Acetolysis of *trans*-2-Tosyloxycyclohexyl-Substituted Benzoates. Kinetics and Oxygen-18 Studies

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Ten 2-tosyloxycyclohexyl benzoates containing various substituents in the *meta* and *para* positions of the benzoyl group were solvolyzed at 97.7° in anhydrous acetic acid containing acetate ions. In addition four of these compounds were solvolyzed at 90.2 and 103.7° in the same reaction medium. Acetolysis was also conducted on three of these compounds which were labeled with oxygen-18 on the carbonyl oxygen. There is excellent correlation between the rates of acetolysis and the Hammett polar substituents σ. Several compounds, whose rates were measured at three different temperatures, provided the data necessary for calculating the entropies, enthalpies, and free energies of activation reported herein. Acetolysis of several compounds with oxygen-18 enrichment in the carbonyl oxygen led to the incorporation of the oxygen-18 in the cyclohexanediol. These results are consistent with reaction pathway that proceeds *via* a symmetrical benzoxonium ion intermediate.

Rate enhancement by a *trans*-acetoxy compared with a *cis*-acetoxy group in the solvolysis of 2-acetoxycyclohexyl tosylate was deomonstrated by Winstein, Grunwald, Buckles, and Hanson.[2] More recently, the *trans*-benzoyloxy group was shown to have a similar effect.[3] Previously, we reported an oxygen-18 study on the acetolysis of *trans*-2-acetoxycyclohexyl tosylate.[4] In this paper, we wish to report our findings on the kinetic and oxygen-18 studies on the acetoylsis of *trans*-2- (*meta*- and *para*-substituted benzoyloxy-) cyclohexyl tosylates.

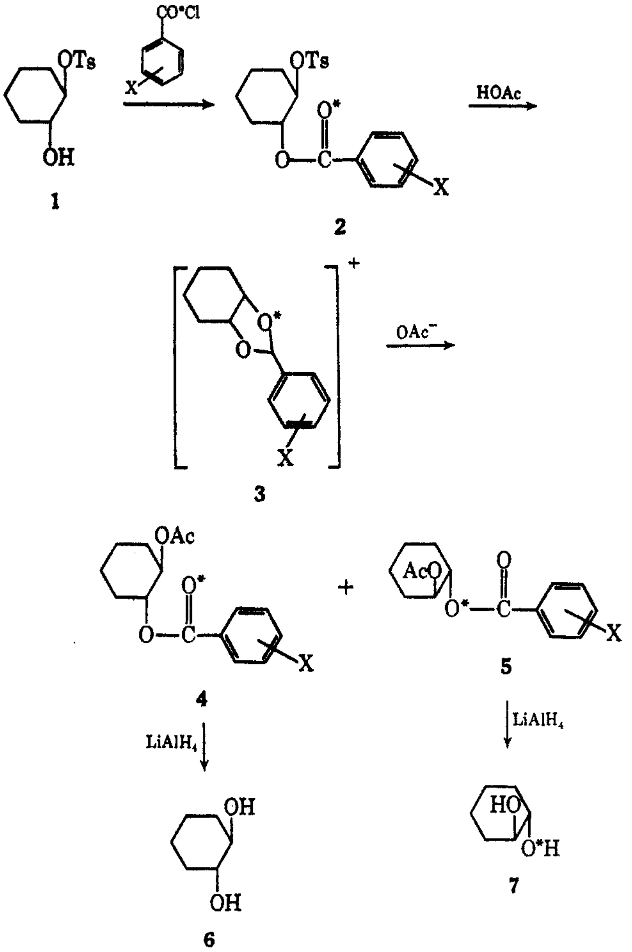
Results and Discussion

A series of compounds (**2a–j**) were prepared and solvolyzed in anhydrous acetic acid with added acetate ion. The resulting (*meta*- and *para*-substituted benzoyloxy)cyclohexyl acetates (**4** and **5**) were isolated and found to be exclusively *trans* and yielded *trans*-1,2-cyclohexanediols (**6** and **7**) upon reductive cleavage by lithium aluminum hydride (Scheme I). The mechanism of the reaction was studied by kinetic techniques and also by labeling the carbonyl oxygen of compounds **2a, c,** and **i** with oxygen-18. The fate of these labeled compounds was ascertained by mass spectroscopy.

The solvolysis rate of **2** was followed by titrating the excess acetate ion with a standardized solution of perchloric acid in glacial acetic acid using a known procedure,[5] except that our titations were conducted with a Metrohm titrimeter.[6] For compounds **2a, c, f,** and **h,** the rates were run at three different temperatures and the thermodynamic parameters of $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta F^{\ddagger}$ were determined from the Arrhenius plot. The kinetic data gave an excellent Hammett $\rho\sigma$ plot. The results of the rate studies are summarized in Table I.

The Hammett $\rho\sigma$ correlation was done using a computer-programmed linear regression analysis. The plot of the first 10 rates measured at 97.7°, listed in Table I, shows a ρ of -1.003 with a correlation coefficient of 0.9953. Although this value for the correlation coefficient is considered excellent,[7] the plot can be greatly improved by eliminating those compounds bearing substituents which are capable of donating electrons by resonance (*p*-OMe, *p*-F, *p*-Cl, and *p*-Br). A Hammett correlation using the six remaining rate constants has ρ -1.001, correlation coefficient 0.9994.

Scheme I



(**a**, X = *p*-OMe; **b**, X = *p*-Me; **c**, X = H; **d**, X = *p*-F; **e**, X = *p*-Cl; **f**, X = *p*-Br; **g**, X = *m*-Cl; **h**, X = *p*-CF$_3$; **i**, X = *p*-NO$_2$; **j**, X = 3,5-di-NO$_2$)

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[1] Taken from the thesis of K. B. G. submitted in partial fulfillment of the requirements for a Ph.D. degree at Arizona State University, June 1969.

[2] S. Winstein, E. Grunwald, R. Buckles, and C. Hanson, *J. Amer. Chem. Soc.*, **70,** 816 (1948).

[3] G. Schneider and L. Kornelia Lang, *Chem. Comm.*, 13 (1967).

[4] K. B. Gash and G. U. Yuen, *J. Org. Chem.*, **31,** 4234 (1966).

[5] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70,** 821 (1948).

[6] Metrohm Potentiograph-Automatic Titrator: Metrohm A. G., Herisau, Switzerland.

[7] H. H. Jaffe, *Chem. Rev.*, **53,** 191 (1953).

TABLE I
FIRST-ORDER SOLVOLYSIS RATE CONSTANTS OF *trans*-2-AROYLOXYCYCLOHEXYL *p*-TOLUENESULFONATES IN ANHYDROUS ACETIC ACID WITH ADDED ACETATE ION

No.	X	[ROTs]	[OAc]	T^a	$10^5\,K$ sec^{-1}
1	*p*-OMe	0.0982	0.0997	97.7	26.4
2	*p*-Me	0.0985	0.120	97.7	17.6
3	H	0.0983	0.116	97.7	13.0
4	*p*-F	0.0944	0.113	97.7	8.48
5	*p*-Cl	0.0945	0.0986	97.7	5.94
6	*p*-Br	0.0846	0.0992	97.7	6.27
7	*m*-Cl	0.0882	0.0977	97.7	4.83
8	*p*-CF_3	0.0647	0.0997	97.7	3.40
9	*p*-NO_2	0.0760	0.120	97.7	2.08
10	3,5-di-NO_2	0.0818	0.0977	97.7	0.463
11	*p*-OMe	0.0991	0.109	90.2	12.4
12	H	0.0965	0.101	90.2	6.03
13	*p*-Br	0.0895	0.110	90.2	3.02
14	*p*-CF_3	0.0921	0.100	90.2	1.58
15	*p*-OMe	0.0980	0.102	103.7	48.7
16	H	0.0977	0.101	103.7	24.3
17	*p*-Br	0.0926	0.101	103.7	12.0
18	*p*-CF_3	0.0970	0.101	103.7	6.10

[a] Temperature ±0.1°.

Brown and Okamoto[8] proposed using σ^+ instead of σ for electron-deficient systems that can be resonance stabilized. The authors were successful in using σ^+ substituent constants in the solvolysis of *para*-substituted phenyldimethylcarbinyl chloride. When σ^+ substituent constants instead of σ were applied to the rate constants 1–10, a value of −0.842 was obtained with a correlation coefficient of 0.9783. The fact that the measured rate constants in these acetolysis reactions gave a better Hammett correlation using σ rather than σ^+ substituent constants can be explained as follows. Although cation **3** is capable of resonance stabilization by electron-donating *para* substituents (*e.g.*, –OMe, –F, –Cl, and –Br), this contribution will be less important in stabilizing **3** than in the case of the phenyldimethylcarbinyl carbonium ion, because the positive charge in **3** is already dispersed over two oxygen atoms as well as the benzylic carbon atom. Some contribution to the stabilization of **3** by electron-donating *para* substituents is quite evident in the Hammett $\rho\sigma$ plot, shown in Figure 1, which shows that the compounds with –OMe, –F, and –Cl in the *para* position do not correlate so well as the others. This additional stabilization accounts for the fact that a better correlation with σ is obtained when the rate constants for the benzoyl compounds with electron-donating groups in the *para* position were excluded from the Hammett $\rho\sigma$ plot.

The rates of the compounds with *p*-methoxy, *p*-bromo, *p*-trifluoromethyl, and hydrogen substituents were run at three different temperatures, 90.2, 97.7, and 103.7°. The activation energy was determined from the Arrhenius equation using a computer-programmed least-squares analysis. The results are listed in Table II.

The acetolysis reaction is accompanied by changes in entropy ranging over five entropy units and changes in enthalpy ranging over a few tenths of a kilocalorie.

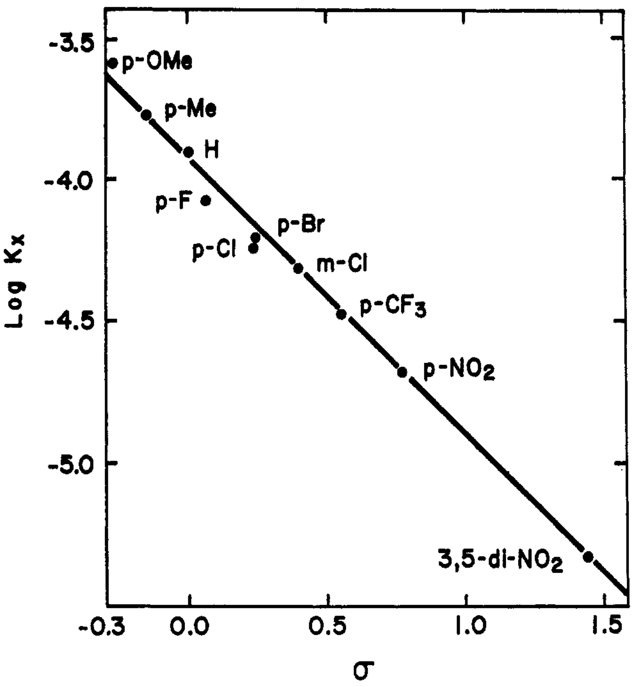

Figure 1.—Plot of log $k_{97.7°}$ against σ for the acetolysis of *trans*-2-tosyloxycyclohexyl *meta*- and *para*-substituted benzoates.

TABLE II
ACTIVATION PARAMETERS

No.	Substituent	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	$\Delta F^\ddagger$, kcal mol^{-1}
1	*p*-OMe	26.8 ± 0.5	−5.0 ± 2	28.7
2	H	27.3 ± 0.5	−5.0 ± 2	29.2
3	*p*-Br	27.0 ± 0.5	−7.3 ± 2	29.7
4	*p*-CF_3	26.5 ± 0.5	−10.0 ± 2	30.2

These results suggest that the reaction is controlled by entropy changes. Several cases have been reported where reactions were controlled by entropy factors;[9–11] for example, Papee, Canady, Zawidzki, and Laidler[12] attributed the increase in entropy of ionization of *para*-substituted phenols with an electron-withdrawing substituent to delocalization of the ionic charge and the consequent release of bound water from the phenoxide ion. Perhaps, to some degree a similar delocalizing effect is operating in **3**, whereby the positive charge is dispersed, in this case, by electron-donating substituents attached to the *para* position. This could explain, in part, the order observed in this work where the entropy becomes more negative as the *para* substituent is varied from –OMe to –CF_3. Additional work is in progress in this laboratory to provide additional data from which more concrete conclusions can be reached on this point.

The isotopic labeling was carried out on three compounds (**2a**, **c**, and **i**). The label was introduced by allowing the appropriate aroyl chloride to react with $H_2{}^{18}O$ to produce the labeled substituted benzoic acid. The acid was then converted into the acid chloride by allowing it to react with either thionyl chloride or oxalyl chloride. The labeled substituted benzoyl

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(8) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

(9) R. W. Hay and L. J. Porter, *J. Chem. Soc., B*, 1261 (1967).

(10) T. C. Bruice and S. J. Benkovic, *J. Amer. Chem. Soc.*, **85**, 1 (1963).

(11) E. Gaetjens and H. Morawetz, *ibid.*, **82**, 5328 (1960).

(12) H. M. Papee, W. J. Canady, T. W. Zawidzki, and K. H. Laidler, *Trans. Faraday Soc.*, **55**, 1734 (1959).

chloride was then allowed to react with mono-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol (**1**) in methylene chloride containing a small amount of pyridine. Acetolysis of **2** was carried out in anhydrous acetic acid with added acetate ion and the acetolysis product (**4** and **5**) was isolated and purified. This was then treated with lithium aluminum hydride in ethyl ether to produce the cyclohexanediols (**6** and **7**). The oxygen-18 content of each of the compounds (**2**, **4**–**5**, and **6**–**7**) was determined by the method of Rittenberg and Ponticorvo[13] as modified by Kashelikar and Ressler.[14] The results of these analyses are listed in Table III, which show that the per cent retention of ^{18}O in the diol is 46 ± 2%. These results indicate that the incorporation of ^{18}O onto the cyclohexane ring from the carbonyl oxygen position through the cyclic intermediate **3** is essentially independent of the rate of the reaction (*i.e.*, independent of the substituent). The inherent accuracy of the analytical procedure is ±3%.

Table III

Results of the Mass Spectroscopic Analysis for Oxygen-18 (At. %)

No.	X	ROTs (**2**)	ROAc (**4** and **5**)	Diol (**6** and **7**)	% retention in diol
1	*p*-OMe	3.16	3.12	1.50	48
2	H	2.59	2.51	1.15	46
3	*p*-NO_2	4.36	4.31	1.88	45

Conclusion

The results of these experiments can be summarized as follows. (1) Acetolysis of *trans*-2-tosyloxycyclohexyl-substituted benzoates in anhydrous acetic acid with added acetate ions yielded exclusively *trans*-2-acetyloxycyclohexyl-substituted benzoates. Complete retention of the *trans* configuration was noted throughout the course of the reaction. (2) An excellent Hammett correlation is obtained using σ values (correlation coefficient 0.9953). In contrast, a poorer Hammett correlation is obtained when σ^+ values were used (correlation coefficient 0.9783). (3) Resonance interaction with electron-donating ring substituents is less in the case of the benzoxonium ion than for the more charge-localized benzyl cation. This is attributable to the fact that the benzoxonium ion can disperse the charge over three atoms—two oxygens and a carbon. (4) In general, the amount of oxygen-18 incorporation onto the cyclohexane ring is independent of the rate of the reaction.

These results are consistent with the reaction pathway that proceeds *via* a symmetrical, cyclic intermediate as represented by **3**.

Experimental Section

The oxygen-18 enrichment analyses were done by mass spectrometry at the Department of Chemistry, Arizona State University, using a Consolidated Electrodynamics 21-130 mass spectrometer. All gas chromatographic (vpc) analyses were done with an Aerograph dual-column, temperature-programmed gas chromatograph, using either a 0.25 in. × 6 ft 2% Carbowax on ABS-70/80 column or a 0.25 in. × 10 ft 20% QF-1 on ABS-70/80 column. All nonaqueous titrations were done on a Metrohm[6] Potentiograph E-336.

Mono-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol (1).—This compound was prepared according to a known procedure.[15a] Recrystallization of the product from Skellysolve C–benzene (1:3) gave a pure sample of the compound with a melting point of 96.2–96.6° (lit.[15b] mp 96–96.4°).

Benzoyl Chloride-^{18}O.—To 0.70 g (0.0385 mol) $H_2{}^{18}O$ was added a solution of 5.50 g (0.039 mol) of freshly distilled benzoyl chloride of 10 ml of dry tetrahydrofuran. The reaction mixture was heated at reflux for 2 hr, at which time the flask was cooled slightly and the solvent removed on a rotary evaporator. The crude acid was treated, without further purification, with 10.0 g of oxalyl chloride (0.079 mol). Evolution of HCl gas began immediately upon the addition of the oxalyl chloride, and the mixture was heated at reflux for 1 hr after evidence of gas formation had stopped. The product mixture was then distilled at water-pump pressure to yield 4.90 g (90%) of slightly yellow product, which was used without further purification.

p-Methoxybenzoyl chloride-*carbonyl*-^{18}O was prepared by the above procedure. *p*-Nitrobenzoyl chloride-*carbonyl*-^{18}O was prepared by the method of Goering and Pombo[16] and purified by the method of Friedman and Wetter.[17]

1-O-Benzoyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol (2c).—To a solution of monotosyldiol starting material 10.0 g (0.037 mol) dissolved in 50 ml of dry pyridine, 5.6 g (0.04 mol) of benzoyl chloride was added slowly with cooling. The solution turned salmon pink and crystals of pyridinium hydrochloride appeared almost immediately. The reaction mixture was stored overnight in a refrigerator (10–16 hr), after which time it was poured into a 400-ml beaker which was filled with crushed ice to which was added about 20 ml (about 0.33 mol) of concentrated sulfuric acid. The mixture was kept cold with occasional stirring for 1 hr, or until the desired product has solidified. At this time it was filtered using suction, washed with 0.5 *M* HCl and then with distilled water, and allowed to air dry. The crude product was obtained in near quantitative yield and was recrystallized twice from 95% ethanol.

This procedure was followed for the preparation of the following substituted benzoates: *p*-methoxy (**2a**), *p*-methyl (**2b**), *p*-fluoro (**2d**), *p*-chloro (**2e**), *p*-bromo (**2f**), *m*-chloro (**2g**), *p*-trifluoromethyl (**2h**), *p*-nitro (**2i**), and 3,5-dinitro (**2j**). Pertinent data for these compounds are listed in Table IV.

Preparation of Acetolysis Solutions.—The solutions in which the acetolysis reactions were carried out were prepared according to the method outlined by Winstein, *et. al.*[18] Reaction progress was monitored by thin layer chromatography (tlc).

1-O-(4-Methoxybenzoyl)-2-O-acetyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O.—Acetolysis of 1-O-(4-methoxybenzoyl)-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol (unlabeled, 4.0 g) yielded 1.6 g (55%) of 1-O-(4-methoxybenzoyl)-2-O-acetyl-*trans*-cyclohexanediol, bp 158–159° (0.25 mm). Acetolysis of the labeled compound yielded product which was not purified, but was found by vpc analyses to be a pure isomer. Small samples were collected from the vpc for analysis.

Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 66.00; H, 7.14; ^{18}O, 3.12 at. % excess.

1-O-Benzoyl-2-O-acetyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O.—Acetolysis of 1-O-benzoyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O (3.0 g) yielded 1.6 g (76%) of product, bp 147–149° (2 mm). Vapor phase chromatography indicated that the product was isomerically pure and a sample of it was collected for analysis.

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.62; H, 7.01; ^{18}O, 2.51 at. % excess.

1-O-(4-Nitrobenzoyl)-2-O-acetyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O.—Acetolysis of 1-O-(4-nitrobenzoyl)-2-O-*p*-toluenesulfonyl-*trans*-cyclohexanediol-*carboxyl*-^{18}O (4.2 g) yielded 2.6 g (84%) of crude solid product. After two crystallizations from

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[13] D. Rittenburg and Ponticorvo, *Intern. J. Appl. Radiation Isotopes*, **1**, 208 (1956–1957).

[14] D. V. Kashelikar and C. Ressler, *J. Amer. Chem. Soc.*, **86**, 2467 (1964).

[15] (a) S. Winstein, H. V. Hess, and R. E. Buckler, *ibid.*, **64**, 2796 (1942); (b) R. Criegee and H. Stanger, *Ber.*, **69B**, 2753 (1936).

[16] H. L. Goering and M. M. Pombo, *J. Amer. Chem. Soc.*, **82**, 2515 (1960).

[17] L. Friedman and W. P. Wetter, *J. Chem. Soc.*, 36 (1967).

[18] S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 812 (1948).

TABLE IV

PROPERTIES OF THE AROYLOXYCYCLOHEXYL p-TOLUENESULFONATES

			Anal, %				
			Calcd		Found		
Compd	Yield, %	Mp, °C	C	H	C	H	^{18}O, at. % excess
2a	86	110–111	62.36	5.98	62.45	6.13	3.16
2b	72	88–89	64.92	6.23	64.83	6.28	
2c	74	112–113	64.15	5.92	64.20	5.92	2.59
2d	78	97–98	61.21	5.39	61.34	5.57	
2e	76	117–118	58.75	5.18	58.63	5.15	
2f	74	120–121	52.99	4.67	53.23	4.82	
2g	80	101–102	58.75	5.18	58.63	5.15	
2h	75	118–119	57.01	4.78	56.93	5.05	
2i	73	125–126	57.27	5.05	57.11	5.13	4.36
2j	83	131–132	51.72	4.34	51.99	4.56	

aqueous methanol and sublimation of the entire product, the yield was 1.60 g (52%), mp 110.0–111.0°.

Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58. Found: C, 58.36; H, 5.58; ^{18}O, 4.31 at. % excess.

Saponification of 1-O-(4-Nitrobenzoyl)-2-O-acetyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O.—Hydrolysis of the labeled diester by a known procedure[2] yielded *trans*-1,2-cyclohexanediol-^{18}O. A pure sample was obtained by one crystallization from carbon tetrachloride followed by sublimation: mp 103.4–104.1°; ^{18}O, 1.88 at. % excess.

Hydrogenolysis of 1-O-Benzoyl-2-O-acetyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O.—One gram of the diester (0.0038 mol) was dissolved in 25 ml of anhydrous diethyl ether. A twofold excess of lithium aluminum hydride (0.008 mol, 0.31 g) was added slowly enough to keep the reaction under control. After a short induction period, the reaction proceeded somewhat vigorously, but it did not require cooling in an ice bath. The reaction was let stand at room temperature for 5 min after the evolution of bubbles of hydrogen had ceased, at which time 1.2 ml of water were added dropwise to break up the complex and to hydrolyze the excess lithium aluminum hydride. The mixture was then vacuum filtered and the white precipitate was digested by boiling with two 25-ml portions of dichloromethane, and the filtrates were combined. Evaporation of the solvent and vapor phase chromatographic analysis of the residue showed that there were two main products along with some very minor (>1%) impurity peaks, which were not identified. Samples of the *trans*-1,2-cyclohexanediol-^{18}O and the benzyl alcohol-^{18}O were collected from the exit port of the vpc. The benzyl alcohol was identified by its ir absorption spectrum and by its nmr spectrum, and the diol had the correct melting point.

Anal. Found for *trans*-1,2-cyclohexanediol-^{18}O: ^{18}O, 1.16 at. % excess. Found for benzyl alcohol: ^{18}O, 1.15 at. % excess.

Hydrogenolysis of 1-O-(4-Methoxybenzoyl)-2-O-acetyl-*trans*-1,2-cyclohexanediol-*carboxyl*-^{18}O.—The hydrogenolysis of this compound was carried out according to the above procedure.

Anal. Found for *trans*-1,2-cyclohexanediol-^{18}O: ^{18}O, 1.50 at. % excess. Found for p-Methoxybenzyl alcohol-^{18}O: ^{18}O, 1.11 at. % excess.

Kinetic Procedure.—The procedure for the rate measurements was essentially the same as that used by Winstein and coworkers.[18] Time was counted from immersion time (+10 sec) to the time when the ampoule was quenched by immersion in ice-water. After being cooled, the ampoule was allowed to come to room temperature and snapped open, and a 2.0-ml aliquot was taken, diluted to *ca.* 15 ml, and titrated with standardized perchloric acid in glacial acetic acid using the Metrohm automatic titrimeter. All titrations (samples and standards) were done with the same titration speed set on the titrimeter. The end point was determined graphically from the titration curve. The titrimeter has a setting so that the differential derivative curve may be obtained, but this gave poor results, and was not used. It was important that the electrode be immersed in distilled water whenever it was not actually being used for a titration, for continuous immersion in glacial acetic acid caused the electrode to behave erratically.

Calculation of Rate Constants.—The rate data was plotted using a linear regression analysis computer program. The program was written in such a way that it would accept data in the form of milliliters of titrant and units of time (seconds, minutes, or hours) or in the form of concentration of some starting material or product at time T. The program would then calculate the specific rate constant from the least-squares line and it would print out values for the statistical correlation, or how well the points actually fall on the line whose slope is represented by the specific rate constant. The program would only calculate first-order rate constants as written, but with little modification it would calculate second-order rate constants as well. The same program was used to calculate Hammett σ–ρ correlations and the activation parameters.

Since the slope of the rate curve tended to drop off after about two half-lives,[18] the program was written in such a way that this could be detected. A subroutine was written which would plot the points and produce an actual graph of the rate curve. It was fairly easy to see from this where the fall off began. In addition to this plot, the program printed out a complete set of answers for the first four points, then for the first five points, and continued in this manner until a set of answers was printed out for all the points. The slope that was used as the specific rate constant for a particular kinetic run was the one which had the best fit for the maximum number of points before the drop off started. On those runs that were duplicated, the deviation from the mean was no greater than ±1% of the value of the rate constant.

Calculation of Activation Parameters.—The Arrhenius plot and the calculation of the enthalpy, entropy, and free energy of activation was done using a computer program similar to that used for the rate data. The difference was in the treatment of the input data before it was subjected to least-squares analysis. The equation used to determine the activation energy (E_a) is $\ln k = -E_a/RT + \ln A$,[19] which, of course, is a linear equation and subject to linear regression analysis. Since $E_a = \Delta H^\ddagger + RT$, the entropy of activation ($\Delta S^\ddagger$) can be calculated from the following equation. The free energy of activation ($\Delta F^\ddagger$) can be calculated from $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.[18] The error in the values for $\Delta S^\ddagger$ is estimated from the rate data to be no greater than ±2 eu.

$$k = k^*T/h \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)^{20}$$

Calculation of Hammett Correlations.—The Hammett σ–ρ correlations were done using the same computer-programmed linear regression analysis that was used in the rate data calculations. The σ constants used were those compiled by McDaniel and Brown.[21]

Analysis of the ^{18}O Content of the Labeled Compounds.—The ^{18}O in the labeled compounds was converted into carbon dioxide and analyzed according to the method of Rittenberg and Ponticorvo,[13] which was modified slightly by Kashelikar and Ressler.[14] The only modification used in this laboratory was that the gas inlet tube was modified so that a bulb of ordinary carbon dioxide could be attached to be used as a blank. The

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[19] W. J. Moore, "Physical Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 297.

[20] L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 7 (1963).

[21] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

^{18}O enrichment was calculated by taking one-half the height of the mass 46 peak times 100 and dividing this result by the sum of the heights of the mass 44 peak and mass 46 peak. The value obtained from the blank sample was subtracted from the value for the enriched sample to compensate for the natural abundance of ^{18}O. Duplicate analyses of the same compounds showed that the analytical procedure was accurate to ±3%.

Registry No.—**2a**, 18888-64-7; **2a**-*carbonyl*-^{18}O, 18893-96-4; **2b**, 18887-40-6; **2c**, 16544-65-3; **2c**-*carbonyl*-^{18}O, 18893-97-5; **2d**, 18887-42-8; **2e**, 18887-43-9; **2f**, 18887-44-0; **2g**, 18887-43-9; **2h**, 18887-46-2; **2i**, 18887-47-3; **2i**-*carbonyl*-^{18}O, 18893-98-6; **2j**, 38887-48-4; **4a**, 18893-99-7; **4c**, 18894-00-3; **4i**, 18902-55-1; **5a**, 18894-01-4; **5c**, 18894-02-5; **5i**, 18894-03-6.

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Notes

Cycloadditions. XXIV. Cycloadducts from Arylaroyldiazomethanes and Carbon Disulfide[1,2]

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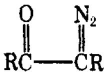
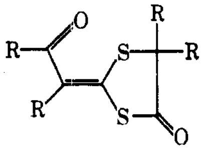
A reinvestigation of the adduct derived from azibenzil (**1a**) and carbon disulfide[5] led Yates and Christensen[6] to assign it structure **2a** (or its geometrical isomer). A supposedly analogous adduct obtained from the reaction of 3-diazobutanone (**1b**) and carbon disulfide was represented by formula **2b**,[7] but a recent X-ray single-crystal structure analysis on this adduct established **3b** as an accurate structural assignment.[8,9]

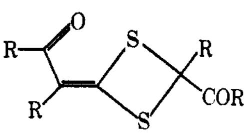


$\overset{O}{\overset{\|}{RC}}-\overset{N_2}{\overset{\|}{C}}R$

1



2



3

a, R = C_6H_5
b, R = CH_3
c, R = p-C_6H_4F

Whether the adduct from azilbenzil might require a similar structural reassignment (**3a** instead of **2a**) was answered through the present work.

Results and Discussion

Structure **2** has two R groups which would be identical by symmetry, whereas in **3** each of the four R groups is distinct. This factor became the basis for an approach to the structural distinction; the adduct in which R = p-C_6H_4F– (**2c** or **3c**) was synthesized and its fluorine nmr spectrum examined.

p-Fluorophenyl-*p*-fluorobenzoyldiazomethane (**1c**) was synthesized through the sequence *p*-fluorobenzaldehyde → *p,p'*-difluorobenzoin → *p,p'*-difluorobenzil → *p,p'*-difluorobenzil monohydrazone → **1c**. Heating the difluoroazibenzil and carbon disulfide to reflux gave a mixture of products from which the adduct $C_{29}H_{16}F_4O_2S_2$ **2c** or **3c**, mp 145–146°, was isolated by fractional crystallization.

The infrared spectra of this tetrafluoro adduct, mp 145–146°, and of the adduct from azibenzil were identical but for three exceptions. One was the expected[10] strong carbon-fluorine bond absorption at 1162 cm^{-1}. The second was a weak band at 945 cm^{-1} in the tetrafluoro adduct, not observed in its unsubstituted analog. The third difference came in the region 1620–1575 cm^{-1}. The compound assigned structure **2a** shows three medium-intensity peaks at 1620, 1598, and 1578 cm^{-1}. In the tetrafluoro adduct, this region is obscured by a very strong band at 1598 cm^{-1} with a shoulder probably containing a band near 1620 cm^{-1}.

The adduct of mp 145–146° showed three absorptions in a ^{19}F nmr spectrum; they had similar fine structure and a 1:1:2 ratio of relative intensities (Figure 1). In tetrahydrofuran, these absorptions appeared

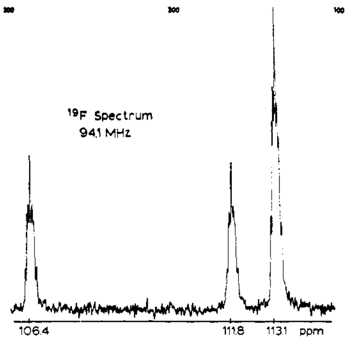


Figure 1.—Fluorine-19 nmr spectrum of adduct **2c**, mp 145–146°, taken as a solution in tetrahydrofuran.

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(2) Paper XXIII in this series: J. E. Baldwin and J. E. Gano, *J. Org. Chem.*, in press.

(3) Alfred P. Sloan Research Fellow.

(4) National Science Foundation Predoctoral Trainee, 1965–1968.

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(9) J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Amer. Chem. Soc.*, **90**, 5800 (1968).

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