THE CONVERSION OF META- AND PARA-SUBSTITUTED BENZALDOXIME ARENESULFONATES TO NITRILES

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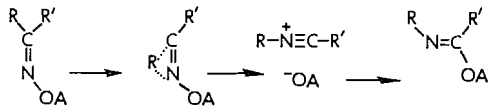
Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

ABSTRACT

The meta- and para-substituted *syn*-benzaldoxime arenesulfonates were prepared from the reaction between the sodium salt of the oxime and the acid chloride in absolute ether. These oxime esters reacted in aqueous alcohol readily to yield the corresponding nitriles exclusively. The reaction rates can be correlated by a Hammett plot with a slope of −0.77. Several para-substituents tended to deviate from the line. Isotope study gives a k_H/k_D ratio of 4.51. The rate was found to be sensitive to the change in the ionizing power of the solvent, and to the change in the strength of the esterifying acid. The addition of lithium perchlorate gives rise to a normal salt effect. Sodium acetate brings about a basic elimination having a Hammett ρ value of +0.44. A mechanism is proposed in the light of these results.

INTRODUCTION

Since Beckmann (1) reported the conversion of oximes to the corresponding amides in acid media, numerous publications have appeared in an attempt to elucidate the mechanism of the transformation. Several authors, Blatt (2), Jones (3), Heldt (4), and Smith (5), have reviewed the Beckmann rearrangement up to 1963. The generally accepted view of the rearrangement involves migration of the hydrocarbon residue *anti* to the leaving group, followed by a rapid tautomerization of the intermediate. The transition state for such a reaction has been described as a pseudo three-membered ring, and the process was viewed as "an internal nucleophilic displacement, and may be described as ionization by rearrangement" (5). Although extensive work has been done on the subject of the



Beckmann rearrangement of ketoximes, the aldoximes have been less frequently investigated. Aldoximes and their derivatives usually undergo fragmentation to nitriles, under the conditions of the Beckmann rearrangement, so readily that examples of normal rearrangement to give amides are quite rare (4). For example, in the presence of phosphorus pentachloride and ether, *syn**-2-chloro-5-nitro-benzaldoxime gave rise to 2-chloro-5-nitrobenzonitrile (6); *syn*-2,6-dichloro-3-nitrobenzaldoxime yielded 2,6-dichloro-3-nitrobenzonitrile (7); and *syn*-α-bromocinnamaldoxime gave α-bromocinnamonitrile (8).

It would appear that aldoximes generally react by a different mode than do ketoximes; thus, "ionization by rearrangement" may not be operative for aldoximes. This paper initiates a general investigation about the difference of aldoxime and ketoxime esters under Beckmann conditions.

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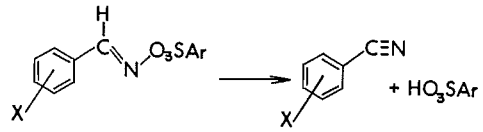
**The use of syn and anti with aldoximes is different from the common convention with ketoximes and refers to cis and trans to the hydrogen, respectively. See ref. 4a, p. 3; 4b, p. 321.*

RESULTS AND DISCUSSION

Aldoxime esters react in aqueous alcohol to give rise to the corresponding nitriles as the sole product. The reaction rates were measured spectrophotometrically by following



the disappearance of the band at the wavelength of maximum absorption of the corresponding aldoxime ester. The products, the nitrile and the acid, have only a small absorption at this wavelength. A correction in the rate expression was made to accommodate this product absorption, and the first-order rate equation becomes

$$\log \frac{(A_0 - A_\infty)}{(A_{obs} - A_\infty)} = \frac{kt}{2.303},$$

where A_0 represents the optical density at the beginning of the reaction, A_{obs} is the observed optical density at time t, and A_∞ is the optical density caused by the products at the end of the reaction. The reaction was found to follow first-order kinetics in aldoxime ester to greater than 90% completion. The first-order rate constants were obtained graphically by plotting $\log (A_0 - A_\infty)/(A_{obs} - A_\infty)$ versus t, and are summarized in Tables I, II, and III. The experimental uncertainty was calculated by the method of average, and found to be ±2.3%. A sample run is given in the Experimental section.

TABLE I

Rate constants for the reaction of substituted *syn*-benzaldoxime *p*-toluenesulfonates at 50.00 ± 0.02 °C in 80% methanol

Run No.	Substituent	$10^5 k$, s^{-1}	Run No.	Substituent	$10^5 k$, s^{-1}
1	*p*-OCH_3	93.5	7	*p*-Cl	10.3
2	*m*-OCH_3	16.3	8	*m*-Cl	10.6
3	*p*-CH_3	27.7	9	*p*-F	12.4
4	*m*-CH_3	25.7	10	*m*-F	10.2
5	—H	20.5	11	*p*-NO_2	7.90
6	*m*-Br	9.74	12	*m*-NO_2	6.33

TABLE II

Rate constants for the reaction of para-substituted *syn*-benzaldoxime *p*-toluenesulfonates at 50.00 ± 0.02 °C in 95% ethanol in the presence of 0.08 *M* sodium acetate

Run No.	Substituent	$10^3 k_2$, $l\ m^{-1}\ s^{-1}$
13	—NO_2	76.9
14	—Cl	26.6
15	—F	24.9
16	—H	23.1
17	—CH_3	19.2
18	—OCH_3	16.2

An examination of the rates in Table III reveals several characteristics of the reaction. First of all, runs 1, 19, and 20 show that the rate is sensitive to solvent change. Varying the solvent from 100% methanol to 60% methanol–water increases the rate by a factor

TABLE III

Rate constants for the reaction of *p*-methoxybenzaldoxime esters under varying conditions

Run No.	Ester	Solvent	Temp., ±0.02 °C	[Added salt]	$10^5 k$, s^{-1}
19	*syn*-*p*-Toluenesulfonate	100% MeOH	50.00	—	23.4
1	"	80% MeOH	"	—	93.5
20	"	60% MeOH	"	—	259
21	"	95% EtOH	"	—	23.5
22	"	"	"	0.20 *M* $LiClO_4$	29.0
23	"	"	"	0.50 *M* "	34.5
24	"	"	"	0.80 *M* "	43.1
25	"	"	"	0.20 *M* HOTs	26.8
26	*syn*-Benzenesulfonate	"	"	—	34.1
27	*syn*-*p*-Bromobenzene-sulfonate	"	"	—	92.9
28	*syn*-Acetate	"	141	—	22.9
29	*anti*-Acetate	"	50.00	—	8.11
30	"	"	60.00	—	16.1
31	"	"	70.00	—	34.3
32	"	"	141	—	1 490*

*Extrapolated rate constant.

of 11.3. This effect can be correlated by the equation proposed by Winstein and co-workers (9), using the scale of solvent-ionizing power derived from ionization of *p*-methoxyneophyl *p*-toluenesulfonate:

$$\log k_r = a \log k_1 + b,$$

where k_r is the rate constant for the reaction being examined, k_1 is the rate constant for the ionization of *p*-methoxyneophyl *p*-toluenesulfonate, and a is a measure of relative sensitivity of the reaction to the ionizing power of the solvent. The a values for several rearrangements have been calculated (9) from data available in the literature, being 0.690 for the ionic rearrangement of 9-decalyl perbenzoate; 0.569 for the allylic rearrangement of 1-phenylallyl 3,4,5-tribromobenzoate; and 0.119 for the Curtius rearrangement of benzoyl azide. In the latter, sensitivity to solvent change is low. Figure 1 shows a

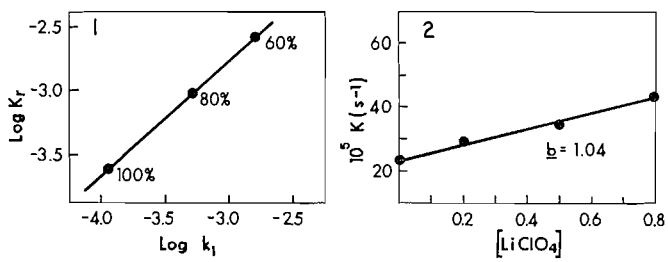


FIG. 1. Plot of log k_r for reaction of *syn*-*p*-methoxybenzaldoxime *p*-toluenesulfonate vs. log k_1 for solvolysis of *p*-methoxyneophyl *p*-toluenesulfonate in methanol at 50 °C.

FIG. 2. Plot of rate constant vs. lithium perchlorate concentration in the reaction of *syn*-*p*-methoxybenzaldoxime *p*-toluenesulfonate in 95% ethanol at 50 °C.

plot of log k_r versus log k_1 in methanol at 50°. The relatively high a value (0.950) indicates that the reaction is sensitive to changes in solvent-ionizing power in a manner similar to that for known ionization reactions.

Secondly, the addition of lithium perchlorate over a range of concentrations up to

0.80 M gives rise to a normal salt effect. This can be described by a linear relation (10) between the rate constant and the molar concentration of lithium perchlorate:

$$k_r = k_0(1 + b[LiClO_4]),$$

where k_r is the observed rate constant, k_0 represents the rate constant at zero salt concentration, and b is the slope of the linear plot representing the % increase in rate constant over k_0 per 0.01 M increment of lithium perchlorate. Figure 2, from runs 21 to 24, shows the linear plot of rate constant versus lithium perchlorate concentration in 95% ethanol at 50°, with a b value of 1.04. The salt effect is quite small, but is that expected in ionizing solvents such as alcohols.

Finally, runs 21, 26, and 27 indicate that the reaction is sensitive to variation of the leaving group. Changing the leaving group from *p*-toluenesulfonate to *p*-bromobenzenesulfonate increases the rate by a factor of 3.9. A comparison of relative rates of the reactions of isopropyl arenesulfonates and *syn*-*p*-methoxybenzaldoxime arenesulfonates in aqueous ethanol at 50° is tabulated in Table IV. Using the three arenesulfonates as

TABLE IV

Comparison of the rates of isopropyl arenesulfonates (11) and *syn*-*p*-methoxybenzaldoxime arenesulfonates

Arenesulfonate	Isopropyl in 50% EtOH at 50°	*syn*-*p*-Methoxybenzaldoxime in 95% EtOH at 50°
p-Toluene	0.63	0.65
Benzene	1.00	1.00
p-Bromobenzene	2.92	2.72

the leaving group, the reaction of the *syn*-aldoxime arenesulfonates varies in the same direction and by approximately the same magnitude as the ionization of isopropyl arenesulfonates.

An inspection of the rate constants from Table I clearly shows that electron-donating groups accelerate the reaction rate and that electron-withdrawing substituents retard it. The effect of meta- and para-substitution on the rate constant can be correlated by the Hammett equation (12)

$$\log k/k_0 = \rho\sigma,$$

where k is the rate constant of the substituted *syn*-aldoxime *p*-toluenesulfonates, k_0 is the rate constant of the unsubstituted compound, ρ is the reaction constant, and σ is the substituent constant. Figure 3 shows a plot of log k/k_0 versus σ, and a ρ value of -0.77 was obtained when only meta-derivatives (σ^n) were considered, as suggested by van Bekkum *et al.* (13). The *p*-OCH_3 substituent deviates significantly from this line (a Hammett σ value of -0.856 would be required to bring it on the line, which means that the σ^+ value of -0.77 would not fit) and a mesomeric para-interaction energy difference ($\Delta\Delta F_p$) of -0.78 kcal mole^{-1} is obtained from the equation

$$-\Delta\Delta F_p = (\sigma - \sigma^n) \times 2.303RT,$$

where ρ is the value derived from the meta-substituents (-0.77), σ is the -0.856 value required to place the point on the line, and σ^n is the value -0.175 suggested by van Bekkum *et al.* (13) for a para-methoxy substituent from the detailed examination of substituent effects.

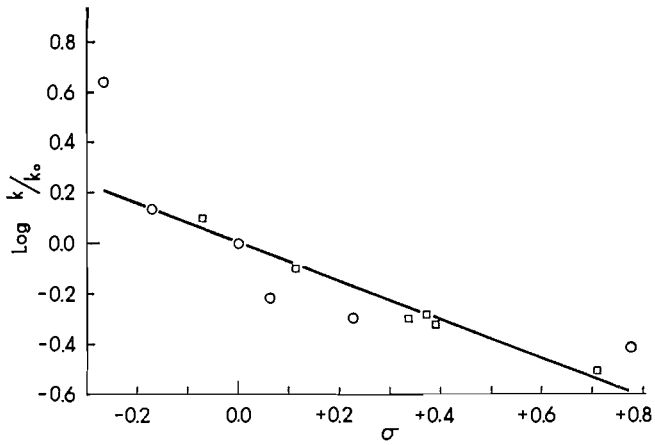
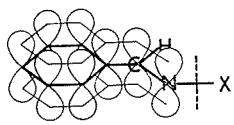
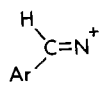


FIG. 3. Plot of log k/k_0 vs. σ for the reaction of meta- (□) and para- (○) substituted *syn*-benzaldoxime *p*-toluenesulfonates in 80% methanol at 50 °C.

It is difficult to envisage a direct resonance interaction between the substituent and the N—O bond in I that is being broken, as it would be expected to be in the nodal plane of the aromatic π orbitals. Thus, ionization to an imidonium species II would not be expected to give rise to a very negative ρ value, nor could we expect a significant resonance interaction with the ring.

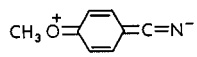


I



II

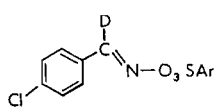
It should be noted, however, that *p*-methoxybenzonitrile, the product, gains additional stabilization from a resonance structure such as III.



III

If the elimination has progressed to the point that the transition state is beginning to resemble the product, then the *p*-methoxy substituent would be expected to stabilize the transition state and thus react at an enhanced rate.

If, indeed, the transition state does resemble the product nitrile, we would expect a considerable amount of C—H bond breaking. In order that we may ascertain the degree of C—H bond breaking in the reaction, the deuterated aldoxime *p*-toluenesulfonate IV was prepared. A rate constant of 1.36×10^{-5} s^{-1} was obtained in 95% ethanol at 50° for the deuterated compound, as compared with 6.16×10^{-5} s^{-1} for the undeuterated ester under the same conditions. This gives rise to a k_H/k_D value of 4.51 at 50°.



IV

An approximation of the theoretical isotope effect was calculated by the following expression (14) (this was necessary because of the sp^2 nature of the C—H bond being broken, a type of rupture not commonly observed):

$$k_D/k_H = \exp \frac{hc}{2kT}(\nu_D - \nu_H),$$

where k_D is the rate constant for the labelled compound, k_H is the rate constant for the unlabelled isomer, h is Planck's constant, c is the velocity of light, k is Boltzmann's constant, T is absolute temperature, and ν_D and ν_H represent the vibrational frequencies associated with a C—D and C—H bond, respectively. From the infrared spectra, the measured vibrational frequency of the C—D bond in *p*-chlorobenzaldoxime *p*-toluenesulfonate is 2 240 cm^{-1}, and that for the C—H bond is 3 030 cm^{-1}. Substituting these values into the above equation gives a theoretical k_H/k_D ratio of 5.81. The observed value of k_H/k_D of 4.51 suggests that the rate-determining step must involve the breaking of the C—H bond.

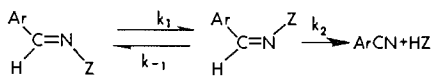
Run 25 in Table III indicates that the reaction is not acid catalyzed. The addition of 0.20 *M* *p*-toluenesulfonic acid had no appreciable effect on the rate. But the rates were observed to be greatly increased by the addition of sodium acetate. The second-order rate constants are calculated by the following equation:

$$k_2 = \frac{k_{obs} - k_1}{[OAc^-]},$$

where k_2 represents the second-order rate constant, k_{obs} is the observed pseudo first-order rate constant, and k_1 is the rate constant in the absence of sodium acetate. The second-order rate constants in the presence of 0.08 *M* sodium acetate are tabulated in Table II. It is interesting to note that the order of reactivity is completely reversed, with a ρ value of +0.44. This is similar to the base-catalyzed dehydrohalogenation of ald-chlorimines (15). A resemblance to this mild base-catalyzed process may also be responsible for the deviation of the *p*-nitro substituent in the uncatalyzed reaction (Fig. 3).

The possibility that the *syn*-aldoxime esters are being isomerized to the corresponding *anti*-ester followed by a *trans*-elimination must also be considered. Thus, in Scheme I,

SCHEME I



the reaction may be represented kinetically by the expression

$$-\frac{d[syn]}{dt} = \frac{k_1 k_2 [syn]}{k_{-1} + k_2}.$$

If k_1 and $k_{-1} > k_2$, then the expression reduces to

$$-\frac{d[syn]}{dt} = k_2 K [syn],$$

where $K = k_1/k_{-1}$, and we would thus obtain the same rate constant for either the *syn*- or the *anti*-ester. As may be seen in Table III, runs 28 to 32, the *anti*-isomer is 65 times faster than the *syn*-isomer. If, however, k_1 is slow and rate determining, we would

not expect to observe a kinetic isotope effect on replacing the oximino hydrogen by deuterium. The intermediate case where $k_{-1} \cong k_2$ reduces the above expression to

$$-\frac{d[syn]}{dt} = \frac{1}{2}k_1[syn]$$

and again no kinetic isotope effect would be observed. The observation of a 65-fold difference in rate between the *syn*- and *anti*-pair, and of a kinetic isotope effect of the magnitude of 4.51, allows us to exclude any possible isomerization mechanism.

A pyrolysis type of mechanism for the arenesulfonate esters may also be ruled out on the basis of the solvent sensitivity and the salt effect. The negative $\Delta S^{\ddagger}$ values in Table V

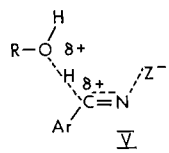
TABLE V

Determination of activation parameters of substituted *syn*-benzaldoxime *p*-toluenesulfonates in 80% methanol

Run No.	Substituent	Temp., ±0.02 °C	$10^5 k$, s^{-1}	$\Delta H^{\ddagger}$, kcal m^{-1}	$\Delta S^{\ddagger}$, e.u.$m.^{-1}$
33	*m*-CH_3	60.07	64.2		
4	*m*-CH_3	50.00	25.7	20.4	−12.0
34	*m*-CH_3	40.04	9.12		
35	—H	60.07	52.0		
5	—H	50.00	20.5	21.0	−10.6
36	—H	40.04	6.99		
37	*m*-Cl	60.07	27.3		
8	*m*-Cl	50.00	10.6	20.3	−14.1
38	*m*-Cl	40.04	3.92		

could readily arise from increased solvent constriction in the transition state and is consistent with ionization processes.

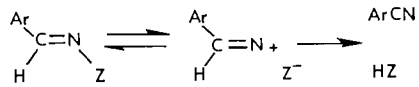
Solvent sensitivity, salt effect, and the dependence of the rate constant upon the leaving group suggest that the reaction is ionic in character. The effect of substituents suggests that a small positive charge may be developed on the conjugated system. The result of isotopic substitution shows that the C—H bond is also considerably stretched. This evidence supports a concerted *cis*-elimination mechanism, and the transition state involving varying degrees of rupture of the N—Z and C—H bonds (V).



V

It is possible that the N—Z bond has been completely broken, and we are measuring the proton loss from species such as II. This suggests the possibility of an ion-pair mechanism (Scheme II) which would involve ionization to the ion pair VI followed by proton abstraction by the gegen ion.

SCHEME II



VI

This suffers from a possible handicap since, to accommodate the kinetic isotope effect, the last step would have to be rate determining and this would suggest that the stronger the arenesulfonate ion as a base the faster the reaction, which is the reverse of that observed in Table IV. This could be overcome by a large change in the prior equilibrium effectively increasing the steady-state concentration of the ion pair, and cannot be rigorously excluded. We are at this time, however, unable to cite any experiment which can satisfactorily differentiate whether the gegen ion or the solvent molecule is acting as base as in V.

EXPERIMENTAL

Preparation of Materials

p-Chlorobenzaldehyde-d

A solution of 40 g (0.37 mole) of N-methyl aniline in 250 ml of benzene was added slowly, with stirring, to a cooled solution of 60 g (0.34 mole) of *p*-chlorobenzoyl chloride in 250 ml of benzene. The mixture was refluxed for 2 h, cooled, and then washed with 250 ml of water, 250 ml of 5% hydrochloric acid, 250 ml of 5% sodium hydroxide, and 250 ml of water, respectively. The benzene solution was dried, the solvent evaporated, and the residue distilled at reduced pressure. The distillate solidified upon cooling in an ice bath. The yield of the pure N-methyl *p*-chlorobenzanilide was 56 g (60%), m.p. 54–56°.

Anal. Calcd. for $C_{14}H_{12}ClNO$: C, 68.5; H, 4.90; N, 5.71. Found: C, 68.1; H, 5.01; N, 5.58.

N-Methyl *p*-chlorobenzanilide (20 g (0.082 mole)) was dissolved in 200 ml of tetrahydrofuran which was redistilled over sodium just before use. The solution was cooled to 4° and 0.89 g (0.022 mole) of lithium aluminium deuteride was added and the mixture stirred at 4° for 15 h, whereupon 400 ml of 7% hydrochloric acid was added. The tetrahydrofuran was evaporated and the residue steam-distilled. The distillate was extracted with ether. The ethereal solution was dried, the solvent evaporated, and the residue distilled at diminished pressure. The distillate solidified on cooling in an ice bath. The yield of *p*-chlorobenzaldehyde-*d* was 7 g (58%), m.p. 47°. The infrared spectrum in chloroform shows that the vibrational frequency of the C—H bond at 2 837 cm^{-1} has been shifted to 2 112 cm^{-1} in the deuterated compound. The n.m.r. spectrum in deuterochloroform shows no absorption at τ 0.30 attributable to aldehydic C—H.

Oximes

All the *syn*-oximes were prepared by the following general procedure.

A 5-g quantity of hydroxylamine hydrochloride was dissolved in 30 ml of water and 20 ml of 10% sodium hydroxide, and 5 g of the aldehyde was then added. Sufficient 95% ethanol was added to the mixture to obtain a homogeneous solution. The mixture was refluxed for 15 min and cooled, and 100 g of crushed ice was added with shaking. If the oxime separated as a solid, the precipitate was filtered and pressed dry. The crude product was recrystallized from a mixture of skelly B and benzene. If the oxime separated as an oil, the oil was extracted with ether. The ethereal solution was dried, the solvent evaporated, and the residue distilled under reduced pressure. The distillate solidified on standing in the freezer. The yield of the pure oximes was in the range of 75–90%. Infrared spectra of the oximes in chloroform show a strong band at 3 580 cm^{-1} caused by O—H absorption (16). The melting point of the oximes together with the reported value (16) are *syn-p*-methoxybenzaldoxime, m.p. 64, reported 64; *syn-m*-methoxybenzaldoxime, m.p. 40, reported 40; *syn-p*-methylbenzaldoxime, m.p. 79, reported 79; *syn-m*-methylbenzaldoxime, m.p. 60, reported 60; *syn*-benzaldoxime, m.p. 35, reported 35; *syn-p*-fluorobenzaldoxime, m.p. 86, reported 86 (17); *syn-m*-fluorobenzaldoxime, m.p. 68, reported 63 (17); *syn-p*-chlorobenzaldoxime, m.p. 110, reported 106; *syn-m*-chlorobenzaldoxime, m.p. 71, reported 70; *syn-p*-chlorobenzaldoxime-*d*, m.p. 109; *syn-m*-bromobenzaldoxime, m.p. 75, reported 72; *syn-p*-nitrobenzaldoxime, m.p. 131, reported 129; *syn-m*-nitrobenzaldoxime, m.p. 124, reported 120; *anti-p*-methoxybenzaldoxime, m.p. 132–133°, reported 133° (18).

Oxime Acetates

A 0.5-g (3.3 mmoles) quantity of *syn-p*-methoxybenzaldoxime was dissolved in 0.5 ml of acetic anhydride. After 10 min, 5 ml of ether and 5 ml of hexane were added. The mixture was cooled and the precipitate was filtered. The yield of *syn-p*-methoxybenzaldoxime acetate was 0.47 g (74%), m.p. 48–49°, after recrystallization from a 50:50 mixture of ether and hexane. Reported m.p. 48–49° (18). The infrared spectrum in chloroform shows a strong band at 1 755 cm^{-1}.

anti-p-Methoxybenzaldoxime acetate was prepared by the same method as that for the *syn*-isomer. Yield 0.52 g (82%), m.p. 64–65°. Reported m.p. 64–65° (18). The infrared spectrum in chloroform shows a strong band at 1 760 cm^{-1}.

Oxime Arenesulfonates

The following general procedure was used for the preparation of the *syn*-aldoxime arenesulfonates except the nitro-substituted compounds.

To a rapidly stirred solution of 3 mmoles of the oxime in 20 ml of absolute ether, 3.1 mmoles of powdered sodium amide was added and the mixture was stirred for about 5 h. The mixture was filtered and the precipitate washed several times with ether.

p-Toluenesulfonyl chloride (0.36 g (2.5 mmoles) in 5 ml of ether) was slowly added to a rapidly stirred slurry of the sodium salt of the oxime in 5 ml of ether. The salt produced was removed by filtration and 10 ml of hexane was added to the filtrate. Upon cooling of the mixture, the oxime arenesulfonate crystallized. Recrystallization from a 50:50 mixture of ether and hexane generally gives a pure sample. Yield 50–60%. The infrared spectra in chloroform show strong bands at 1 380 and 1 170 cm^{-1}, characteristic of sulfonate esters (16).

Since the meta- and para-substituted *syn*-nitrobenzaldoximes gave a mixture of the original oxime and the corresponding nitrile when the above method was followed, the procedure was modified. The sodium salt of the oximes was prepared as previously. The salt was dissolved in 5 ml of 50% acetone–water and added slowly with stirring to a cooled solution of *p*-toluenesulfonyl chloride in 2 ml of acetone. The oxime ester separated was collected, washed with 50% acetone, and recrystallized as before. The yield was about 45%.

The relevant data for these *syn*-aldoxime arenesulfonates are summarized in Table VI.

TABLE VI

Summary of data for X—C_6H_4—CH=N—O—SO_2—C_6H_4—Y—*p*

	m.p.,* °C	Max., mμ	Molecular formula	Anal. calcd. C	H	N	Anal. found C	H	N
Y = CH_3									
X =									
p-OCH_3	99–100	274.5	$C_{15}H_{15}NO_4S$	59.0	4.91	4.59	59.1	5.02	4.50
p-CH_3	100–102	261.0	$C_{15}H_{15}NO_3S$	62.3	5.19	4.84	62.5	5.50	4.91
—H	85–86	255.0	$C_{14}H_{13}NO_3S$	61.1	4.41	5.08	61.3	4.56	5.03
p-F	98–99	253.5	$C_{14}H_{12}FNO_3S$	57.4	4.10	4.78	57.4	4.33	4.73
p-Cl	102–103	260.5	$C_{14}H_{12}ClNO_3S$	54.4	3.90	4.52	54.4	4.40	4.44
p-Cl-*d*	105–107	260.0	$C_{14}H_{11}DClNO_3S$						
p-NO_2	111–112	276.0	$C_{14}H_{12}N_2O_5S$	52.5	3.77	8.74	52.5	3.83	8.50
m-OCH_3	85–86	257.5	$C_{15}H_{15}NO_4S$	59.0	4.91	4.59	58.9	4.86	4.39
m-CH_3	83–84	256.0	$C_{15}H_{15}NO_3S$	62.3	5.19	4.84	62.4	5.13	4.71
m-F	95–96	252.0	$C_{14}H_{12}FNO_3S$	57.4	4.10	4.78	57.4	4.51	4.54
m-Cl	94–95	252.5	$C_{14}H_{12}ClNO_3S$	54.4	3.90	4.52	54.3	4.44	4.61
m-Br	106–107	254.5	$C_{14}H_{12}BrNO_3S$	47.4	3.39	3.96	47.2	3.58	4.07
m-NO_2	110–111	228.5	$C_{14}H_{12}N_2O_5S$	52.5	3.77	8.74	52.5	4.14	8.52
Y = H									
X = OCH_3	99–100	272.5	$C_{14}H_{13}NO_4S$	57.7	4.47	4.81	57.4	4.63	4.67
Y = Br									
X = OCH_3	104–105	274.0	$C_{14}H_{12}BrNO_4S$	54.5	3.25	3.78	54.5	3.59	3.70

*Melted with decomposition.

Product Analysis

syn-p-Chlorobenzaldoxime *p*-toluenesulfonate (0.50 g (1.6 mmoles)) was suspended in 10 ml of 95% ethanol at 50°. The suspension dissolved within 12 h, and the mixture was kept at 50° for an additional 24 h, whereupon 20 g of crushed ice was added. The solid separated was filtered and recrystallized from skelly B. The yield of *p*-chlorobenzonitrile was 0.13 g (80%), m.p. 92–93°. Reported m.p. 94–96° (17). The infrared spectrum in chloroform shows a strong band at 2 230 cm^{-1} caused by C≡N absorption (16). *p*-Methoxybenzonitrile, m.p. 61–62°, reported 61–62° (17), was similarly isolated from *syn-p*-methoxybenzaldoxime *p*-toluenesulfonate in 87% yield.

Kinetic Measurements

Absorption curves of the *syn*-aldoxime esters in the ultraviolet region were obtained on a Cary recording spectrophotometer model 14M. Kinetic measurements were taken from a Beckman model DU spectrophotometer at the wavelength of maximum absorption of the corresponding oxime ester. The spectrophotometer is equipped with a double set of thermospacers connected to a circulating constant temperature bath, thermostated within ±0.02° of the particular temperature. All kinetic runs were extrapolated back to zero time, and the small absorption caused by the products of the reaction was corrected in the rate expression. Good first-order curves were observed in every case. As an example, the reaction of the unsubstituted compound is recorded in Table VII, and the results are plotted in Fig. 4.

Reaction of *syn-p*-methoxybenzaldoxime acetate was carried out by the sealed-tube technique. A standard solution of the acetate (2 mg per 100 ml of the solvent) was made up. Samples of approximately 5 ml volume were sealed in ampoules and placed in the temperature bath. The reaction was followed by withdrawing and cooling ampoules at intervals of time, and the optical density was measured.

TABLE VII

Reaction of *syn*-benzaldoxime *p*-toluenesulfonate in 80% methanol at 50.0° and 255.0 mμ

Time, min	A_{obs}	$\frac{A_0 - A_\infty}{A_{obs} - A_\infty}$	$\log \frac{A_0 - A_\infty}{A_{obs} - A_\infty}$	$10^5 k$, s^{-1}
0	1.140	1.09/1.09	0.000	—
10	1.025	1.09/0.973	0.0493	18.6
20	0.905	1.09/0.853	0.106	20.3
30	0.815	1.09/0.763	0.154	19.7
40	0.722	1.09/0.670	0.211	20.3
50	0.647	1.09/0.595	0.263	20.2
60	0.580	1.09/0.548	0.300	19.3
98	0.328	1.09/0.330	0.519	20.3
125	0.288	1.09/0.235	0.666	20.4
144	0.237	1.09/0.185	0.747	20.0
∞	0.052			

NOTE: Average $k = 19.9 \pm 0.05 \times 10^{-5}$ s^{-1}.

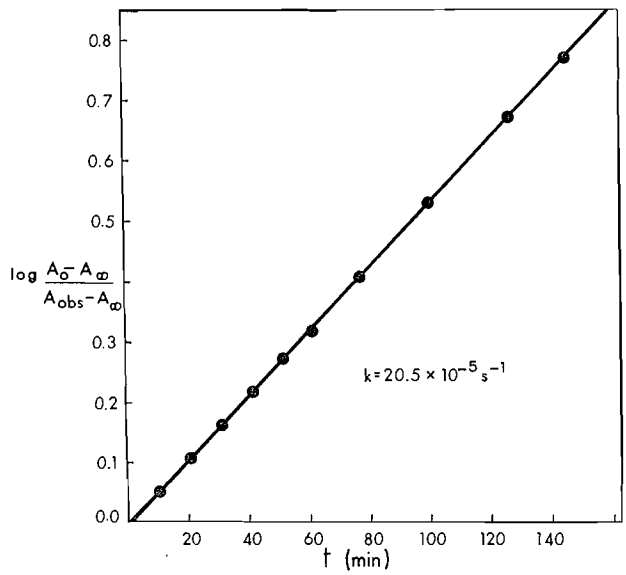


FIG. 4. Plot of log $(A_0 - A_\infty)/(A_{obs} - A_\infty)$ vs. t for the reaction of *syn*-benzaldoxime *p*-toluenesulfonate in 80% methanol at 50° and 255.0 mμ.

Infrared Spectra

The infrared spectra of *p*-chlorobenzaldoxime *p*-toluenesulfonate and the deutero-derivative were measured at 1% concentration in carbon tetrachloride solution using the same cells in each case. The spectrum of the deuterated compound has a C—D stretching band at 2 240 cm^{-1} that was not in the spectrum of the undeuterated ester. It also lacked a band at 3 030 cm^{-1}, which is present in the spectrum of the undeuterated aldoxime ester.

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