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Beckmann Rearrangement. II. Salt Effects in the Acetolysis of Cyclopentanone and Cyclohexanone Oxime *p*-Toluenesulfonate

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The rate-determining step in the acetolysis of cyclopentanone oxime *p*-toluenesulfonate is the dissociation of an ion pair, presumably an ion pair containing an azacyclopropene ring system as the cation. Exchange of the *p*-toluenesulfonate ion with perchlorate and chloride ions yields intermediates which show characteristic rates of acetolysis. The normal primary salt effect is relatively small in the acetolysis of cyclopentanone and cyclohexanone oxime *p*-toluenesulfonates.

Pearson[1] and more recently Huisgen[2] and coworkers studied the kinetics of rearrangement of substituted acetophenone and cycloalkanone oximes in sulfuric acid and 1,4-dichlorobutane, respectively, and suggested that the rearrangement proceeds with the anchimeric assistance of the migrating group. Such anchimeric assistance of the migrating group would give rise to the azacyclopropene ring system in the transition state. The azacyclopropene ring system was identified by Neber[3] as a reaction intermediate in the Neber rearrangement and more recently by Cram[4] and coworkers. This paper describes the kinetic isolation of a stable ion pair in the acetolysis of cyclopentanone oxime *p*-toluenesulfonate, the cation of which is believed to contain the azacyclopropene ring system.

Experimental

Starting Materials.—The synthesis of oxime *p*-toluenesulfonates was described in a previous paper.[5] The pure oxime *p*-toluenesulfonates could be stored in the refrigerator for more than a year without any decomposition. Cyclopentanone oxime *p*-bromobenzenesulfonate was synthesized from *p*-bromobenzenesulfonyl chloride (21.8 g., 0.1 mole) and sodium cyclopentanone oxime (13.3 g., 0.11 mole) as described previously for the *p*-toluenesulfonate esters.[5] After three recrystallizations from carbon tetrachloride the yield of pure cyclopentanone oxime *p*-bromobenzenesulfonate was 78%, m.p. 67.5–68.0°.

Anal. Calcd. for $C_{11}H_{12}NO_3SBr$: C, 41.52; H, 3.80; N, 4.40. Found: C, 41.90; H, 4.31; N, 4.56.

Solvents.—Acetic acid (100%) was prepared by refluxing 99.7% acetic acid (du Pont Co., C.P.) with the calculated amount of acetic anhydride for 24 hours. The freezing point of the acetic acid prepared in this way was 16.65°. (The reported freezing point of 100% acetic acid is 16.65°.)[6]

Absolute methanol was prepared by the method of Fieser[7] by refluxing methanol (Baker Chemical Co., analyzed reagent grade) with metallic magnesium and subsequently distilling the pure methanol. Karl Fischer determination[8] indicated that the methanol contained 0.0218% or less water. Chloroform (J. T. Baker Chemical Co., reagent grade) was distilled over phosphorus pentoxide. The heart cut, b.p. 61°, $n^{25}D$ 1.4992, was used for the rate experiments.

Acetic acid, methanol and chloroform were stored in automatic buret assemblies which were protected from moisture by Drierite[9] tubes.

Inorganic Salts.—Sodium *p*-toluenesulfonate and sodium *p*-bromobenzenesulfonate (Eastman Chemical Co.) were recrystallized three times from distilled water and dried for 41 hours at 100°. Sodium perchlorate and lithium chloride (J. T. Baker Chemical Co., C.P.) were dried, without further purification, for about 40 hours at 100°. Karl Fischer determination[8] in absolute methanol showed that the salts did not contain more than 0.0005% water.

Rate Determination in Glacial Acetic Acid.—The rates of acetolysis in 100% acetic acid were determined in a Bartlett–Swain titration cell[10] by the method of Roberts and coworkers,[11] *i. e.*, the *p*-toluenesulfonic acid produced was titrated intermittently with standard sodium acetate using one ml. of a 0.1% brom phenol blue solution in 100% acetic acid as indicator. To provide a better contrast for reading the end-point, a white stripe was painted on the outside of the cell. Standard sodium acetate was prepared by dissolving a calculated amount of sodium acetate (anhydrous C.P., freshly dried for two hours at 100°) in 100% acetic acid and standardizing the solution against an analyzed sample of *p*-toluenesulfonic acid monohydrate as the primary standard. The normality of the sodium acetate used throughout the experiments was 0.07. A 10-ml. micro-buret standardized to A. H. Thomas specification was used.

The following is a typical run: 65 ml. of 100% acetic acid and one ml. of 0.1% brom phenol blue were thermostated to 35.82 ± 0.05°. With rapid stirring 199 mg. of cyclopentanone oxime *p*-toluenesulfonate was added to the thermostated cell; the time of addition was considered to be zero time. The rate of reaction was followed by titration with 0.0696 *N* sodium acetate in 100% acetic acid until the faint yellow color of the indicator appeared. The rate of *p*-toluenesulfonic acid formation which is equal to the rate of acetolysis was evaluated from the first-order equation

$$k = \frac{2.303}{(t - t_0)} \log \frac{V_\infty - V_0}{V_\infty - V}$$

where

V_∞ = vol. of NaOAc consumed at infinite time
V_0 = vol. of NaOAc consumed at zero time, t_0
V = vol. of NaOAc consumed at given time, t

The results of a typical rate determination are presented in Table I. The averate mean deviation when 88.5% of the reaction was complete was found to be $k = 6.06 \times 10^{-4} \pm 0.25$ by calculating the rate constant for each adjacent pair of points from the integrated equation. All rates were calculated by the least-squares method (see Table I).

Salt effects were measured by addition of the salt (weighed to the nearest mg. or 1%, whichever was the more accurate method) to 64 ml. of 100% acetic acid and employment of the analytical technique described previously. The measurement of salt effects generally was limited by the solubility of the salt in 100% acetic acid and by indicator–salt error.[12] Beyond certain initial salt concentrations the indicator change was too sluggish for accurate determination. The determinations of salt effects of sodium perchlorate upon the

(1) (a) D. E. Pearson and W. E. Cole, *J. Org. Chem.*, **20**, 488 (1955); (b) D. E. Pearson, J. F. Baxter and J. C. Martin, *ibid.*, **17**, 1511 (1952); (c) D. E. Pearson and E. D. Watts, *ibid.*, **20**, 494 (1955); (d) D. E. Pearson and F. Greer, THIS JOURNAL, **77**, 6649 (1955).

(2) (a) R. Huisgen, I. Ugi, M. Assemi, J. Witte, H. Walz and W. Jira, *Chimia (Switz.)*, **11**, 266 (1956); (6) R. Huisgen, I. Ugi, M. Assemi and J. Witte, *Ann.*, **602**, 127 (1957).

(3) P. W. Neber and A. Friedelsheim, THIS JOURNAL, **449**, 109 (1926), and later papers.

(4) D. J. Cram and M. L. Hatch, *ibid.*, **75**, 35 (1953).

(5) W. Z. Heldt, Part I, *ibid.*, **80**, 5880 (1958).

(6) A. Weissbergber, "Technique of Organic Chemistry," Interscience Publishers Inc., New York, N. Y., 1955, Vol. VII, p. 145.

(7) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 359.

(8) J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

(9) W. A. Hammond Drierite Co., Xenia, Ohio.

(10) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **71**, 1406 (1949).

(11) J. D. Roberts, W. E. Young and S. Winstein, *ibid.*, **64**, 2157 (1942).

(12) W. Rieman, III, J. D. Neuss and B. Naiman, "Quantitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1942, p. 74.

TABLE I

DETERMINATION OF THE RATE CONSTANT OF ACETOLYSIS OF CYCLOPENTANONE OXIME *p*-TOLUENESULFONATE (193 MG.) IN 65 ML. OF 100% HOAc at 35.82 ± 0.05°

Time, sec.	0.0696 *N* NaOAc added, ml.	$k \times 10^4$, sec.$^{-1}$
60	1.04	..
115	1.37	5.99
185	1.78	6.01
250	2.08	..
350	2.62	5.99
450	3.16	6.42
525	3.52	..
650	4.08	5.96
775	4.60	5.96
1025	5.49	5.71
1210	6.17	6.72
1360	6.64	6.40
1700	7.48	5.41
2130	8.39	6.33
2325	8.73	6.38
2680	9.21	5.97
3050	9.59	5.30
3700	10.00	6.22
		Av. 6.06 ± 0.25

rate of solvolysis were inaccurate when the ionic strength at zero time was greater than 0.125 for cyclopentanone oxime *p*-toluenesulfonate and 0.154 for cyclohexanone oxime *p*-toluenesulfonate because of the indicator error. For lithium chloride, the indicator error became very large when the initial ionic strength was greater than 0.050. Determinations of salt effects with sodium *p*-bromobenzenesulfonate were limited by the solubility of the salt in 100% acetic acid.

Rate Determinations in 100% Methanol.—The rates of methanolysis of oxime *p*-toluenesulfonates were determined in a Bartlett–Swain titration cell.[10] The upper part of the cell was modified slightly to provide two openings into which the glass and the calomel electrodes fitted tightly and dipped into the solution. The reaction rate was measured by potentiometric titrations of the *p*-toluenesulfonic acid evolved with standard sodium methoxide (Humphrey Wilkinson Chemical Manufacturers) to *p*H 8.0. Sodium methoxide was standardized potentiometrically by means of glass and calomel electrodes against hydrochloric acid as a primary standard. The normality of the sodium methoxide used was 0.07. The cell was thermostated in the following solvents at their freezing points: *p*-xylene, m.p. 13.35°; benzene, m.p. 5.3°; water, m.p. 0°. The rates at high temperature were measured in a constant temperature water-bath. In a typical run, 398 mg. of cyclohexanone oxime *p*-toluenesulfonate was added to a rapidly stirred solution of 65 ml. of 100% methanol thermostated at 13.30 ± 0.05°. The solution was titrated intermittently with 0.069 *N* sodium methoxide from a calibrated 10-ml. buret (A. H. Thomas) to *p*H 8.0. The results of a typical run are summarized in Table II.

Up to about 80% of completion of the reaction, the average deviation in the rate constant in the example given was about ±0.053 or ±6%. All rates were calculated by the least-square method, which reasonably agreed with the rates as calculated from the plots of log $(V_\infty - V)$ *vs.* time. Salt effects were measured as described previously.

Partial Rearrangement of Cyclopentanone Oxime *p*-Toluenesulfonate.—Cyclopentanone oxime *p*-toluenesulfonate (1.1 g., 4.348 mmoles) was dissolved in 30.0 g. of dry chloroform and tubes containing 5.5 g. of this solution were sealed and kept at 90.2 ± 1.0° for various lengths of time. The content of each tube was analyzed spectrophotometrically[13] for the presence of the starting material. The chloroform was then evaporated under vacuum (about 0.1 mm.) and the residue was weighed, placed into 100% acetic acid, and the rate of acetolysis was determined by titration with standard sodium acetate at 35.0 ± 0.5° as described above. Since the final product of rearrangement does not solvolyze under these conditions, the untitratable part of the products of rearrangement in chloroform was assumed to be N-(*p*-toluenesulfonyl)-valerolactam. The amount of O-(*p*-toluenesulfonyl)-valerolactim was calculated by the difference between the total standard solution of sodium acetate consumed and the amount of oxime *p*-toluenesulfonate as determined by infrared measurement.

(13) W. Z. Heldt, being submitted to THIS JOURNAL, Part III.

TABLE II

DETERMINATION OF THE RATE CONSTANT OF METHANOLYSIS OF CYCLOHEXANONE OXIME *p*-TOLUENESULFONATE (393 MG.) IN 65 ML. OF 100% METHANOL AT 13.30 ± 0.05°

Time, sec.	0.0690 *N* $NaOCH_3$ added, ml.	$k \times 10^4$, sec.$^{-1}$
94	4.71	..
165	5.70	8.43
272	7.03	8.08
377	8.24	8.18
520	9.70	9.60
757	11.74	6.84
885	12.73	8.27
1020	13.68	8.22
1160	14.48	7.46
1310	15.20	7.37
1490	16.02	8.34
1635	16.61	7.51
1835	17.30	7.21
1960	17.70	7.51
		Av. 7.89 ± 0.53

The amount of O-(*p*-toluenesulfonyl)-valerolactim calculated in this manner agreed with the amount as determined from the difference between V_0 and V_1, V_1 being the intercept of the titration curve, extrapolated to zero time, with the log $(V_\infty - V_0)$ axis. The results are summarized in Table III.

Results and Discussion

Acetolyses of Oxime *p*-Toluenesulfonates.—In the preceding paper in the series[5] it was reported that the only primary product of acetolysis was apparently the O-acetylimine which yields with an excess of acetic acid, the amide and acetic anhydride. The rate was strictly first order up to at least 85–90% completion of the reaction. No curvature was observed up to at least 85% of reaction when the rate was evaluated from a plot of log $(V_\infty - V)$ *vs.* time. The relative mean deviation of the rate constant was ±4% (see Table I). A 2.5-fold increase in the initial concentration of cyclohexanone oxime *p*-toluenesulfonate from 80 to 200 mg. per 65 ml. of 100% acetic acid increased the rate constant from $14.27 \pm 0.42 \times 10^{-4}$ to $15.13 \pm 0.58 \times 10^{-4}$ sec.$^{-1}$ or still within experimental error. Therefore, we may assume reaction was first order in oxime tosylate.

Pearson[1] and more recently Huisgen[2] pointed out that in concentrated sulfuric acid and 1,4-dichlorobutane, the transition state of Beckmann rearrangement may have an azacyclopropene ring system if the migrating group is phenyl or substituted phenyl. The suggestion of Pearson and Huisgen was based upon determination of electronic effects of the migrating group and considerations of the stereochemistry of the initial and transition state. Further evidence for such transition state was clearly desirable. The acetolysis of I may proceed in the several ways indicated below, each of which may generate *p*-toluenesulfonic acid.

The rate as determined here is necessarily the slow step in the acetolysis. We wished definitely to

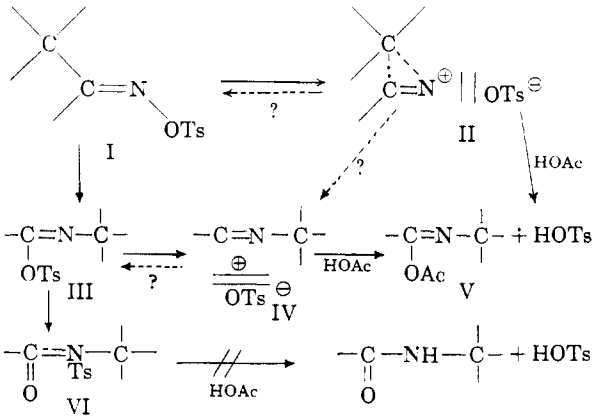
TABLE III

PARTIAL REARRANGEMENT OF CYCLOPENTANONE OXIME *p*-TOLUENESULFONATE (1.100 g.) IN CHLOROFORM (30.000 g.) AT 90.2 ± 1.0°

Run	Reacn. time in $CHCl_3$ at 90.2°	Absorption at 11.55 μ	Final oxime *p*-toluenesulfonate %	M mole	Total mixture, mmole	O-(*p*-Toluenesulfonyl) lactim, mmole	N-(*p*-Toluenesulfonyl) lactam,[a] mmole	Rate constant of acetolysis in 100% HOAc at 35.5 ± 0.05° $k \times 10^4$, sec.$^{-1}$
1	10	0.510	88.6	0.609 (.605)[b]	0.690	0.082	...	6.45
2	25	.460	77.7	.533	.690	.088	0.077	6.47
3	60	.338	55.8	.383	.690	.105	.160	5.76
4	80	.305	50.5	.340 (.338)[b]	.690	.175	.157	6.68

[a] N-*p*-(Toluenesulfonyl)-valerolactam is assumed to be the material which does not solvolyze in acetic acid. [b] Determination of oxime *p*-toluenesulfonate by titration to V_∞.

determine whether the solvolysis of I, III or VI is rate determining.



Rearrangement of cyclopentanone oxime *p*-toluenesulfonate (I) in chloroform, and possibly in other chlorinated solvents, proceeds with initial formation of the O-(*p*-toluenesulfonyl)-valerolactim (III) which rearranges slowly to the corresponding N-(*p*-toluenesulfonyl)-valerolactam (VI).[13] The transitory intermediate in the reaction can be clearly identified in the infrared spectrum.[13] Kuhara[14] has shown that the imine derivatives solvolyze in water and Bordwell[15] and Huisgen[2b] demonstrated that the N-substituted amide is quite stable under these conditions. Similarly, we found that N-(*p*-toluenesulfonyl)-valero- and caprolactam do not solvolyze when heated to the boiling point in 100% acetic acid.

To determine whether III precedes the rate-determining step, as suggested above, compound I was partially rearranged in chloroform to III and VI (Table III).

The amounts of I and III after 60 minutes at 90.2° (run 3, Table III) in the partially rearranged mixture were 55.8 and 15.2%, respectively. Since the rate constant of solvolysis of this mixture was equal to that of I, either I or III must solvolyze very rapidly as compared to the other one. Since the amount of the material solvolyzing at a slow rate as determined by titration (Fig. 1) is equivalent to the amount of I as determined by an infrared spectroscopic method, the slow step in the acetolysis must be the acetolysis of I. The rate-determining step must, therefore, *precede* the formation of III.[16] The rate constants of four acetolyses of partially rearranged I are represented in Table III. Run 3 of Table III is plotted in Fig. 1.

Salt Effects and Ion Pairs in Acetolyses of Oxime *p*-Toluenesulfonates.—Winstein and co-workers[18] investigated the salt effects in the acetolysis of a number of anchimerically assisted bridged carbonium ions by a combination of salt effects and polarimetric measurements. They were able to isolate kinetically the ion pairs involved in the rearrangement.[19] This technique appears to be a very useful tool in the kinetic isolation of other anchimerically assisted bridged carbonium ions in systems where such ions could be determined only with difficulty.

As pointed out in the above equation, the acetolyses of oxime *p*-toluenesulfonates proceed *via* II which could represent either the transition state or conceivably a fairly stable reaction intermediate. The rate-determining step in the reaction could then be the acetolysis of II or the acetolysis of VII to products.[18a]

The rate constant of acetolysis of cyclopentanone oxime *p*-toluenesulfonate (Ia) was 6.06 ± 0.25 × 10^{-4} at 35.82° and that of cyclopentanone oxime

(14) M. Kuhara, a monograph edited by S. Komatsu incorporating the complete work of Kuhara and entitled: "M. Kuhara on the Beckmann Rearrangement," Imperial University, Tokyo, 1926 (in English).

(15) F. G. Bordwell and B. B. Lampert, THIS JOURNAL, **73**, 2369 (1951).

(16) Addition of sodium acetate to the acetolysis of I did not produce an oxime acetate. Several additional attempts were made to isolate other oxime derivatives such as cyclohexanone oxime brosylate and chloride in the acetolysis of cyclohexanone oxime *p*-toluenesulfonate in excess of sodium brosylate and sodium chloride, respectively. No such derivatives of oximes were detected. Therefore, the formation of II from I must be irreversible. The added anion $OBr^\ominus$ did not displace $OTs^\ominus$ in Ia by an S_N2 process since *syn*-methylphenyl ketoxime yielded only acetanilide as the only reaction product. Since the group *anti* to the departing $OTs^\ominus$ group migrates in the Beckmann rearrangement[17] and a S_N2 process on the nitrogen of the oxime implies an inversion of *syn* to *anti* preceding the rearrangement, no such inversion could have occurred under the reaction conditions employed.

As reported previously,[5] acetolysis of 5 *M* solution of I yields *p*-toluenesulfamido-δ-valeric acid in 8% conversion. This result indicates that in concentrated solution the formation of III, which probably proceeds *via* an ion return: I → II → IV → III, competes favorably with the acetolysis of II or IV.

(17) J. Meisenheimer, *Ber.*, **54**, 3206 (1921).

(18) (a) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (c) S. Winstein and K. C. Schreiber, *ibid.*, 2171 (1952); (d) S. Winstein, E. Clippinger, A. Fainberg and G. C. Robinson, *Chemistry & Industry*, 664 (1954), and subsequent papers.

(19) Winstein distinguishes two types of ion pairs which may occur in the acetolysis of an alkyl halide or sulfonate ester: an "intimate ion pair" and a "solvent separated ion pair." Since we do have experimental evidence only for an ion pair, no distinction is made between these two types of ion pairs.

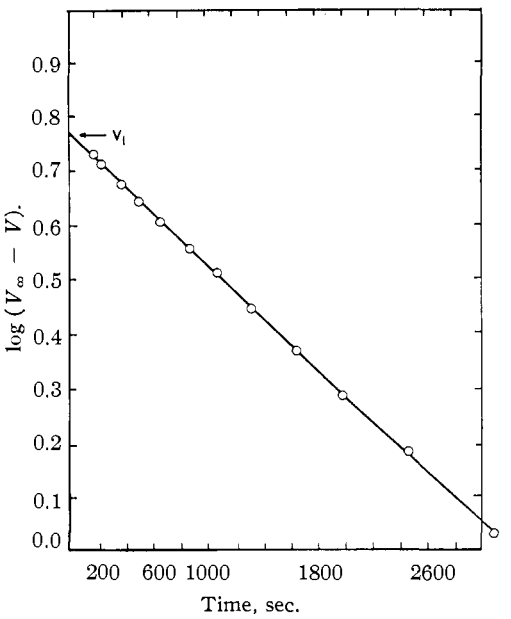
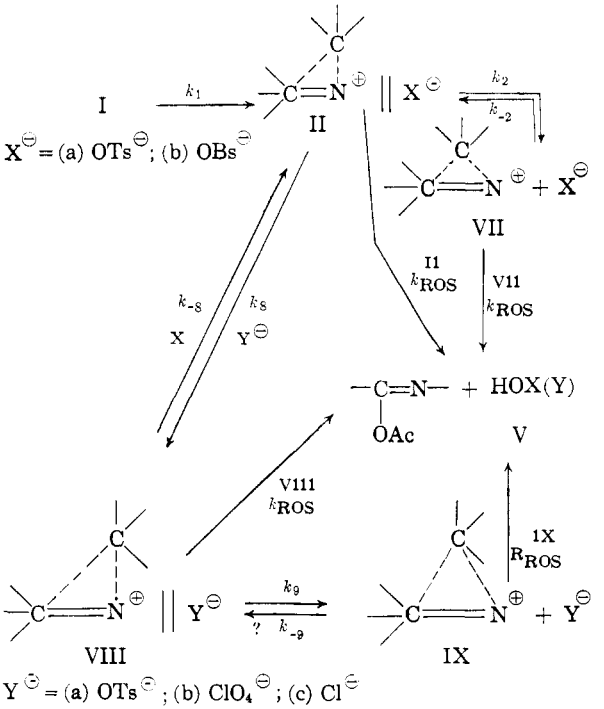


Fig. 1.—Table III, run 3; acetolysis of partially rearranged cyclopentanone oxime *p*-toluenesulfonate: NaOAc = 0.07 *N*, V_∞ = 9 ml., V_1 = 1.5 ml., T = 35.50 ± 0.05°.

p-bromobenzenesulfonate (Ib), 17.47 ± 0.70 × 10^{-4} sec.$^{-1}$ at the same temperature. When Ia was solvolyzed in the presence of sodium *p*-bromobenzenesulfonate, essentially no change in the rate of reaction was observed (6.35 ± 0.30 × 10^{-4} at μ_{0NaOBs} = 2.1 × 10^{-2}) which probably indicates that no exchange occurred or that the exchange was slow. Unfortunately, the low solubility of sodium *p*-bromobenzenesulfonate excluded an increase of the concentration of the salt to more significant amounts. However, when Ib was solvolyzed in the presence of sodium *p*-toluenesulfonate, a slow



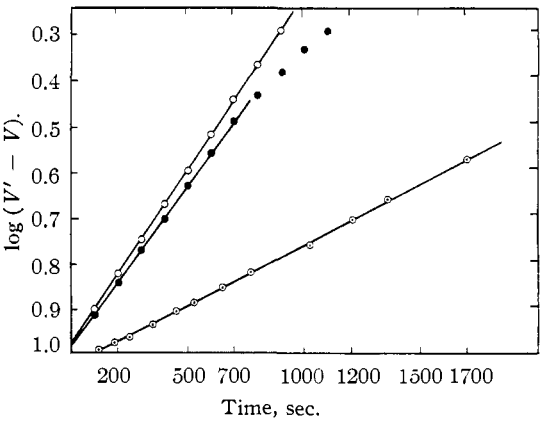


Fig. 2.—Effect of sodium tosylate on the acetolysis of cyclopentanone oxime *p*-toluenesulfonate at T = 35.5 ± 0.1°: ⊙, 0.0122 *M* cyclopentanone oxime *p*-toluenesulfonate (k = 6.06 × 10^{-4} sec.$^{-1}$); ○, 0.0122 *M* cyclopentanone oxime *p*-bromobenzenesulfonate (k = 17.4 × 10^{-4} sec.$^{-1}$); ●, 0.0122 *M* cyclopentanone oxime *p*-bromobenzenesulfonate in the presence of 0.03 *M* NaOTs.

exchange reaction occurred. The rate up to 62% of the reaction was between the rate of reaction of Ia and Ib indicating a composite rate of Ia and Ib. Beyond 62% of reaction, the rate declined (Fig. 2 and Table IV). Apparently an exchange between $OTs^\ominus$ and $OBs^\ominus$ is taking place. As the concentration of added $OTs^\ominus$ was increased in the acetolysis of Ib, the rate was linear for decreasing percentages of complete reaction (62% of reaction at initial ionic strength μ_{0NaOTs} = 3.0 × 10^{-2} to about 54% of reaction at μ_{0NaOTs} = 9.3 × 10^{-2}). Apparently the rate-determining step in the acetolysis is the solvolysis of the ion pair II or the ion VII. If the foreign ions are added, an exchange may occur (k_8/k_{-8}).

TABLE IV

ACETOLYSIS OF 1.22 × 10^{-2} *M* CYCLOPENTANONE OXIME *p*-BROMOBENZENESULFONATE IN THE PRESENCE OF 3.0 × 10^{-2} *M* SODIUM TOSYLATE

Time, sec.	Reacn., %	0.0700 *N* NaOAc added, ml.	k × 10^4, sec.$^{-1}$	
100	14	1.35	...	
200	26	2.55	15.69	
300	37	3.55	16.10	
400	47	4.50	16.23	16.02
500	55	5.25	15.87	
600	62	5.85	14.84	
700	67	6.45	17.41	
800	71	6.80	12.83	
900	74	7.15	12.10	
1000	77	7.40	10.74	
1100	79	7.60	9.56	

The rate lying between the rates of acetolysis of Ia and Ib but having no curvature up to about 60% reaction can be reationalized by assuming a rapid equilibrium of the ion pair II with ion pair VIII compared to the rate of solvolysis (which equilibrium is solely dependent upon the ratio of the rates of exchange (k_8/k_{-8}). Since the exchange reaction is rapid as compared to solvolysis and the ratio $X^\ominus/Y^\ominus$ will remain constant during an initial period of a run, the relative ratios k_8/k_{-8} will remain con-

stant and the rate should show no curvature during an initial period of the run.[20,21])

Added sodium perchlorate considerably increased the initial rate of acetolysis of Ia. The rate was again constant up to about 60–70% reaction; thereafter the rate drifted upward. (The higher the initial concentration of sodium perchlorate the earlier the drifting of the rate occurred, as described above.) The rate constant increased linearly with increase of initial ionic strength μ_{0NaClO_4} = 0.43 to about $\mu_{0NaClO_4} = 6.5 \times 10^{-2}$ leveling off at a rate of $11.5 \pm 0.4 \times 10^{-4}$ sec.$^{-1}$. At this ionic strength, all of Ia appears to be converted into VIIIb and the rate is essentially the rate of acetolysis of VIIIb.

Addition of lithium chloride to the acetolysis of Ia decreases the initial rate. When $\mu_{0LiCl} = 2.0 \times 10^{-2}$ the rate constant leveled off at $4.3 \pm 0.2 \times 10^{-4}$ sec.$^{-1}$, apparently the rate of acetolysis of VIIIc. Sample runs which demonstrate such exchange of anions in the ion pair are summarized in Table V and are plotted in Fig. 3.

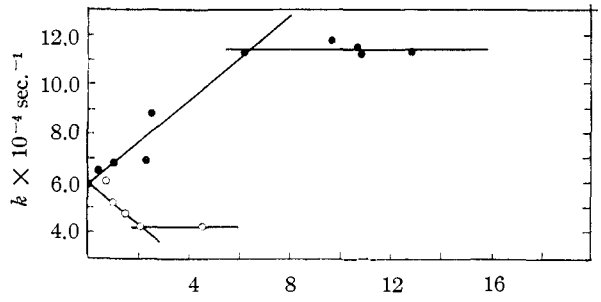


Fig. 3.—Effect of $NaClO_4$ and LiCl on the rate of acetolysis of cyclopentanone oxime *p*-toluenesulfonate at T = 35.35 ± 0.05°: •, $NaClO_4$; O, LiCl.

Superimposed upon the exchange reaction is the so-called "normal salt effect."[22] This is an increase in the rates of acetolysis due to an increase of dielectric constant of the medium with increasing ionic strength.[23] Addition of sodium perchlorate to the solvolysis increases the rate by both an exchange reaction and "normal salt effect." The sum of these two effects may be established qualitatively from the slope of the rate constant *vs.* μ_{0NaClO_4} which indicates the increase of rate per 0.01 *M* of sodium perchlorate added. The "normal salt effect" is probably $NaClO_4$ > NaOTs.[22a] The "normal salt effect" is furthermore approximately additive for a mixture of salts.[24] When a salt mixture of two salts was added to the acetolysis of Ia and the initial ionic strength was kept constant (Table VI), no curvature was observed in the plot of the rate constant *vs.* μ_{0NaClO_4} (at $\mu_0 = \Sigma\mu_{0NaClO_4} + \mu_{0NaOTs}$ = const.) with increasing amount of

(20) (a) For a similar case see S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 333 (1956); (b) *ibid.*, footnote 18.

(21) The author is indebted to Dr. G. R. Coraor, who suggested this explanation.

(22) (a) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2780 (1956); (b) S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).

(23) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 360.

(24) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2763 (1956).

TABLE V

EFFECT OF SALTS ON RATES OF ACETOLYSIS OF OXIME SULFONATE ESTERS

Temp., °C.	Salt added, meq.		$\mu_0 \times 10^2$ (at zero time)	$k \times 10^4$, sec.$^{-1}$
Cyclopentanone oxime brosylate,[a] 0.079 meq.				
35.35 ± 0.05°	...	...	...	17.50
35.35 ± 0.05°	...	...	...	17.27
35.35 ± 0.05°	NaOTs	1.01	1.55	16.72
35.35 ± 0.05°	NaOTs	2.00	3.07	16.12
35.35 ± 0.05°	NaOTs	3.99	6.14	15.77
35.35 ± 0.05°	NaOTs	6.06	9.32	15.54
Cyclopentanone, oxime tosylate, 0.079 meq.				
35.35 ± 0.05°	...	...	...	6.06
35.35 ± 0.05°	NaOBrS	0.235	0.36	5.32
35.35 ± 0.05°	NaOBrS	0.514	0.79	5.57
35.35 ± 0.05°	NaOBrS	1.012	1.56	5.62
35.35 ± 0.05°	$NaClO_4$	0.28	0.43	6.56
35.35 ± 0.05°	$NaClO_4$	0.68	1.04	6.95
35.35 ± 0.05°	$NaClO_4$	1.54	2.37	7.00
35.35 ± 0.05°	$NaClO_4$	1.64	2.52	8.92
35.35 ± 0.05°	$NaClO_4$	4.05	6.23	11.34
35.35 ± 0.05°	$NaClO_4$	6.00	9.23	11.88
35.35 ± 0.05°	$NaClO_4$	6.97	10.7	11.54
35.35 ± 0.05°	$NaClO_4$	7.04	10.8	11.34
35.35 ± 0.05°	$NaClO_4$	8.41	12.9	11.38
35.35 ± 0.05°	LiCl	0.50	0.77	6.14
35.35 ± 0.05°	LiCl	0.67	1.03	5.25
35.35 ± 0.05°	LiCl	1.00	1.53	4.88
35.35 ± 0.05°	LiCl	1.95	2.10	4.26
35.35 ± 0.05°	LiCl	3.00	4.61	4.37
Cyclohexanone oxime tosylate, 0.074 meq.				
18.35 ± 0.05°	LiCl	...	...	15.13
18.35 ± 0.05°	$NaClO_4$	0.29	0.446	17.82
18.35 ± 0.05°	$NaClO_4$	1.58	2.43	19.16
18.35 ± 0.05°	$NaClO_4$	3.44	5.22	28.20
18.35 ± 0.05°	$NaClO_4$	4.48	6.89	28.79
18.35 ± 0.05°	$NaClO_4$	5.93	9.12	32.24
18.35 ± 0.05°	$NaClO_4$	6.02	9.25	33.16
18.35 ± 0.05°	$NaClO_4$	6.54	10.1	30.63
18.35 ± 0.05°	$NaClO_4$	10.00	15.3	41.45

[a] Brosylate = BrS = *p*-$BrC_6H_4SO_2$-; tosylate = Ts = *p*-$CH_3C_6H_4SO_2$-.

μ_{0NaClO_4} (Table V). Such curvatures should appear in the plot, if the "normal salt effect" is considerable and the effect of sodium perchlorate is larger than the effect of sodium tosylate provided the effects of both ions are additive. Furthermore, the slope of the rate constant *vs.* μ_{0NaClO_4} at increasing μ_{0NaClO_4} should be larger than the slope of the rate constant *vs.* μ_{0NaClO_4} at constant ionic strength ($\mu_0 = \Sigma\mu_{0NaClO_4} + \mu_{0NaOTs}$ = const.). For Ia the slope of the rate constant *vs.* μ_{0NaClO_4} at increasing μ_{0NaClO_4} is 1.17×10^{-2} (Table V), for the rate constant *vs.* μ_{0NaClO_4} at constant ionic strength the slope is 0.47×10^{-2} indicating either a very large primary salt effect, which is improbable since addition of NaOTs does not increase the rate constant (Table V and VI), or that an increase in the tosylate ion concentration at constant ionic strength decreases the composite rate of solvolysis of II and VIII, probably by reversing the equilibrium k_8/k_{-8} in favor of II. Acetolysis of cyclohexanone oxime *p*-toluenesulfonate (X) does not

show any "normal salt effect" (Table V and VI). But here the slope of the rate constant *vs.* μ_{0NaClO_4} at increasing μ_{0NaClO_4} is smaller than when plotted *vs.* μ_{0NaClO_4} at constant ionic strength (*ca.* 2.2×10^{-2} and 3.8×10^{-2}, respectively). This effect is at present not yet understood (see Table VII).

TABLE VI

EFFECT OF NaOTs UPON ACETOLYSIS OF CYCLOPENTANONE AND CYCLOHEXANONE OXIME *p*-TOLUENESULFONATES AT CONSTANT IONIC STRENGTH ($\mu_{0NaClO_4} + \mu_{0NaOTs} = \Sigma\mu_0$ = CONSTANT)

OTS derivs. meq.	$NaClO_4$ Meq.	$\mu_0 \times 10^2$	NaOTs Meq.	$\mu_0 \times 10^2$	$\Sigma\mu_0 \times 10^2$	$k \times 10^4$, sec.$^{-1}$
A. Cyclopentanone derivative at T = 35.35 ± 0.05°						
0.79	..	..	4.11	6.32	6.32	6.31
.79	1.11	1.61	2.60	4.00	5.61	7.14
.79	2.11	3.25	2.01	3.10	6.34	7.58
.79	3.10	4.77	0.99	1.52	6.29	8.61
.79	3.59	5.53	0.50	0.77	6.30	8.89
B. Cyclohexanone derivative at T = 13.35 ± 0.05°						
0.74	3.25	5.00	..	..	5.00	22.81
.74	2.25	3.46	1.00	1.54	5.00	22.75
.74	1.78	2.76	1.50	2.30	5.05	21.86
.74	1.26	1.94	1.99	3.06	5.00	18.42
.74	0.79	1.22	2.51	3.86	5.05	15.62
.74	..	..	3.28	5.05	5.05	14.97

TABLE VII

EFFECTS OF (A) $NaClO_4$ AND (B) NaOTS + $NaClO_4$ AT CONSTANT IONIC STRENGTH ON METHANOLYSIS OF CYCLOHEXANONE OXIME *p*-TOLUENESULFONATE AT 13.35 ± 0.05°

OTs derivative, meq.	$NaClO_4$, meq.	$\mu_0 \times 10^2$ (at zero time)	$k \times 10^4$ sec.$^{-1}$
0.74	..	..	7.58
.74	1.19	1.8	8.01
.74	3.27	5.0	8.57
.74	6.46	9.9	9.23

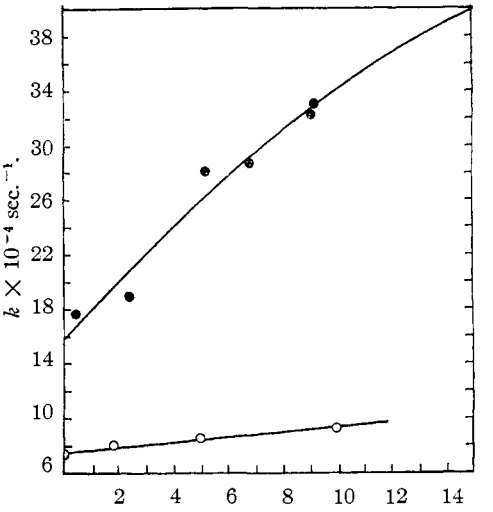
OTs derivative, meq.	$NaClO_4$ Meq.	$\mu_0 \times 10^2$	NaOTs Meq.	$\mu_0 \times 10^2$	$\Sigma\mu_0 \times 10^2$	$k \times 10^4$, sec.$^{-1}$
0.74	6.48	9.96	..	..	9.96	10.23
.74	5.36	8.25	0.98	1.51	9.76	9.95
.74	4.84	7.45	1.99	3.66	10.50	9.76
.74	3.45	5.31	3.00	4.61	9.92	9.86
.74	2.41	3.70	4.00	6.15	9.85	9.86

Rate-determining Step.—Either k_{ROS}^{II} or k_{ROS}^{VII} could actually be the rate-determining step in the acetolysis of Ia. As pointed out above, the solvolysis may proceed by an *exchange* reaction when foreign anions are added but shows no common ion effect (Table VI, VII). This evidence would favor k_{ROS}^{II} as being rate determining. The absence of a common ion effect is not a sufficient condition for the elimination of VII. Winstein[20a] gives three conditions under which the common ion effect will not be visible during a kinetic run as a result of added ion or common ion generated during the reactions: case 1, $k_{ROS}^{VII} >> k_2$, VII is not formed; case 2, $k_{ROS}^{III} >> k_{-2}(X^-)$, VII is formed but not returned; and case 3, $k_{-2}(X^-) >> k_{ROS}^{VII}$, return from VII to II is essentially complete.

Addition of water to 100% acetic acid increases the nucleophilicity of the solvent appreciably.[25] Case 3 requires that the rate of solvolysis of VII be increased with the increase of the nucleophilicity of the solvent. Addition of water does not increase the rate of solvolysis to any extent.[18] Case 3, therefore, does not apply to the acetolysis of Ia.

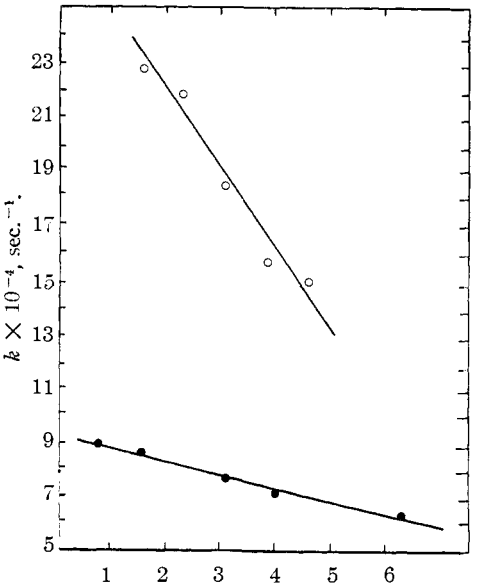
No definite choice can be made between case 1 and case 2 at the present time, but the evidence accumulated thus far appears to favor k_{ROS}^{II} as the rate-determining step.

Effect on Structure.—The rate of acetolysis of cyclohexanone oxime *p*-toluenesulfonate (X) increased with increasing μ_{0NaClO_4}. The rate did not level off at any particular rate in the range of μ_{NaClO_4} investigated as in the case of Ia (Fig. 4).



Initial ionic strength of $NaClO_4$ added ($\mu_0 \times 10^2$).

Fig. 4.—Effect of $NaClO_4$ on the rate of acetolysis and methanolysis of cyclohexanone oxime *p*-toluenesulfonate: ●, acetolysis; ○, methanolysis.



Initial ionic strength of NaOTs added ($\mu_0 \times 10^2$).

Fig. 5.—Effect of NaOTs upon the rate of acetolysis of cyclopentanone and cyclohexanone oxime *p*-toluenesulfonate at constant ionic strength ($\Sigma\mu_0 = \mu_{0NaClO_4} + \mu_{0NaOTs}$ = const.): ○, cyclohexanone oxime *p*-toluenesulfonate, $\Sigma\mu_0$ = 0.05; ●, cyclopentanone oxime *p*-toluenesulfonate, $\Sigma\mu_0$ = 0.063.

(25) (a) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2770 (1956), and earlier papers; (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

Apparently here the exchange of II to VIIIb is rapid as compared to the solvolysis of II, and VIIIb must solvolyze much faster than II.

It is interesting to compare the rates of acetolysis of Ia and X at constant ionic strength. Figure 5 shows the plots of rate constants of Ia and X *vs.* μ_{0NaOTs} at constant ionic strength ($\Sigma\mu_0 = \mu_{0NaClO_4} + \mu_{0NaOTs}$ = const.).

The slope of the rate constant *vs.* μ_{0NaOTs} at $\Sigma\mu_0 = \mu_{0NaClO_4}$ = 0.063 for Ia is 0.48 × 10^{-2} and for X the corresponding slope at $\Sigma\mu_0 = \mu_{0NaClO_4} + \mu_{0NaOTs}$ = 0.052 is 0.726. Although the constant ionic strength at which the solvolyses reactions were investigated is higher for Ia than X, the slope is considerably steeper for X. This result again indicated that II is considerably more ionized in X than for Ia and that for X, $k_{ROS}^{VIII} >> k_{ROS}^{II}$ and $k_8/k_{-8} >> k_{ROS}^{II}$.

Salt Effects in Methanol.—The solvolysis of X in absolute methanol was strictly first order and no rate depression was observed due to common ion effect during the reaction. There was a slight increase of the rate due to primary salt effect (Table VII). An increase in μ_{0NaOTs} in $\Sigma\mu_0 = \mu_{0NaClO_4} + \mu_{0NaOTs}$ = const. did not decrease the rate, but the rate remained essentially constant. In methanol the solvolysis, therefore, appears not to proceed with anion exchange, or $k_{ROS}^{II} > k_8$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. XXXII. The Synthesis of Azulenes *via* the Interactions of Arylacetylenes with Sulfenyl Halides. Part 1. 1,2,3-Triphenylazulene[1,a,b,c]

BY STEVEN J. ASSONY[2] AND NORMAN KHARASCH

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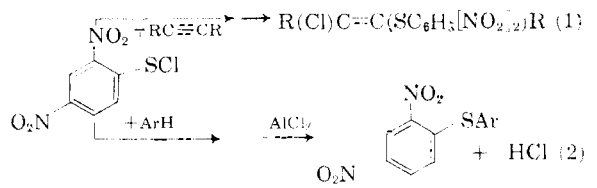
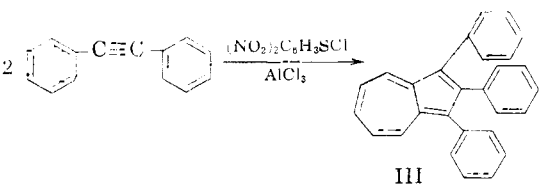
In the presence of 2,4-dinitrobenzenesulfenyl chloride and aluminum chloride, both of which are required, diphenylacetylene is dimerized to 1,2,3-triphenylazulene. This novel reaction appears to be the first recorded instance wherein a benzene ring is expanded to a seven-membered carbocyclic ring under ionizing conditions. The best yield in the one-step conversion was 25%. The structure of the azulene was established by an alternate synthesis, which involved formation and fusion of a triphenylcyclopentane ring onto the seven-membered ring of cycloheptanone.

Introduction.—In previous papers of this series, the reactions of 2,4-dinitrobenzenesulfenyl chloride (I) with symmetrical alkynes[3] and with aromatic hydrocarbons[4] were examined. It was demonstrated that I adds to symmetrical alkynes to form the 1:1 adducts (equation 1) and that the aluminum chloride-catalyzed substitution (equation 2, Ar = aryl) with aromatic hydrocarbons is a general reaction. It was also shown that the reaction of 1 with acetylene to yield the 1:1 adduct (equation 1, R = H) required aluminum chloride, whereas such catalysis was not required with 2-butyne, 3-hexyne or diphenylacetylene.



The present paper reports the reaction whereby, under critical conditions which require the presence of *both* the sulfenyl chloride I and aluminum chloride, diphenylacetylene (II) is dimerized to 1,2,3-triphenylazulene (III).



Initial Evidence for the Structure of III.—The following results, obtained in the initial period of study, led to the prediction[6] that the product was 1,2,3-triphenylazulene (III). In the second phase of the work, described below, the structure of III was confirmed by alternate synthesis from cycloheptanone.

(a) The molecular formula of III, a deep blue, crystalline hydrocarbon, m.p. 215.5–216°, is $C_{28}H_{20}$. It is, therefore, a dimer of diphenylacetylene, $C_{14}H_{10}$. The molecular weight was also confirmed by the mass spectral analysis of III, which was kindly carried out by the Houston laboratory group of the Shell Oil Co.

(1) (a) Presented before the Division of Organic Chemistry, 131st Meeting of the American Chemical Society, Miami, Fla., April 11, 1957. (b) Abstracted from a dissertation presented to the Faculty of the Graduate School, University of Southern California, by Steven J. Assony, in partial fulfillment of the requirements for the degree Doctor of Philosophy, January, 1957. (c) This study was sponsored, in part, by the Office of Ordnance Research, United States Army, under Contract DA-04-495-Ord. 306.

(2) Richfield Oil Corp., Predoctoral Fellow, 1955-1956.

(3) N. Kharasch and S. J. Assony, THIS JOURNAL, **75**, 1081 (1953).

(4) C. M. Buess and N. Kharasch, *ibid.*, **72**, 3529 (1950); also ref. 5b.

(5) (a) The *trans* structure for the adducts reported has been suggested[3] but not yet fully established. The Friedel-Crafts reactions of 2,4-dinitrobenzenesulfenyl chloride with aromatic hydrocarbons and their derivatives provides an excellent method for characterizing these substances[4] and also is the first step in the synthesis of aromatic thiols by the procedure of Kharasch and Swidler, *J. Org. Chem.*, **19**, 1704 (1956). (b) *Cf.* also N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956).

(6) S. J. Assony and N. Kharasch, *Chemistry & Industry*, 1388 (1954).