

copy. Several samples of the same 0.3 M solution of V were sealed in Pyrex tubes, all of which were placed into the 258.0° bath simultaneously. Samples were removed at various times, cooled to room temperature, and diluted with chloroform, and the amount of V remaining was determined by infrared spectroscopy. By these semiquantitative methods, rate constants for the rearrangements of these imidates could be determined and are given in Table I.

Registry No.—II, 16240-81-6; III, 16240-82-7; IV, 16240-83-8; V, 16240-84-9; VI, 16240-85-0; VII, 16240-86-1; VIII, 16240-87-2; IX, 16240-88-3.

Acknowledgment.—The author acknowledges many encouraging and stimulating thoughts contributed to this work by A. S. Hay.

Steric Rate Enhancement in the Newman-Kwart Rearrangement. A Comparison with the Chapman Rearrangement

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A series of O-aryl dimethylthiocarbamates have been prepared and their rates of rearrangement to the corresponding S-aryl dimethylthiocarbamates have been determined. Steric acceleration of rates due to hindered rotation (as found also in the Chapman rearrangement) appeared to be present in the *ortho*-substituted compounds in this series. A correlation of the rates with substituent constants and a separation of polar and steric effects were achieved.

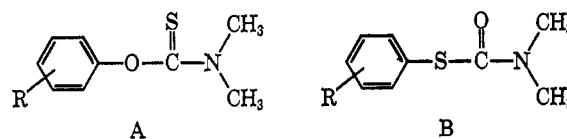
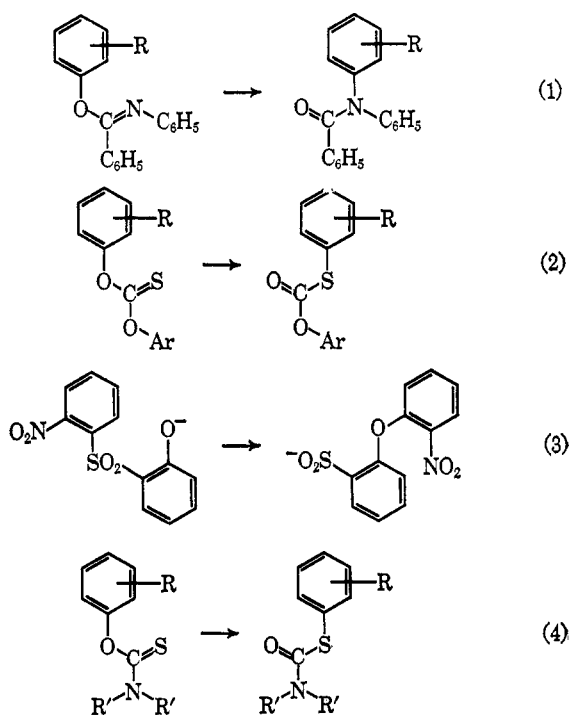
Intramolecular migration of aryl groups between adjacent atoms occurs quite commonly in organic chemistry. Much less common, however, are intramolecular migrations between nonadjacent atoms. Some examples of this latter type of reaction are the Chapman rearrangement¹ (reaction 1), the Schönberg rearrangement² (reaction 2), the Smiles rearrangement³ (reaction 3), and the recently reported conversion of O-aryl dialkylthiocarbamates into S-aryl dialkylthiocarbamates⁴ (reaction 4), hereinafter referred to as the Newman-Kwart rearrangement. The

present paper is concerned mainly with the Newman-Kwart and Chapman rearrangements.

It has been reported⁵ that the Chapman rearrangement is an intramolecular nucleophilic-aromatic substitution reaction and that *ortho* substituents in the migrating aromatic ring enhance the rate⁵⁻⁷ (steric acceleration due to hindered rotation (SAHR) effect⁶). The apparent similarity between this reaction and the Newman-Kwart rearrangement prompted a kinetic investigation of the latter in order to determine whether or not the postulated SAHR effect in the Chapman rearrangement was evident in the Newman-Kwart rearrangement also.

Results

The O-aryl dimethylthiocarbamates (A1-A13) used in the present study were prepared from the corresponding phenols by the method of Newman and Karnes.⁴ The previously unknown materials (A2, A4-A10, A12, and A13) were identified by their nmr and infrared spectra and by their elemental analyses.



- | | |
|---|---|
| 1, R = 4-OCH ₃ | 8, R = 2,6-(CH ₃) ₂ |
| 2, R = 4-CH ₃ | 9, R = 2- <i>t</i> -C ₄ H ₉ |
| 3, R = 4- <i>t</i> -C ₄ H ₉ | 10, R = 2- <i>t</i> -C ₄ H ₉ -4-CH ₃ |
| 4, R = H | 11, R = 2,6-(<i>t</i> -C ₄ H ₉) ₂ -4-CH ₃ |
| 5, R = 4-Br | 12, R = 2-C ₆ H ₅ |
| 6, R = 4-C ₆ H ₅ | 13, R = 2,6-(C ₆ H ₅) ₂ |
| 7, R = 2-CH ₃ | 14, R = 4-NO ₂ |

These same previously unknown compounds were each heated neat at 258° for times necessary for

(1) For a recent review, see J. W. Schulenberg and S. Archer, *Org. Reactions*, **14**, 1 (1965).

(2) H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Amer. Chem. Soc.*, **77**, 2479 (1955); D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).

(3) J. F. Bunnett and T. Okamoto, *ibid.*, **78**, 5363 (1956).

(4) M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966); H. Kwart and E. R. Evans, *ibid.*, **31**, 410 (1966).

(5) K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, **77**, 2205 (1955).

(6) H. M. Relles, *J. Org. Chem.*, **33**, 2245 (1968).

(7) Conversely, in intermolecular nucleophilic-aromatic substitution reactions, *ortho* substituents sterically cause rate depressions (absence of SAHR effect). See, for example, (a) A. M. Porto, L. Altieri, A. J. Castro, and J. A. Brieux, *J. Chem. Soc., Sect. B*, 963 (1966); (b) N. E. Sbarbati, *J. Org. Chem.*, **30**, 3365 (1965); (c) P. Van Berk, J. O. M. Van Langen, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, **75**, 1137 (1956); (d) P. J. C. Fierens and A. Halleux, *Bull. Soc. Chim. Belges*, **64**, 696 (1955).

their complete rearrangement to the corresponding S-aryl dimethylthiocarbamates (B2, B4–B10, B12, and B13, respectively). In every case, the product was found to be essentially pure by nmr spectroscopy. Each was recrystallized and identified by its elemental analysis and nmr and infrared spectra. The conversions of A1, A3, A11, and A14 into B1, B3, B11, and B14, respectively, have been reported⁴ previously.

In agreement with the recent study of Neuman, Roark, and Jonas,⁸ it was observed that the nmr spectrum of each A isomer displayed a well-resolved doublet at room temperature for the $(\text{CH}_3)_2\text{N}$ group, whereas each corresponding B isomer showed, for this group, a single sharp peak shifted upfield somewhat from the doublet of A. This type of nmr spectral difference was also noted by Newman and Karnes⁴ for the isomeric pairs which they prepared. This difference provided a relatively simple method for following the rates of rearrangement of the A isomers to the corresponding B isomers in diphenyl ether. The observed rate constants are listed in Table I.

TABLE I

RATE CONSTANTS FOR THE NEWMAN-KWART REARRANGEMENT IN A 0.3 M SOLUTION OF DIPHENYL ETHER AT 258.2°

Compd	$k \times 10^4, \text{sec}^{-1}$
A1	1.09 ± 0.05
A2	2.80 ± 0.10
A3	3.25 ± 0.05
A4	5.70 ± 0.20
A5	11.3 ± 0.2
A6	7.95 ± 0.15
A7	5.45 ± 0.25
A8	4.75 ± 0.05
A9	1.09 ± 0.03
A10	0.595 ± 0.005
A11	0.0390 ± 0.0010
A12	4.80 ± 0.05
A13	4.70 ± 0.10

In one case, A9 → B9, a fourfold increase in the initial concentration gave no change in the k value, thus indicating that the rearrangement was first order in A9. Newman and Karnes found⁴ that the rearrangement of A14 was also unimolecular. It, therefore, does not seem unreasonable to assume that the other A isomers studied herein rearranged by unimolecular processes also.⁹

The rates of rearrangement of A2, A4, A7, and A8 were similarly determined at 232.3°. These k values are similarly determined at 232.3°. These k values are listed in Table II along with the calculated enthalpy and entropy of activation.

Discussion

Evidence that (at least) A2, A4, A7, and A8 rearrange by a common mechanism is provided by the excellent straight-line plot of $\log k_{258.2^\circ}$ against $\log k_{232.3^\circ}$ (correlation coefficient = 0.990), which fulfills Exner's criterion.¹⁰

(8) R. C. Neuman, Jr., D. N. Roark, and V. Jonas, *J. Amer. Chem. Soc.*, **89**, 3412 (1967).

(9) Powers and Tarbell showed² that the structurally similar Schönberg rearrangement of bis(4-chlorophenyl)thioncarbonate to bis(4-chlorophenyl)thiolcarbonate displayed first-order kinetics. Furthermore, Wiberg and Rowland found³ that the Chapman rearrangement proceeded by first-order kinetics.

TABLE II
ACTIVATION PARAMETERS AND RATE CONSTANTS
FOR THE NEWMAN-KWART REARRANGEMENT IN 0.3 M SOLUTIONS
OF DIPHENYL ETHER AT 232.3°

Compd	$k \times 10^4, \text{sec}^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$
A2	4.35 ± 0.15	37.3 ± 1.5	-6.0 ± 2.5
A4	8.0 ± 0.25	39.5 ± 1.5	-0.4 ± 2.5
A7	7.9 ± 0.20	38.8 ± 1.5	-1.7 ± 2.5
A8	6.60 ± 0.10	39.7 ± 1.5	-0.2 ± 2.5

It is apparent from a comparison of the rate constants for A2, A7, and A8 that there is a rate-enhancing effect present in A7 and A8 which is considerably more important than the rate-depressing inductive and steric-compressive effects of methyl groups. This is most likely the SAHR effect previously found^{5,6} to be of importance in the Chapman rearrangement. Although there is considerable uncertainty involved, the trend in the ΔS^\ddagger values for A2, A7, and A8 (Table II) indicates that the rate enhancements of A7 and A8 arise from decreased ΔS^\ddagger . That is, the *o*-methyl substituents cause an entropy loss in A7 and A8, relative to A2, even before rearrangement occurs by hindering free rotation around the carbon-oxygen bonds. The restriction of this mode of rotation is precisely that which is required for the formation of the four-membered ring during rearrangement.

Also as in the Chapman rearrangement, steric compression apparently overrides the SAHR effect for *t*-butyl groups in the Newman-Kwart rearrangement. Thus, A9 rearranges only one-third as fast as A3.

The above discussion serves to indicate somewhat qualitatively that the same sort of effects are operative in the Chapman and Newman-Kwart rearrangement. However, the separation of polar and steric contributions to *ortho* substituent constants in both rearrangements can be achieved by a more quantitative approach, as follows.

Since direct attack occurs on a ring carbon during the rearrangements, the use of a set of substituent parameters other than σ seems desirable. Indeed, when the logarithms of the rate constants for A1–A6 (in which no steric effects are involved) were plotted against the corresponding σ values,¹¹ a least-squares line was obtained which had a correlation coefficient of only 0.839. Similarly, in the Chapman rearrangement, the plot of $\log k$'s for C1–C9 vs. σ gave a correlation coefficient of 0.925.

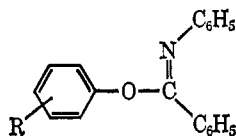
Intermolecular nucleophilic-aromatic substitution reactions resemble the Chapman and Newman-Kwart rearrangements in that they also involve direct attack on a ring carbon and placing of negative charge in the ring. From the kinetics of four different series of these reactions, Brioux and coworkers^{7a,12} were able to calculate *para* substituent constants by using the ρ values obtained from plots of $\log k$'s of *meta*-substituted compounds against σ values obtained from the literature. Where comparisons could be made, the *para* substituent constants obtained in this way much more closely resembled σ^- (Hammett's constants obtained from the reactions of anilines and phenols)

(10) O. Exner, *Collect. Czech. Chem. Commun.*, **29**, 1094 (1964).

(11) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 89 (1963).

(12) W. Greizerstein, R. A. Bonelli, and J. A. Brioux, *J. Amer. Chem. Soc.*, **84**, 1026 (1962).

than σ . For the present discussion, Brioux's series of substituent constants have been designated as " σ^- " constants.



C1, R = 4-OCH ₃	C9, R = 3-CH ₃
2, R = 4-CH ₃	10, R = 2-CH ₃
3, R = 4- <i>t</i> -C ₄ H ₉	11, R = 2,6-(CH ₃) ₂
4, R = H	12, R = 2- <i>t</i> -C ₄ H ₉
5, R = 4-C ₂ H ₅	13, R = 2,6-(<i>t</i> -C ₄ H ₉) ₂
6, R = 4- <i>i</i> -C ₃ H ₇	14, R = 2,6-(C ₆ H ₅) ₂
7, R = 4-Cl	15, R = 2-CH ₃ -6-C ₆ H ₅
8, R = 4-Br	16, R = 2- <i>i</i> -C ₃ H ₇

When these σ^- values were plotted against the log k 's for the Newman-Kwart rearrangement of A1-A6, the correlation coefficient was found to be 0.954 and $\rho = 1.62^{13}$ (see Figure 1). For the Chapman rearrange-

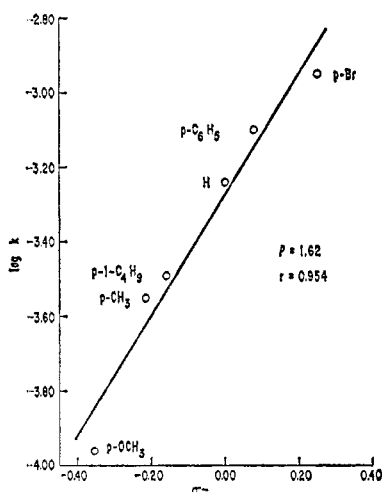


Figure 1.—Least-squares plot of log k for the Newman-Kwart rearrangement of 4-substituted A at 258.2° vs. σ^- .

ment of C1-C4 and C7-C9,^{5,14} the correlation coefficient was 0.970 and $\rho = 1.63^{13}$ (see Figure 2). (No improvement in these correlations was found when log k 's were plotted against linear combinations of σ^- and σ .¹⁵) From these ρ values, it was possible to calculate the substituent constants for the *ortho*-substituted compounds in the Newman-Kwart (A7-A13) and in the Chapman (C10-C16) rearrangements. Furthermore, according to Taft¹⁶

$$\sigma_{ortho}^{polar} \cong \sigma_{para}^{polar} \quad (5)$$

Using this same approximation for σ^- values, it was possible to calculate *steric* substituent constants for the two rearrangements. These results are tabulated in Tables III, IV, and V.

(13) The similarity in the ρ values further supports the proposal that the mechanisms for the two rearrangements are the same.

(14) C5 and C6 were omitted from the plot because σ^- values for *p*-C₂H₅ and *p*-*i*-C₃H₇ are not available.

(15) The use of linear combinations of substituent constants for improved rate correlations has been reported: (a) A. A. Humfray and J. J. Ryan, *J. Chem. Soc., Sect. B*, 468 (1967); (b) J. J. Ryan and A. A. Humfray, *ibid.*, 842 (1968); (c) Y. Tsuno, T. Ibata, and Y. Yukawa, *Bull. Chem. Soc. Jap.*, **32**, 960 (1959); (d) Y. Tsuno and Y. Yukawa, *ibid.*, **32**, 965, 971 (1959).

(16) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 556.

TABLE III
SEPARATION OF POLAR AND STERIC EFFECTS
IN THE NEWMAN-KWART REARRANGEMENT IN 0.3 M SOLUTIONS
OF DIPHENYL ETHER AT 258.2°

Compd	Log k	σ_{para}^- ^a	σ_{para}^- polar ^a	σ_{para}^- steric ^a
A1	-3.96	-0.354	-0.354	0.0
A2	-3.55	-0.216	-0.216	0.0
A3	-3.49	-0.160	-0.160	0.0
A4	-3.24	0.0	0.0	0.0
A5	-2.95	0.251	0.251	0.0
A6	-3.10	0.078	0.078	0.0
		Newman-Kwart σ_{ortho}^- ^b	σ_{ortho}^- polar ^{a,c}	Newman-Kwart σ_{ortho}^- steric
A7	-3.26	-0.012	-0.216	0.204
A8	-3.32	-0.049	-0.432	0.383
A9	-3.96	-0.444	-0.160	-0.284
A10	-4.23	-0.611	-0.376 ^d	-0.235
A11	-5.41	-1.340	-0.536 ^d	-0.804
A12	-3.32	-0.049	0.078	-0.127
A13	-3.33	-0.056	0.156	-0.212

^a Average values for four intermolecular reactions; see ref 7a and 12. ^b Calculated from $\rho = 1.62$. ^c Assume that total σ^- equals the sum of the individual σ^- 's; see ref 16; σ_{ortho}^- polar \cong σ_{para}^- polar. ^d Includes σ_{para}^- for 4-CH₃ group.

TABLE IV
SEPARATION OF POLAR AND STERIC EFFECTS
IN THE CHAPMAN REARRANGEMENT IN 0.3 M SOLUTIONS
OF DIPHENYL ETHER AT 255°

Compd	Log k	σ_{ortho}^- ^a	σ_{ortho}^- polar ^{a,e}	σ_{ortho}^- steric ^a
C1	-4.80 ^b	-0.354	-0.354	0.0
C2	-4.45 ^b	-0.216	-0.216	0.0
C3	-4.42 ^b	-0.160	-0.160	0.0
C4	-4.12 ^b	0.0	0.0	0.0
C5	-4.43 ^b	(-0.19) ^c	(-0.19) ^c	0.0
C6	-4.42 ^b	(-0.19) ^c	(-0.19) ^c	0.0
C7	-3.86 ^b	0.212	0.212	0.0
C8	-3.74 ^b	0.251	0.251	0.0
C9	-4.15 ^b	-0.069	-0.069	0.0
		Chapman σ_{ortho}^- ^d	σ_{ortho}^- polar ^{a,e}	Chapman σ_{ortho}^- steric
C10	-4.05 ^b	0.043	-0.216	0.259
C11	-3.91 ^b	0.129	-0.432	0.561
C12	-4.64 ^b	-0.319	-0.160	-0.159
C13	-5.51 ^b	-0.853	-0.320	-0.533
C14	-3.73 ^b	0.239	0.156	0.083
C15	-3.81 ^b	0.190	-0.138	0.328
C16	-4.17 ^b	-0.031	(-0.19) ^c	(0.16) ^c

^a Average values for four intermolecular reactions, see ref 7a and 12. ^b Data from ref 5. ^c No data reported in ref 7a and 12. Assumed that values would be intermediate between CH₃ and *t*-C₄H₉ to a first approximation. ^d Calculated from $\rho = 1.63$. ^e Assume that total σ^- equals the sum of the individual σ^- 's (see ref 16); σ_{ortho}^- polar \cong σ_{para}^- polar. ^f Data from ref 6.

TABLE V
COMPARISON OF STERIC EFFECTS IN THE NEWMAN-KWART
AND CHAPMAN REARRANGEMENTS

<i>ortho</i> substituent(s)	Newman-Kwart σ_{ortho}^- steric	Chapman σ_{ortho}^- steric
2-CH ₃	0.204	0.259
2,6-(CH ₃) ₂	0.383	0.561
2- <i>t</i> -C ₄ H ₉	-0.284, -0.235	-0.159
2,6-(<i>t</i> -C ₄ H ₉) ₂	-0.804	-0.533
2-C ₆ H ₅	-0.127	
2,6-(C ₆ H ₅) ₂	-0.212	0.083
2-CH ₃ -6-C ₆ H ₅		0.328
2- <i>i</i> -C ₃ H ₇		(0.16)

TABLE VI
 O-ARYL DIMETHYLTHIOCARBAMATES

Compd	Mp, °C	Proton nmr τ values (no. of protons)				Characteristic ir bands, ^a cm ⁻¹
		Aromatic multiplet	N(CH ₃) ₂ Doublet	Ar-CH ₃ singlet	Ar-C(CH ₃) ₃ singlet	
A2	86-88 ^b	2.72-3.22 (4 H)	6.63, 6.74 (6 H)	7.77 (3 H)		1539, 1200
A4 ^c	170-175 (0.25) ^d	2.47-3.1 (5 H)	6.68, 6.80 (6 H)			1527, 1200
A5	84-86 ^b	2.23-3.16 (4 H)	6.60, 6.74 (6 H)			1542, 1208
A6	139-141 ^b	2.27-3.01 (9 H)	6.55, 6.67 (6 H)			1534, 1205
A7 ^c	163-168 (0.2) ^d	2.68-3.18 (4 H)	6.63, 6.77 (6 H)	7.92 (3 H)		1528, 1212
A8	80-82 ^b	2.94 (3 H)	6.55, 6.64 (6 H)	7.83 (6 H)		1535, 1172
A9	63-65 ^{b,e}	2.53-3.28 (4 H)	6.60, 6.67 (6 H)		8.66 (9 H)	1533, 1193
A10	72-74 ^b	2.72-3.1 (3 H)	6.52, 6.63 (6 H)	7.67 (3 H)	8.65 (9 H)	1522, 1208
A12	102-104 ^b	2.47-2.9 (9 H)	6.72, 6.94 (6 H)			1533, 1194
A13	132-133 ^{b,f}	2.40-2.85 (13 H)	7.08, 7.13 (6 H)			1535, 1197

^a Characteristic bands were reported to be 1530-1560 and 1190-1230 cm⁻¹ for a series of 29 compounds (see ref 4). ^b Recrystallized from ethanol. ^c Some S-aryl compound was formed on distillation and remained as a small impurity in the O-aryl compound. Its presence was taken into account in the kinetic runs but did not affect the elemental analysis. ^d Boiling point (millimeter). ^e Recrystallized after distilling; the boiling point was 174-182° (0.13 mm). ^f Recrystallized after eluting from an alumina column with 1:3 hexane-benzene.

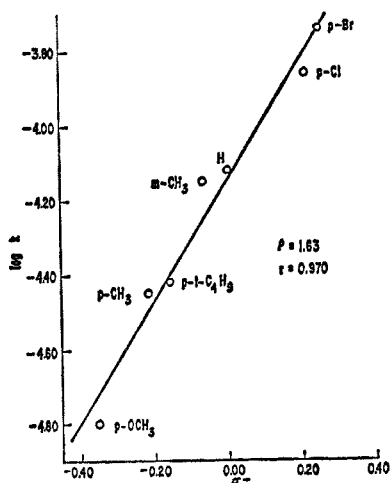


Figure 2.—Least-squares plot of $\log k$ for the Chapman rearrangement of 4-substituted C at 255° vs. σ^- .

Despite the approximations made above, the values for σ^-_{ortho} in both rearrangements are in agreement with the previously discussed (*vide supra*) competition between rate enhancement (SAHR effect) and rate depression. The rate-enhancing steric effect of a single *o*-methyl group is almost the same in both rearrangements and, in each case, addition of a second *o*-methyl group causes further steric rate enhancement by a factor of approximately two (see Table V).

Steric compression during rearrangement would be expected to be much more severe with *t*-butyl groups than with methyl groups and the negative sign of the σ^-_{ortho} values for the *t*-butyl compounds shows that this rate-retarding compression overrides the SAHR effect. Although the σ^-_{ortho} values for the *t*-butyl compounds are not the same in the two rearrangements, the ratio of the values for two *t*-butyl groups and one *t*-butyl group in both cases is *ca.* 3. This more-than-cumulative effect has been discussed previously⁶ and given a tentative structural interpretation.

A single isopropyl group has a σ^-_{ortho} value between

those for methyl and *t*-butyl in agreement with the expected order of steric compression for the three groups (*t*-butyl > *i*-propyl > methyl). The positive sign of this σ^-_{ortho} indicates that here, as in the methyl case, the SAHR effect is more important than steric compression.

It is probable that the compounds containing *o*-phenyl substituents give rise to small σ^-_{ortho} values because of the approximate balance between steric compression and the SAHR effect. But the errors incurred through the approximations used are apparently magnified in these cases since the sign of the σ^-_{ortho} cannot even be stated.

There is another internal consistency which arises from the σ^-_{ortho} values for the Chapman rearrangement. The calculated value for 2-CH₃-6-C₆H₅ is 0.328. This is very close to that which is obtained, 0.301, by adding the value for 2-CH₃ to one-half of the value for 2,6-(C₆H₅)₂ (see Table V).

Experimental Section

All new compounds gave satisfactory elemental analysis and molecular weight determinations consistent with the assigned structures. Known compounds gave correct melting points and the expected spectral data.

Preparation of O-Aryl Dimethylthiocarbamates.—These compounds (A1-A13) were prepared under nitrogen from the appropriate phenol by the sodium hydride-DMF-dimethylthiocarbonyl chloride method of Newman and Karnes.⁴ Their corrected melting points (or boiling points) and spectral data are given in Table VI. Infrared spectra were recorded as KBr pellets or in chloroform or carbon disulfide solution. Nmr spectra were taken in CCl₄ or CDCl₃ using tetramethylsilane as an internal standard.

Preparation of S-Aryl Dimethylthiocarbamates.—These compounds were all obtained in high yield by heating the corresponding O-aryl dimethylthiocarbamate at 258° for the appropriate time (determined in the kinetic runs). Their physical constants and spectral data are given in Table VII. Infrared and nmr spectra were recorded as described for the O-aryl dimethylthiocarbamates.

Kinetic Runs.—A 0.3 M solution of each A isomer in diphenyl ether was prepared, sealed in an nmr tube, and heated in a refluxing diphenyl ether bath at 258.2° (cor.). The nmr tube was removed at various intervals and its nmr spectrum was recorded at room temperature. The relative amounts of A and B isomers present as a function of time at 258.2° were thus determined. Control experiments showed that no changes in the

(17) It should be noted that these steric substituent constants can only apply to intramolecular reactions of the types shown in eq 1-4 since they include SAHR effects. SAHR effects would not be expected to occur in intermolecular nucleophilic-aromatic substitutions.

TABLE VII
 S-ARYL DIMETHYLTHIOCARBAMATES

Compd	Mp, °C	Proton nmr τ values (no. of protons)				Thiol ester carbonyl ir band, cm^{-1} ^a
		Aromatic multiplet	N(CH ₃) ₂ Singlet	Ar-CH ₃ singlet	Ar-C(CH ₃) ₂ singlet	
B2	31-33 ^b	2.50-2.96 (4 H)	6.97 (6 H)	7.65 (3 H)	1669	
B4	c	2.50-2.67 (5 H)	6.98 (6 H)		1668	
B5	81-83 ^d	2.40-2.77 (4 H)	6.97 (6 H)		1660	
B6	136-137.5 ^d	2.32-2.83 (9 H)	6.98 (6 H)		1665	
B7	c	2.73 (4 H)	6.94 (6 H)	7.67 (3 H)	1668	
B8	35-37 ^b	2.86 (3 H)	7.00 (6 H)	7.59 (6 H)	1664	
B9	75-77 ^b	2.45-3.00 (4 H)	7.07 (6 H)	8.53 (9 H)	1662	
B10	70-73 ^d	2.68-2.98 (3 H)	6.95 (6 H)	7.67 (3 H)	1662	
B12	83-85 ^d	2.68 (9 H)	7.19 (6 H)		1663	
B13	127-129 ^d	2.56-2.91 (13 H)	7.42 (6 H)		1660	

^a Reported as occurring near 1675 cm^{-1} by L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 188. ^b Recrystallized from 30-60° petroleum ether. ^c Liquid. ^d Recrystallized from ethanol.

 TABLE VIII
 REARRANGEMENT OF (2-*t*-BUTYL-4-METHYL)PHENYL
 DIMETHYLTHIOCARBAMATE (A10) AT 258.2°

Time at 258.2° min	% of A10 remaining	$k \times 10^5$ ^a sec ⁻¹
0	100	
30	89.4	6.2
90	74.0	5.6
150	58.6	6.0
210	48.5	5.7
270	39.6	5.7
450	19.3	6.1
1350	ca. 0	$\text{Av } k = 5.9 \pm 0.2$

^a Calculated from the equation $k = 2.303/t \times \log a/(a-x)$ where t = seconds, a = initial concentration, and $(a-x)$ = concentration at time t .

amounts of A and B isomers occurred over a period of days at room temperature. Duplicate runs in each case agreed within 4% (the precision of the nmr integrator). The rearrangements were followed kinetically to at least 75% completion and no drifts in the rate constants were noted. The results are listed in Table I.

In every case, after many half-lives, no O-aryl compound could be detected by nmr.

The results of a typical kinetic run are illustrated in Table VIII.

Registry No.—A2, 16241-02-4; B2, 7322-85-2; A4, 16241-04-6; B4, 7304-68-9; A5, 16241-06-8; B5, 7305-13-7; A6, 16241-08-0; B6, 16241-09-1; A7, 10345-39-8; B7, 7305-14-8; A8, 16241-12-6; B8, 16241-13-7; A9, 16241-14-8; B9, 16241-15-9; A10, 16214-91-8; B10, 16214-92-9; A12, 10345-41-2; B12, 16241-17-1; A13, 16241-18-2; B13, 16241-19-3.

Hydrolysis Kinetics for *p*-Dimethylaminophenyl Isocyanate in Aqueous Solutions

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p-Dimethylaminophenyl isocyanate hydrolyzes, giving *p*-dimethylaminoaniline. The rate-limiting reaction at pH < 9 is hydration of the isocyanate to give the carbamic acid (or carbamate ion). Rate data for the hydration indicate three reaction paths which are first order in unprotonated isocyanate: (1) pH independent; (2) first order in [H⁺]; (3) first order in [OH⁻]. Approach of the rate to pH independence as the pH is lowered is attributed to protonation of the isocyanate. The rate decreases with increasing acetate buffer concentration. In phosphate buffers, fast reaction of the phosphate with the isocyanate competes with hydration. An interpretation of the yields of *p*-dimethylaminoaniline in phosphate buffers indicates that there is no important catalysis of isocyanate hydrolysis by phosphate. The yield experiments also gave the rate constant for the reaction of the isocyanate with *p*-dimethylaminoaniline to form 1,3-bis(*p*-dimethylaminophenyl)urea. Arsenate reacts with the isocyanate even more rapidly than does phosphate. The product goes to *p*-dimethylaminoaniline very rapidly. Above pH 9, decarboxylation of the carbamate ion is the rate-limiting reaction in the hydrolysis of the isocyanate. It is proposed that decarboxylation proceeds *via* protonation of the nitrogen of the carbamate group.

Hydrolysis kinetics for organic isocyanates in aqueous solution appear not to have been reported. The present communication describes the hydrolysis kinetics for *p*-dimethylaminophenyl isocyanate in aqueous solutions containing 1% acetonitrile. This isocyanate gave a product (*p*-dimethylaminoaniline) that could be monitored conveniently at a rotating platinum anode, and reaction rates were not prohibitively high. Since the rotating electrode is a very sensitive analytical probe, low isocyanate concentrations could be used. It was thus possible to avoid almost completely the reaction of the isocyanate with *p*-dimethylaminoaniline to

give 1,3-bis(*p*-dimethylaminophenyl)urea.¹ Eliminating this reaction simplified the kinetics.

Results and Discussion

Below pH 11, reactions were monitored with the rotating platinum electrode. At higher pH values, reactions were slow and were best followed spectrophotometrically. Observed pseudo-first-order rate constants, k_{obsd} , were calculated from slopes of $\log (X_{\infty}$

(1) H. Staudinger and R. Endle, *Ber.*, **50**, 1042 (1917); C. Naegeli, A. Tyabji, L. Conrad, and F. Litwan, *Helv. Chim. Acta*, **21**, 1100 (1938).