Effects of Ring Substituents on the Reactivity of Thionphenoxide Ions towards Some Nitro-activated Thiophene Derivatives

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The rates of nucleophilic substitution of bromine on 3-bromo-2-nitrothiophene (I) and 2-bromo-3-nitrothiophene (II) by *o*-, *m*-, and *p*-substituted thiophenoxide ions have been measured in methanol at 20.02°.

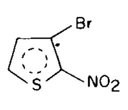
The rate of thiophenoxy-debromination is always higher when the reaction center is in the β-position (substrate I) rather than in α-position (substrate II). Plots of the log k against σ°-constants for the reaction of the substituted thiophenoxides towards I and II have ρ-values of -0.78 (for substrate I) and -0.76 (for substrate II). Deviations from linearity for *p*-substituents with strong +M and -M effect are discussed.

A comparison of proton basicity, carbon basicity, and nucleophilicity of the thiophenoxide ions has also been made.

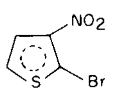
The mechanism of nucleophilic substitution on aromatic and heteroaromatic substrates has been investigated intensively during recent years and an extensive literature is available (1). However, despite the large amount of information accumulated on the influence of the polar and steric effects of *p*-, *m*-, and *o*-substituents on the aromatic substrate (1,2), few data are available in the literature on the effects of substituents on the nucleophile (1,3).

The importance of a quantitative study of the effect of substituents on the nucleophile is that, through the ρ-parameter of the Hammett relationship, it is possible to obtain information on the charge density at the reaction center and on the degree of bond-formation between the nucleophile and the substrate at the rate-limiting transition state (3).

Therefore, as part of our broad concern with structure-reactivity correlations and of our continuing research in the field of sulfur derivatives (4), we report now the results of a kinetic study of the substituent effects on the reactivity of *p*-, *m*-, and *o*-substituted sodium thiophenoxides towards 3-bromo-2-nitrothiophene (I) and 2-bromo-3-nitrothiophene (II).



I



II

The choice of I and II as substrates was due to the fact that for many years we have been interested in nucleophilic substitutions on heterocyclic aromatic compounds and particularly on thiophene derivatives (4) [The proposed mechanism of nucleophilic substitution of the bromine in the substrates I and II is the addition-elimination mechanism typical of nucleophilic aromatic substitution (1,5).]. Therefore, the isomers I and II differ in the relative position of the bromine atom and nitro group with respect to the heteroatom of the thiophene

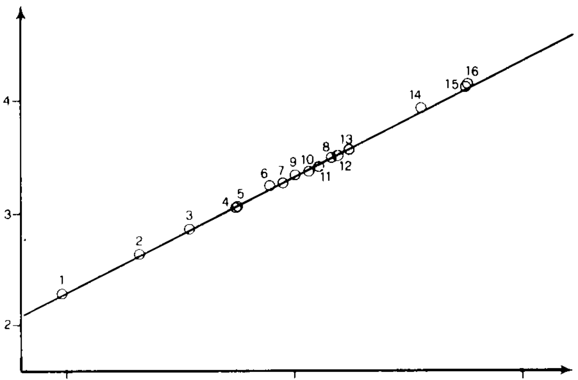


Figure 1. Relationship between log k for the reaction of a series of substituted thiophenoxides with bromonitrothiophenes I and II. 4 + log k_{I} is plotted against 3 + log k_{II}. For k values see Table 1. The slope calculated from all the substituents is 1.06 (r = 0.999).

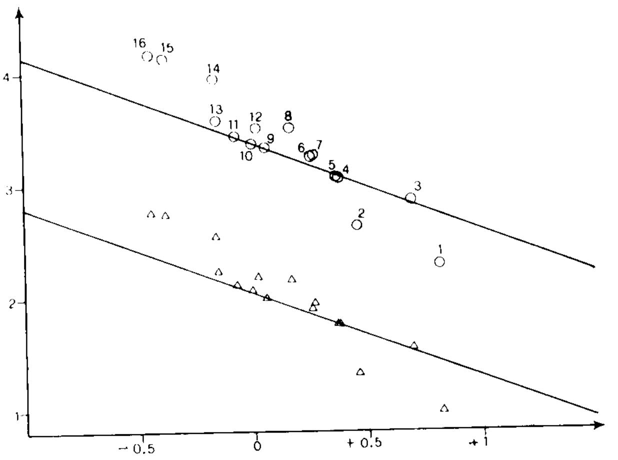


Figure 2. Hammett plot for the reaction of substituted sodium thiophenoxides with bromonitrothiophenes I and II. 4 + log k_I (open circle) and 3 + log k_{II} (triangles) are plotted against σ°-constant. For k values see Table I. The slopes calculated from *m*-substituents are the following:

ρ_I = -0.78 r = 0.995
ρ_{II} = -0.76 r = 0.996

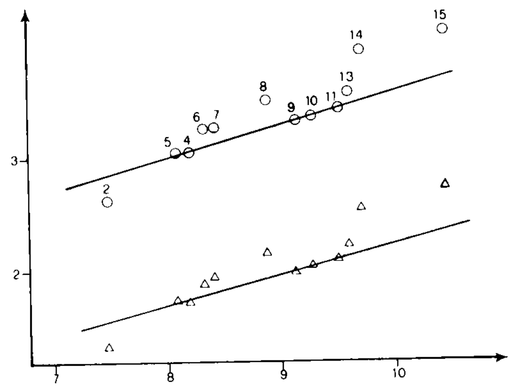


Figure 3. Plot of log k for the reaction of I and II (as in Figure 2) with sodium thiophenoxide *versus* pK_a of the corresponding thiophenol. The slopes calculated from *m*-substituents are the following:

slope_I = 0.28 r = 0.997
slope_{II} = 0.27 r = 0.996

ring; thus, while in I the reaction of the thiophenoxy-debromination occurs in the β-position with respect to the sulfur atom of the ring, in II the reaction center is in α-position. Furthermore, this research has been done in order to examine the influence of the position of the reaction center with respect to the sulfur atom of the thiophene ring on the effect of the substituent in the

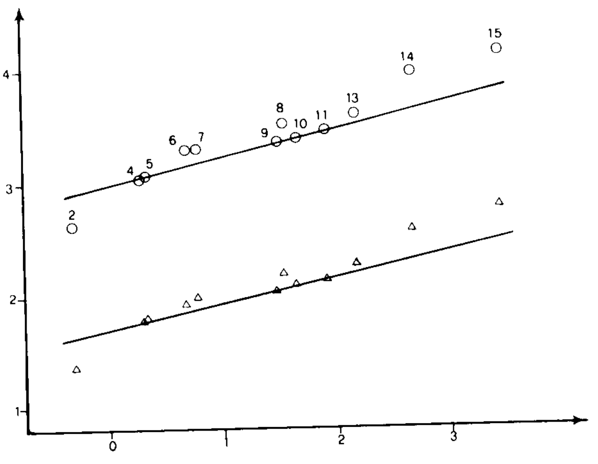


Figure 4. Plot of log k for the reaction of I and II (as in Figure 2) with sodium thiophenoxide *versus* the carbon basicity (C.B.)TNB (log K) of the corresponding thiophenoxide ion. The slopes calculated from *m*-substituents are the following:

slope_I = 0.25 r = 1
slope_{II} = 0.24 r = 0.999

TABLE I

Rate Constants in M^{-1} sec^{-1} for the Reactions of 3-Bromo-2-nitrothiophene (I) and 2-Bromo-3-nitrothiophene (II) with Substituted Sodium Thiophenoxides at 20.02° in Methanol.

Substituent	I	II
(1) *p*-NO_2	0.0195	0.0095
(2) *p*-$COCH_3$	0.043	0.021
(3) *m*-NO_2	0.072	0.035
(4) *m*-Br	0.112	0.055
(5) *m*-Cl	0.114	0.056
(6) *p*-Br	0.183	0.077
(7) *p*-Cl	0.186	0.089
(8) *p*-F	0.318	0.145
(9) *m*-OCH_3	0.221	0.102
(10) H	0.234 (a)	0.116 (a)
(11) *m*-CH_3	0.273	0.128
(12) *p*-SCH_3	0.322	0.156
(13) *p*-CH_3	0.383	0.174
(14) *p*-OCH_3	0.890	0.355
(15) *p*-NH_2	1.310	0.560
(16) *p*-$N(CH_3)_2$	1.450	0.570
(17) *o*-CH_3	0.36	0.143
(18) 2,4,6-$(CH_3)_3$	0.37	0.130

(a) Data from reference (13).

TABLE II

Physical, Analytical, and Spectroscopic (uv) Data of X-Phenyl 3-(2-Nitro)thienyl Sulphides

X (a)	M.p., °C	Crystallization Solvent	Found %		Formula	Required %		λ max (b) (nm)	log ε (b)
			N	S		N	S		
p-NO_2	174	Methanol-dioxane	9.98	22.69	$C_{10}H_6N_2O_4S_2$	9.92	22.72	368	4.11
p-$COCH_3$	163	Benzene-light petr. (80-100°)	5.08	22.86	$C_{12}H_9NO_3S_2$	5.02	22.96	372	4.06
m-NO_2	154	Benzene-light petr. (60-80°)	10.02	22.60	$C_{10}H_6N_2O_4S_2$	9.92	22.72	364	4.05
m-Br (c)	109	Benzene-light petr. (60-80°)	4.54	20.38	$C_{10}H_6BrNO_2S_2$	4.43	20.28	370	4.04
m-Cl (d)	112	Light petroleum (80-100°)	5.22	23.27	$C_{10}H_6ClNO_2S_2$	5.16	23.60	368	4.03
p-Br (e)	190	Light petroleum (100-120°)	4.35	20.48	$C_{10}H_6BrNO_2S_2$	4.43	20.28	370	4.05
p-Cl (f)	179	Light petroleum (110-130°)	5.16	23.56	$C_{10}H_6ClNO_2S_2$	5.16	23.60	370	4.05
p-F	120	Benzene-light petr. (75-120°)	5.54	24.73	$C_{10}H_6FNO_2S_2$	5.49	25.12	370	4.01
m-OCH_3	133	Benzene-light petr. (60-80°)	5.35	24.14	$C_{11}H_9NO_3S_2$	5.24	23.98	372	4.03
m-CH_3	101	Light petroleum (100-120°)	5.69	25.27	$C_{11}H_9NO_2S_2$	5.57	25.57	374	4.03
p-SCH_3	129	Light petroleum (110-130°)	5.08	33.77	$C_{11}H_9NO_2S_3$	4.95	33.95	374	4.06
p-CH_3	118	Methanol	5.52	25.28	$C_{11}H_9NO_2S_2$	5.57	25.57	374	4.03
p-OCH_3	135	Ethanol	5.38	23.95	$C_{11}H_9NO_3S_2$	5.24	23.98	374	4.03
p-NH_2	179	Benzene-light petr. (80-100°)	11.20	25.18	$C_{10}H_8N_2O_2S_2$	11.10	25.42	368	4.03
p-$N(CH_3)_2$	180	Benzene	9.93	22.52	$C_{12}H_{12}N_2O_2S_2$	9.99	22.87	368	4.02
o-CH_3	68	Methanol	5.69	25.38	$C_{11}H_9NO_2S_2$	5.57	25.27	372	4.04
2,4,6-$(CH_3)_3$	156	Ethanol	5.10	22.76	$C_{13}H_{13}NO_2S_2$	5.01	22.98	378	4.06

(a) Data for X = H are reported in reference (13). (b) In methanol. (c) Br%: Found, 25.23. Required 25.27. (d) Cl%: Found, 13.29. Required 13.05. (e) Br%: Found, 25.37. Required 25.27. (f) Cl%: Found, 13.09. Required 13.05.

TABLE III

Physical, Analytical (a), and Spectroscopic (uv) Data of X-Phenyl 2-(3-Nitro)thienyl Sulphides

X (b)	M.p., °C	Crystallization Solvent	Found %		λ max (c) (nm)	log ε (c)
			N	S		
p-NO_2	142	Ethanol	10.07	22.38	364	3.89
p-$COCH_3$	125	Benzene-light petr. (80-100°)	5.12	22.88	366	3.88
m-NO_2	131	Benzene-light petr. (60-80°)	10.08	22.60	358	3.84
m-Br (d)	95	Light petroleum (100-120°)	4.53	20.52	364	3.84
m-Cl (e)	77	Light petroleum (80-100°)	5.19	23.99	362	3.83
p-Br (f)	148	Light petroleum (80-100°)	4.49	20.08	364	3.86
p-Cl (g)	148	Light petroleum (110-130°)	5.42	23.55	364	3.86
p-F	130	Benzene-light petr. (75-120°)	5.51	24.94	364	3.82
m-OCH_3	101	Benzene-light petr. (60-80°)	5.30	23.97	368	3.85
m-CH_3	67	Light petroleum (80-100°)	5.63	25.30	368	3.84
p-SCH_3	129	Light petroleum (110-130°)	5.00	33.86	368	3.91
p-CH_3	127	Methanol	5.57	25.27	368	3.85
p-OCH_3	143	Ethanol	5.30	23.64	368	3.87
p-NH_2	141	Benzene-light petr. (60-80°)	11.18	25.22	362	3.83
p-$N(CH_3)_2$	182	Benzene-light petr. (60-80°)	10.13	22.68	366	3.84
o-CH_3	117	Methanol	5.53	25.51	368	3.85
2,4,6-$(CH_3)_3$	87	Ethanol	5.09	22.62	370	3.89

(a) For formulas and required analysis of these sulphides, see Table II. (b) Data for X = H are reported in reference (13). (c) In methanol. (d) Br%: Found, 25.38. (e) Cl%: Found, 13.20. (f) Br%: Found, 25.18. (g) Cl%: Found, 13.25.

nucleophile for the reaction of thiophene substrates with sodium thiophenoxide.

Results and Discussion.

In Table I the rate constants of I and II with substituted sodium thiophenoxides are listed; the electron-donating substituents increase the reaction rate, whereas the electron withdrawing substituents have the opposite effect. For a given ring-substituent in the thiolate, the reactivity of derivatives of I is always higher than that of derivatives of II.

In order to compare the substituent effects in the thiophenoxide ion with change of the thiophene substrate, the values of 4 + log k_I have been plotted against the values of 3 + log k_{II} for each substituent in the thiophenoxide ion and the least square regression line has been calculated. The good correlation and the slope found (*ca.* equal to one, see Figure 1) suggest that the change in the electronic interaction between the sulfur atom and the substituents in the thiophenoxide ion is almost independent of the position of the electrophile reaction centers with respect to the heteroatom of the thiophene ring. Therefore, since from previous studies (5) it has been found that the change of the leaving group did not cause any large change of rate in the reaction of sodium thiophenoxide with 3-X-2-nitrothiophenes and with 2-X-3-nitrothiophenes (X = Cl, Br, I, $SO_2C_6H_5$), we can conclude that in nucleophilic substitution with thiophenoxide ion on nitro-activated thiophene substrates, the change of the position of the reaction center with respect to the sulfur atom of the thiophene ring (*cf.* isomers I and II) does not cause any significant change of the degree of bond-forming and bond-making of the rate-limiting transition state.

The rate data can be now profitably examined through the ρ-σ relationship. In Figure 2 the values of log k for the reaction of the substituted thiophenoxides with I and II are plotted against the Taft's $\sigma°$-values (6). The plots reveal that all the points corresponding to the *m*-substituents lie on straight lines, whereas the points corresponding to the *p*-substituents deviate more or less significantly from linearity. In Figure 2 the least square regression lines obtained from the *m*-substituents are drawn and the relative slopes and correlation coefficients are reported. Similar ρ-values were obtained in the two cases.

Concerning the magnitude of ρ-parameters it is to be pointed out that the comparison of the ρ-values obtained from the other data available in literature on the effect of the substituents in nucleophiles involved in nucleophilic aromatic substitution is not easy owing to the different conditions of solvent and temperature used in experiments. Knowles, *et. al* (3) reported a ρ-value of -1.8 for the reaction of 1-chloro-2,4-dinitrobenzene with substituted phenoxide ions in 80% dioxane-water at 65°. W. Tagaki, *et. al* (3) found a ρ-value of -2.11 for C-O bond cleavage in the reaction of *p*-nitrophenylbenzenesulfonates with substituted thiophenoxides in 80% dioxane-water at 50°. Ricci, *et. al* (3) found a ρ-value of -0.72 for the reaction of 2-halobenzothiazoles with substituted thiophenoxides in methanol at 25°. From these data the ρ-values for the reaction we studied (ρ_I = -0.78 and ρ_{II} = -0.76) seem to be not high, indicating, thus, not very advanced degrees of bond-formation at the rate-limiting transition states [For a better validity of these conclusions more homoegneous and comparable data are needed: to this purpose, researches are in progress in our laboratory on various nucleophiles and substrates. Many reactivity data have been reported on the nucleophilicity of substituted thiolates involved in S_{N_2} reactions on aliphatic substrates (8) and in addition reactions to ethylene and acetylene substrates having an electron-withdrawing group (9): The ρ-values are generally higher than those found in the present study. However, the fact that different experimental conditions are often used and the most suitable substituents have not always been chosen to calculate the slopes must be carefully taken into account.]. This fact is confirmed if the ρ-values are compared with that obtained by Crampton *et. al* (7) (-3.33) from measurements of equilibrium constants for formation of 1:1 covalently bound addition complexes of the substituted thiophenoxides with 1,3,5-trinitrobenzene in 95% ethanol at 22°: in this case, the C-S bond between the substrate and the thiophenoxide is completely formed.

Concerning the *p*-substituents it is evident from Figure 2 that the observed reactivities of various *p*-substituted thiophenoxides towards I and II do not agree with the values predicted by $\sigma°$-constants. The points corresponding to *p*-substituents with -M effect (*p*-NO_2 and *p*-$COCH_3$) fall below the straight line, whereas the points corresponding to the substituents with +M effect (*p*-Br, *p*-Cl, *p*-F, *p*-SCH_3, *p*-CH_3, *p*-OCH_3, *p*-NH_2, and *p*-N-$(CH_3)_2$ lie above the straight line.

Let us examine separately the two classes of substituents.

Substituents with a -M Electronic Effect.

The negative deviations observed for *p*-NO_2 and *p*-$COCH_3$ indicate that substituents with a strong -M electronic effect when they are in the *p*-position with respect to the thiol group of the thiophenoxide cause a decrease of the nucleophilicity with respect to the parent compound greater than that predicted by $\sigma°$-constants. This fact indicates that there is a large decrease of resonance interaction across the phenyl group between the sulphur atom and *p*-NO_2 and *p*-$COCH_3$ groups in passage from the ground state to the rate-limiting transition state.

Substituents with a +M Electronic Effect.

The magnitude of the positive deviations from linearity of the points corresponding to these substituents are clearly dependent on the capability of the substituent to release electrons by a mesomeric effect: thus, *p*-Br, *p*-Cl, and *p*-CH_3 (substituents with a small +M effect) give negligible deviations from linearity; whereas, *p*-F, *p*-SCH_3, *p*-OCH_3, *p*-NH_2, and *p*-N-$(CH_3)_2$ (substituents with strong +M effect) deviate significantly from linearity. Analogous anomalous behavior for similar *p*-substituted thiophenoxides has been reported by other authors (7,8,9) and different interpretations have been proposed. In our opinion, an important factor to keep in mind in the study of the nucleophilic reactivity of the thiophenoxide ion is its polarizability which would be expected to be particularly influenced by the mesomeric electronic effect of the *p*-substituents of the benzene ring. Therefore, the present findings could be rationalized on the basis of the fact that, according to a mechanism of nucleophilic attack of the sulfur atom of the thiolates ion on the thiophene substrates, *p*-substituents with a +M effect in the *p*-position of the benzene ring of the thiophenoxide, reducing the possibility of conjugation from the sulfur atom into the benzene ring, enhance the ability of the nucleophile to interact with the substrate to form a partial bond at a considerable distance. This implies a nucleophilicity of these *p*-substituted thiophenoxides higher than that expected from the $\sigma°$-constants.

Valence shell expansion of the sulfur atom of the thiolate ion in the transition state of these displacements ought to be taken into account; evidence of such an expansion has been presented in other cases (10) and shown to increase as the X-group attached to sulfur becomes more electron-withdrawing.

However, the fact that in the rate-limiting transition state of our reaction, the bond order between S and X is less than one and there is the anionic charge dispersed over the thiophene system (X = I or II) as well as the thiophenoxide system, makes doubtful this possibility.

Recently Crampton and coworkers (7) have measured the equilibrium constants for formation of 1:1 covalently bound addition complexes between thiophenoxides and 1,3,5-trinitrobenzene. They concluded that the values of these constants could be taken as measure of carbon basicity of thiophenoxide ions and compared to nucleophilicity to see whether carbon basicities may better correlate the nucleophilicities of thiophenoxide ions than do their proton basicities.

With the purpose to verify this suggestion and to clarify the origin of the deviations of Figure 2, the values of log k for the reactions of the thiophenoxides towards I and II have been plotted against the acidity constants (pK_a) of the thiophenols (7) (Figure 3) and also against the equilibrium constants for complex formation (7) of the corresponding thiophenoxides with 1,3,5-trinitrobenzene (C.B.)TNB (Figure 4) [Unfortunately our results and those of Crampton and coworkers are not in the same solvent (methanol and 95% ethanol respectively) but we think that these differences should not appreciably affect the considerations which follow.]. From the least squares regression lines obtained for *m*-substituents, the following points emerge:

(a) The slopes observed in the two cases are small and, for a given thiophene substrate, they are a little higher when calculated with respect to the pK_a than with respect to (C.B.)TNB (respectively 0.28 and 0.25 for the substrate I and 0.27 and 0.24 for the substrate II).

These results suggest that the change in electron density at the sulfur atom of the thiophenoxide ion is greater in the reaction with 1,3,5-trinitrobenzene than in the reaction with a proton and that, moreover, these changes are much larger than those occurring in nucleophilic substitution rates with I and II. Brønsted plot for reactions of substituted phenoxides with chloro-2,4-dinitrobenzene in dioxane-water 80% at 65° has a β-value nearly close the unity. A β-value of 0.63 has been found from Biggi and Pietra (11) for the reaction of a series of amines with 2,4-dinitrochlorobenzene in 3:2 dioxane-water at 25.4°. This, according to the significance generally attached to the Brønsted β-value, seems to indicate that at rate-limiting transition state more bond-formation is involved in the reaction of phenoxides or amines with 2,4-dinitrochlorobenzene than in the reaction of thiophenoxide with thiophene deviations I and II [The slopes of the curves in Figure 3 are practically the β-values of the well-known Brønsted equation. They have been calculated from the points corresponding to the *m*-substituents since these points lie on a straight line, whereas the other points corresponding to the *p*-substituents show more or less significant deviations from linearity. If the slopes are calculated from all the points, the found values (slopeI = 0.437, r = 0.935, slopeII = 0.418, r = 0.944 (Figure 3); slopeI = 0.364, r = 0.976, slopeII = 0.346, r = 0.981 (Figure 4)) are always rather low when compared to the other similar data reported in literature: this confirms that a low degree of bond formation occurs at the rate-limiting transition state in the studied reactions.].

(b) The deviations from the linearity observed for *p*-$COCH_3$, *p*-CH_3, *p*-OCH_3, *p*-NH_2, and *p*-halogens indicate that the electronic effects of these substituents are stronger when the thiophenoxide ions are involved in the reaction rates (nucleophilicity) rather than in equilibrium constants (proton and carbon basicity). However, it is interesting to note that the deviations from linearity observed from electron-donating groups, are lower when the rate constants for a given thiophene substrate are compared with (C.B.) (Figure 4) rather than with pK_a (Figure 3). This indicates that thiophenoxide ions having *p*-substituents with strong +M effect have a nucleophilicity higher than that expected from the values of carbon basicity and even higher than that expected from the values of proton basicity.

Steric Effects.

We have also examined the effects of *o*-substituents in the benzenethiolate ion on the reaction rates. As it can be seen from Table I, the reactions are not strongly affected by steric hindrance; the observed rate decreases on introduction of methyl groups in the *o*-position of the thiol group is low.

EXPERIMENTAL

Solvent and Reagents.

Methanol was purified by a method reported in the literature (12). Compounds I and II were prepared as previously described (13). The substituted thiophenols were prepared by standard procedure.

Products.

The sulphides were prepared according to the method described in previous paper (13). The physical, analytical, and spectroscopic data of sulphides are reported in Tables II and III.

Kinetic Measurements.

The reaction rates were followed by uv spectroscopy as previously described (13). The probable error of rate constants is ± 4%. The kinetic data are the average of two or more separate runs conducted with different concentrations of the reagents in the range $10^{-3}M$-$10^{-4}M$. In all cases, second-order coefficients were observed and the actual formation of the expected substitution products in an appreciable amount (more than 95%) was checked.

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