichloroethylene (III), trichloroethylene (IV), and tetrachloroethylene (V) were commercial materials distilled from Drierite, and center cuts were used for all relative rate runs. Olefin I was stored over a few crystals of hydroquinone to prevent polymerization. Olefins II and III each contained $<0.5\%$ of the other by g.l.c. analysis. Cyclohexane was washed with sulfuric acid, washed with water, dried, and distilled from sodium. 1,1,2-Trichlorotrifluoroethane, benzene, carbon disulfide, and carbon tetrachloride were commercial materials distilled from appropriate drying agents. Chlorine was passed through sulfuric acid before being condensed in appropriate traps. Bromotrichloromethane was distilled and a center cut retained. Cyclohexene and 1-octene were distilled from sodium; cyclopentene (Matheson Coleman and Bell) was used without further purification.

Yields of 1:1 Addition Products.—The olefin in question (~ 5 ml.) was placed in a 15-ml., three-necked flask equipped with a condenser, nitrogen inlet tube, and magnetic stirring bar and immersed in a constant temperature bath at 25.0°. After the solution was flushed with nitrogen, a measured aliquot of chlorine solution in carbon tetrachloride (~ 5 ml., ~ 1.75 mmoles of chlorine) was added; at the same time, an aliquot was added to excess aqueous potassium iodide solution and the iodine released titrated with standard sodium thiosulfate solution. The contents of the flask were stirred and illuminated with a 275-watt sunlamp at 12-18 in. to induce reaction. When the reaction mixture was colorless (2-5 min.), a measured amount of cyclohexyl chloride was added as an internal standard for g.l.c. analysis. Analyses were performed at 125° on Perkin-Elmer column "B" (bis(2-ethylhexyl) sebacate). Areas were determined from the product of peak height and retention time and corrected to molar ratios by calibration factors determined from standard mixtures of cyclohexyl chloride, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, and hexachloroethane. The response of the latter was nonlinear and analyses were performed with peak areas as close as possible to those in calibration runs. From a knowledge of the number of millimoles of chlorine added compared to the number of millimoles of product formed (based on the number of millimoles of cyclohexyl chloride added), the yields shown in Table I were determined.

Competitive Chlorination of Pairs of Olefins.—Mixtures of the olefins in question, carbon tetrachloride, and the appropriate solvent were made up volumetrically. Initial concentrations (compared to the internal standard carbon tetrachloride) were determined by g.l.c. An aliquot (~ 2 ml.) was placed in a small combustion tube, frozen with liquid nitrogen, and evacuated to <0.1 mm. Chlorine was distilled into the tube from a trap and frozen above the sample. The tube was then pressurized

(39) M. L. Poutsma, unpublished results.

(40) M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.*, **86**, 233, 238, 242 (1964).

to 1 atmosphere with nitrogen, sealed, and quickly brought to 25.0° in a constant temperature bath in subdued light. Reaction was induced with a 275-watt sunlamp at 12–18 in. Final concentrations were determined by g.l.c.; two chlorinations were performed for each initial mixture. Most analyses were performed at 55° (70° for mixtures containing V) on column "B"; Perkin-Elmer columns "A" (diisodecyl phthalate) and "R" (polypropylene glycol) are also suitable in most cases. Areas were determined from the product of peak height and retention time (essentially no changes in the latter) and used to solve eq. 10 to give the results shown in Tables II and V.

Competitive Chlorination of Olefins and Cyclohexane.—The appropriate mixture of olefin, cyclohexane, and solvent was placed in a flask equipped as for the yield determinations. After the solution was flushed with nitrogen, chlorine (previously measured out in a graduated cold trap) was swept into the solu-

tion with nitrogen in the dark; reaction was initiated with illumination as before; g.l.c. analyses for cyclohexyl chloride and the appropriate polychloroethane were performed on column "A"; areas were determined by planimeter and corrected to molar ratios by calibration factors as before; the calibration factors for areas determined by planimeter and determined from the product of peak height and retention time were determined separately and were almost identical. These values were used to solve eq. 13 to give the results listed in Tables III and VI.

Bromotrichloromethane-Olefin Reactions.—The procedure was essentially identical to that of Huyser²⁷; g.l.c. analyses were carried out on Perkin-Elmer column "O" (silicone grease) at 78° for bromotrichloromethane, chloroform, and the solvent which served as an internal standard; areas were determined by planimeter and, after proper calibration, used to solve eq. 14 to give the results listed in Table VIII.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

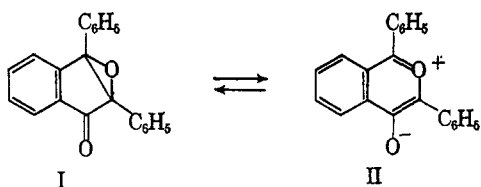
Photochemical and Thermal Valence Tautomerization of 2,3-Diphenylindenone Oxide. II¹

BY EDWIN F. ULLMAN AND JOHN E. MILKS

RECEIVED APRIL 8, 1964

Heat or ultraviolet light partially converts 2,3-diphenylindenone oxide (I) to an aromatic valence tautomer, the red 1,3-diphenyl-2-benzopyrylium 4-oxide (II). Both the thermal and photochemical processes are reversible. The chemistry of the red species is discussed.

Numerous indenone oxide derivatives have been reported to display unusual photochromic and thermochromic properties.² These phenomena have generally been dismissed as evidence for thermal and photochemical decomposition and have not been carefully studied. The existence of these color reactions suggested the possibility of a reversible valence tautomerization of the pyrylium oxide II with the structure I, which is *formally* a canonical form of II. At the outset of this study such a valence tautomerization of a benzenoid system was without precedent, although the photochemical interconversion of *o*-di-*t*-butylbenzene to its "Dewar" bicyclo[2.2.0]hexadiene tautomer has since been reported.³



Since 2,3-diphenylindenone oxide (I) was readily accessible and was the only indenone oxide derivative which had been subjected to even a limited study in regard to its color-forming properties, this compound was chosen for the present investigation. The compound was first described by Weitz and Scheffer,^{2a} who reported that on strong heating in an inert solvent or on exposure to diffuse daylight it turned red, and that this red coloration faded on cooling or standing in the dark. Rapid cooling of the hot solutions led to a longer

lifetime of the red color, but rewarming accelerated the fading process. These data led these authors to conclude that the red species was probably a transient radical-like intermediate which was present in very low concentrations. This conclusion was supported by the observation that after 24–48 hr. a refluxing xylene solution was no longer red and the indenone oxide I could not be recovered.

Reinvestigation of the properties of I confirmed these observations. The red species observed on heating or on ultraviolet irradiation of the solid compound or its solutions proved to be very sensitive to numerous reagents. While fading generally occurred in benzene solution in a few minutes at room temperature, the rate could be greatly reduced by careful exclusion of oxygen, or greatly accelerated by peroxides, halogens, acids, bases, and mercaptans, all of which presumably reacted directly with the red compound.

Intensely colored solutions could be developed by rapid heating up to near 200° or by long irradiation in deoxygenated benzene solutions with filtered (3200–3900 Å.) light from a high pressure mercury arc. The color intensity attained by irradiation proved to be very dependent on wave length. Unfiltered light was less effective in producing the colored species while visible radiation (>4500 Å.) led to rapid and complete decoloration of previously colored solutions. Thus the photostationary state concentrations of the red species appeared to be dependent principally on the ratio of light absorbed by the red compound to that absorbed by the indenone oxide I, and represented steady-state concentrations of either an intermediate in an irreversible rearrangement or a tautomer in true photoequilibrium with I.

Ultraviolet irradiation (2600–3900 Å.) of a benzene solution of the indenone oxide I led to the appearance of a sharp new peak in the infrared at 6.38 μ suggestive of the enolate-like C–O grouping in II together with a weaker peak at 8.03 μ . A simultaneous and

(1) A preliminary report of this work has appeared previously: E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **84**, 1315 (1962).

(2) (a) E. Weitz and A. Scheffer, *Chem. Ber.*, **54**, 2327 (1921); (b) C. F. H. Allen and J. W. Gates, Jr., *J. Am. Chem. Soc.*, **65**, 1230 (1943); (c) R. DeFazi and A. Banchetti, *Gazz. chim. ital.*, **76**, 283 (1946); (d) A. Banchetti *ibid.*, **76**, 459 (1946); (e) R. DeFazi and S. Carboni, *ibid.*, **78**, 567 (1948); (f) S. Carboni, *ibid.*, **81**, 225 (1951); (g) L. A. Shchukina and E. P. Semkin, *J. Gen. Chem. USSR*, (Eng. trans.), **32**, 476 (1962).

(3) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).