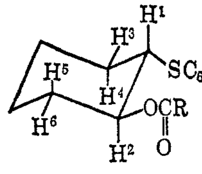
By a similar procedure, the other acid anhydrides were obtained from the corresponding mercuric and silver carboxylates (see Table II).

General Procedure for the Preparation of the Adducts (6–8).—To a stirred mixture of an olefin (0.02 mol) and a mercuric carboxylate (0.01 mol) in 20 ml of methylene chloride was added a solution of **5** (0.02 mol) in 10 ml of methylene chloride at room temperature over a period of 20 min. A slightly exothermic reaction took place soon. Stirring was continued for 20 min at room temperature. A white precipitate of mercuric chloride (1.8–2.2 g, 67–76%) was collected by filtration. The filtrate was concentrated and chromatographed on alumina (80 g) using ether as an eluent. After removal of ether, the residual oil was distilled to give the corresponding adduct. Yields, physical properties, and analytical data are listed in Table III. The infrared spectra of **6a**, **6b**, **7a**, **7b**, and **8** showed carbonyl absorptions at 1740, 1720, 1740, 1725, and 1740 cm^{-1}, respectively. The nmr[15] spectrum of **6a** showed peaks at τ 7.6–8.9 (complex, 8 H), 5.25 (sextet, 1 H, CH),[16] and 6.88 (sextet, 1 H, CH);[16] that of **6b** showed peaks at τ 7.6–8.9 (complex, 8 H), 5.01 (sextet, 1 H, CH),[16] and 6.71 (sextet, 1 H, CH).[16] The nmr spectrum of **7a** showed peaks at τ 6.73 (quartet, 1 H, CH_2),[17] 6.97 (quartet, 1 H, CH_2),[17] and 4.16 (quartet, 1 H, CH);[17] that of **7b** showed peaks at τ 6.57 (quartet, 1 H, CH_2),[17] 6.84 (quartet, 1 H, CH_2),[17] and 3.93 (quartet, 1 H, CH);[17] that of **8** showed peaks at τ 6.92 (doublet, 2 H, J = 6 cps, CH_2) and 4.13 (triplet, 1 H, J = 6 cps, CH).



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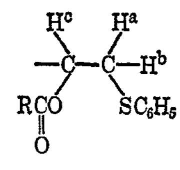

7, 8

Hydrolysis of 7b.—A solution of **7b** (3.34 g, 0.01 mol) and sodium hydroxide (0.60 g, 0.015 mol) in 25 ml of water and 25 ml of ethanol was heated on the steam bath for 10 hr. After removal of ethanol, the residue was diluted with 30 ml of water, extracted repeatedly with ether, and dried over anhydrous sodium sulfate. After removal of ether, the residual oil was distilled to give **9** (1.60 g, 70%): bp 138–139° (0.06 mm) [lit.[8] bp 168° (2 mm)]; ν_{max} 3410 (OH) cm^{-1}; nmr (CCl_4), two quartets centered at τ 7.00 (1 H) and 7.06 (1 H) with J_{ab} = 13 cps, a singlet at 6.45 (1 H, OH), a quartet at 5.48 (1 H, J_{ac} and J_{bc} = 5 and 8 cps), a multiplet centered at 2.88 (10 H, aromatic protons).

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.02; H, 6.13. Found: C, 73.26; H, 6.00.

The aqueous, alkaline solution was acidified with dilute hydrochloric acid to give benzoic acid (1.00 g, 82%), mp 118–120°.

Reaction of Mercuric Thiobenzoate with 5.—To a stirred suspension of mercuric thiobenzoate (4.75 g, 0.01 mol) in 20 ml of methylene chloride was added a solution of **5** (2.90 g, 0.02 mol) in 10 ml of methylene chloride at room temperature. After stirring was continued for 10 min, a white precipitate of mercuric chloride (2.22 g, 82%) was filtered off. The filtrate was concentrated and distilled to give benzoyl phenyl disulfide[18] (3.96 g, 80%): bp 147–148° (0.1 mm); ν_{max} 1695, 1200, 885, 690, and 680 cm^{-1}.

Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.36; H, 4.09. Found: C, 63.65; H, 4.18.

Similarly, mercuric chloride (89%) and diphenyl disulfide (97%) were obtained from the reaction of mercuric benzenethiolate with **5**.

Reaction of Mercuric Benzenethiolate with 1.—To a stirred suspension of mercuric benzenethiolate (4.19 g, 0.01 mol) in 20 ml of methylene chloride was added **1** (2.96 g, 0.01 mol) at room temperature. A reaction took place immediately, and a clear yellow solution was formed. The reaction mixture was concentrated *in vacuo* to dryness and treated with ether. The yellow crystal of **2** (4.76 g, 95%), mp 134–136°, was collected by filtration. The filtrate was evaporated and chromatographed on alumina (80 g) to remove residual **2**. Elution with ether gave diphenyl disulfide (2.10 g, 98%), mp 59–60°.

Registry No.—**1**, 97-77-8; **2**, 16162-55-3; **5**, 931-59-9; **6a**, 16162-54-2; **6b**, 16162-48-4; **7a**, 16162-49-5; **7b**, 16162-50-8; **9**, 16162-51-9; benzoyl phenyl disulfide, 5718-98-9; mercuric thiobenzoate, 16162-53-1.

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[15] The nmr spectra were measured at 100 Mcps in CCl_4 solution with TMS as an internal standard, and these data were obtained by first-order analysis.

[16] $J_{12} = J_{14} = J_{25}$ = 8 cps, $J_{13} = J_{26}$ = 4 cps.

[17] J_{ab} = 14 cps, J_{ac} and J_{bc} = 6 and 8 cps.

[18] H. Böhme and M. Clement, *Ann.*, **576**, 61 (1952).

Steric Rate Enhancement in the Chapman Rearrangement

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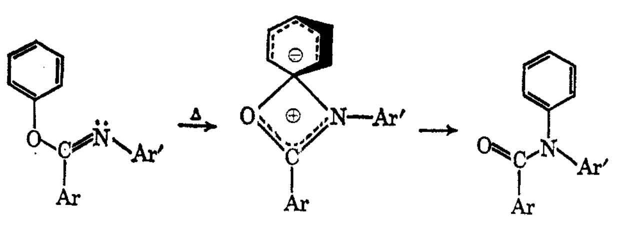
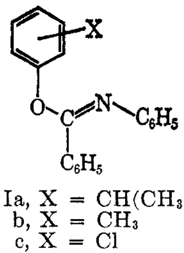
N-Phenylbenzimidates of 2,6-dimethyl-, 2,6-di-*t*-butyl-, 2,6-diphenyl-, and 2-methyl-6-phenylphenol have been prepared and have been found to undergo the Chapman rearrangement to give the corresponding N-arylbenzanilides. Kinetic measurements have been obtained and are discussed in terms of the competition between steric acceleration and steric deceleration of the rates of rearrangement.

An elegant study by Wiberg and Rowland[1] indicated that the Chapman rearrangement[2] obeyed first-order kinetics and that the mechanism involved an intramolecular, nucleophilic–aromatic substitution.



It was also reported[1] that the ratios of the rate constants for corresponding *ortho*- and *para*-substituted compounds (Ia–d) were greater than unity. It was assumed that the *ortho* substituent hindered free ro-



Ia, X = $CH(CH_3)_2$
b, X = CH_3
c, X = Cl
d, X = OCH_3
e, X = $C(CH_3)_3$
f, X = H

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

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

tation of the aromatic ring to which it was attached; the restriction of this mode of rotation was precisely that which was required for the formation of the four-membered ring in the transition state. That is, the introduction of an *ortho* substituent lessens the entropy decrease on proceeding from the reactant to the transition state. Indeed, it was found that the entropies of activation for *p*-Ib and *o*-Ib were −9.7 and −3.6 eu, respectively. In the case of Ie, k_{ortho}/k_{para} was 0.60. Here it was suggested that the steric requirement of the *o*-*t*-butyl group was large enough to overcome the rate-enhancing effect resulting from hindered rotation. The $\Delta S^{\ddagger}$ value for *o*-Ie was indeed about 8 eu more negative than that for *o*-Ib.

An extension of these arguments predicts that the rate of the Chapman rearrangement should be greater with two *ortho* substituents on the migrating aromatic ring than with one, provided that overriding steric compression is not attained. Successful Chapman rearrangements, in which the migrating aromatic ring contained two *ortho* substituents, have been reported[2] only in cases where the substituents were halogens, and no kinetic data were reported. Even if a kinetic study revealed that these di-*o*-halo compounds rearranged faster than the corresponding mono-*o*-halo compounds, it would be difficult to separate the rate enhancement due to the hindrance to rotation in the reactant and that due to the inductive electron-withdrawing effect of the halogens.

A study of the Chapman rearrangement of imidates of some 2,6-disubstituted phenols, in which the substituents were not electron-withdrawing groups, was expected to provide an increased understanding of the competition between steric acceleration and steric deceleration of rates. Therefore, four aryl N-phenylbenzimidates (II, III, IV, V) were prepared from N-phenylbenzimidoyl chloride and the corresponding phenol in the presence of base. The rearrangement of these imidates occurred readily at 300° and the corresponding amides (VI, VII, VIII, IX) were obtained in high yield (Scheme I).

In order to compare the rates of rearrangement of II–V with literature values[1] for other imidates, samples of II–V were dissolved in diphenyl ether and heated at 258.0°. The rearrangements of II, III, and IV were followed by nuclear magnetic resonance spectroscopy; the rearrangement of V was followed by an infrared method. The semiquantitative results are given in Table I.[3-5] The $\Delta H^{\ddagger}$ values[1] for the Chapman rearrangement of five very different aryl N-phenylbenzimidates range from 36.7 to 39.5 kcal/mol. The average of these values was used to calculate the rate constants at 255° corresponding to those given in Table I. These are listed in Table II together with some other rate constants selected from the literature[1] for comparison.

Scheme I

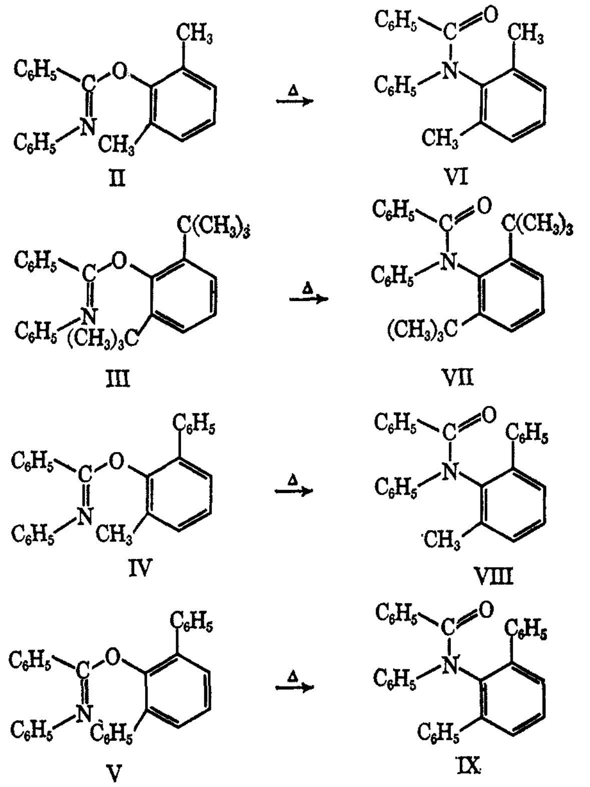

Table I

Rate Constants of Chapman Rearrangements at 258.0° in Diphenyl Ether

Imidate	Substituent[a]	Concn, M[b]	$k \times 10^5$, sec^{-1}
II	2,6-di-CH_3	0.303	15.1 ± 0.1
III	2,6-(t-C_4H_9)$_2$	0.303	0.38 ± 0.04
IV	2-CH_3-6-C_6H_5	0.301	19.0 ± 2.2
V	2,6-(C_6H_5)$_2$	0.302	23.1 ± 1.1

[a] In O-aryl ring. [b] Concentrations of the solutions at 25°.

Table II

Rate Constants for Chapman Rearrangements at 255° in Diphenyl Ether

Imidate	Substituent[a]	$k \times 10^5$, sec^{-1}	k/k_{If}
II	2,6-di-CH_3	12.3	1.61
III	2,6-(t-C_4H_9)$_2$	0.31	0.040
IV	2-CH_3-6-C_6H_5	15.5	2.02
V	2,6-(C_6H_5)$_2$	18.8	2.45
If	H	7.66[b]	1.00
o-Ib	2-CH_3	8.87[b]	1.16
p-Ib	4-CH_3	3.55[b]	0.46
o-Ie	2-t-C_4H_9	2.30[b]	0.30
p-Ie	4-t-C_4H_9	3.82[b]	0.50

[a] In O-aryl ring. [b] Obtained from 0.3 M solutions of the imidate in diphenyl ether at 255° by a perchloric acid titration method.[1]

From the rate constants for If and *o*-Ib, it is apparent that the combined polar and steric decelerating effects of an added *o*-methyl group on the rearrange-

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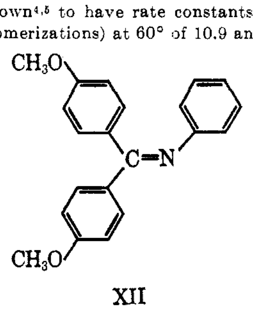
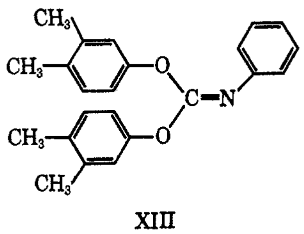
(3) Implicit in a discussion of the Chapman rearrangement and its kinetics is that, regardless of which form (*syn* or *anti*) of the imidate reacts, the equilibrium between these forms is rapid compared to the rate of rearrangement. This assumption is quite credible since XII and XIII have been shown[4,5] to have rate constants for inversion of nitrogen (pseudo-*syn*-*anti* isomerizations) at 60° of 10.9 and *ca.* 1.6 × 10^{-3} sec^{-1}, respectively.


XII


XIII

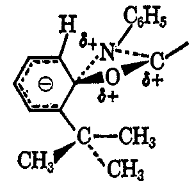
(4) D. Y. Curtin and C. G. McCarty, *Tetrahedron Lett.*, 1269 (1962).

(5) N. P. Marullo and E. H. Wagener, *J. Amer. Chem. Soc.*, **88**, 5034 (1966).

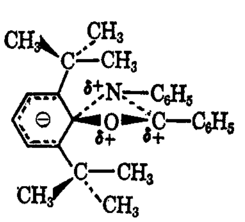
ment are outweighed by the steric acceleration due to hindered rotation (SAHR) effect. The combination of these factors leads to a 16% increase in *k*. More striking is the observed 61% increase in *k* in placing two *o*-methyl groups on the migrating aryl ring (compare *k*'s for If and II). If all substituent effects were additive,[6] a 35% rate increase would have been expected. Since all polar and steric effects, other than the SAHR effect, should inhibit the rearrangement (compare *k*'s for If and *p*-Ib), the large rate enhancement observed must be due to the fact that two *o*-methyl groups exhibit more of an SAHR effect than would be predicted from the effect of one *o*-methyl group alone. That is, two *o*-methyl groups hinder free rotation around the ether linkage of II more than twice as much as the methyl group in *o*-Ib.

On the other hand, with one *o*-*t*-butyl group (*o*-Ie), the steric compression which is introduced on proceeding to the transition state is slightly more important than the SAHR effect (assuming approximately the same polar effect for an *o*- and a *p*-*t*-butyl group) since the rate constant for *o*-Ie is slightly less than that for *p*-Ie.[7]

From the rate constants for If and *o*-Ie, if all substituent effects were additive, one would predict that the addition of another *o*-*t*-butyl group, giving III, would depress the rearrangement rate constant to *ca.* 0.69×10^{-5} sec^{-1}. The fact that the observed rate constant was 0.31×10^{-5} sec^{-1} indicates that the decelerating effect of steric compression is more than twice as important for two *o*-*t*-butyl groups as for one. A possible structural explanation for this more than cumulative effect is that bond-angle distortion occurs to relieve nonbonded strain in the rearrangement of *o*-Ie (see X) but cannot occur in III because of the presence of the second *o*-*t*-butyl group (see XI).



X



XI

From the available data, it is not possible at present to discuss the magnitude of the SAHR effect on the rates of the Chapman rearrangement of IV and V. It can be seen, however, that the combination of resonance, inductive, and SAHR effects, enhancing the rates of rearrangement of these two compounds over that of If, was apparently much more than enough to offset the rate-depressing effect arising from steric compression in the transition state.

Experimental Section

N-Phenylbenzimidoyl Chloride.—A mixture of 105 g (0.532 mol) of benzanilide and 100 ml of thionyl chloride was stirred and heated at reflux for 1.5 hr. Gas evolution began almost immediately. After the resulting black solution had been allowed to stand at room temperature overnight, the excess thionyl chloride was removed by distillation at atmospheric pressure. Further distillation under reduced pressure afforded 112.6 g (98%) of N-phenylbenzimidoyl chloride: bp 119–121° (0.15 mm); mp 41–42° [lit. bp 115–120° (0.3 mm);[9] mp 40°[10]].

2,6-Dimethylphenyl N-Phenylbenzimidate (II).—Exactly 6.097 g (0.0500 mol) of 2,6-xylenol was dissolved in 50 ml of 1.02 *M* sodium ethoxide in ethanol. Then, 10.774 g (0.0500 mol) of N-phenylbenzimidoyl chloride in 45 ml of ethyl ether was added with continuous stirring. A slight exotherm was noted and a precipitate appeared. After the system had been stirred at room temperature for 5 hr, it was mixed with 250 ml of ethyl ether. This ether solution was extracted three times with water and dried with anhydrous sodium sulfate. Removal of the solvent on a steam bath gave 14.91 g of a viscous, orange oil which soon became entirely crystalline. Three recrystallizations from hexane afforded 6.17 g (41%) of pure V, mp 93–94.5°. The nuclear magnetic resonance (nmr) spectrum (CCl_4) consisted of a multiplet for the aromatic protons (τ 2.35–3.60; integral 13.0) and a single peak for the methyl protons (7.72; integral 6.1). The infrared spectrum[11] ($CHCl_3$) displayed C=N absorption at 1670 cm^{-1} and aryl ether absorption at 1253 cm^{-1}.

Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.9; H, 6.0; N, 4.6.

N-(2,6-Dimethylphenyl)benzanilide (VI).—A sample of 1.935 g (0.00643 mol) of V was sealed in a partially evacuated Carius tube under nitrogen and then heated at 300° for 30 min. The very slightly yellow material thus obtained was shown spectroscopically and by thin layer chromatography to be devoid of any starting material (II). The nmr spectrum (CCl_4) displayed a complex multiplet, entirely different from that of II, between τ 2.44 and 3.30 (integral 13.0) and a single sharp peak at 7.85 (integral 5.8). The infrared spectrum[11] ($CHCl_3$) showed a tertiary amide carbonyl absorption at 1645 and a tertiary phenyl amine band at 1345 cm^{-1} and none of the characteristic bands of II. The spectra are consistent with the structure of VI. One recrystallization from hexane (starting with 1.66 g) gave 1.21 g (73%) of pure VI, mp 95–97°.

Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.6; H, 6.4; N, 4.5.

Identical results were obtained (as indicated by the nmr spectrum) when the reaction was carried out in air or in nitrogen (in Carius tubes sealed at atmospheric pressure). Interestingly, the nmr spectrum of VI was found to be temperature dependent. As the sample temperature was decreased below 38°, the peak for the methyl protons (w_h = 1.4 cps at 38°) gradually broadened and at *ca.* 7.5° two broad peaks appeared and these became sharper as the temperature was lowered. At −31°, the width at half-height for each was 1.5 cps. The ratio of the areas of the low-field and high-field peaks was 56:44. This phenomenon is undoubtedly the result of hindered rotation around the C—N amide bond.

2,6-Di-*t*-butylphenyl N-Phenylbenzimidate (III).—Exactly 10.00 g (0.0486 mol) of 2,6-di-*t*-butylphenol and 0.1 g of triphenylmethane were dissolved in 150 ml of tetrahydrofuran. While the solution was stirred under nitrogen, *ca.* 31 ml of 1.6 *M* butyllithium in hexane was added whereupon the red color of the triphenylmethyl carbanion just appeared. Then 10.47 g (0.0486 mol) of N-phenylbenzimidoyl chloride in 75 ml of tetrahydrofuran was added and the system was stirred overnight at room temperature under nitrogen. After the reaction mixture was combined with 400 ml of ethyl ether, it was extracted with water, dried with anhydrous magnesium sulfate, and freed of solvent on a rotary evaporator. A viscous, red oil (19.35 g) was thus obtained. Chromatography on 400 g of alumina, using hexane as elution solvent, afforded some 2,6-di-*t*-butylphenol and another impure compound which exhibited infrared absorption at 1670 and 1270 cm^{-1}, typical of 2,6-disubstituted phenyl N-phenylbenzimidates. Two recrystallizations from methanol afforded 4.28 g (23%) of colorless plates, mp 127.5–128.5°. The spectra of this material were consistent with the structure of III.

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[6] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 575, 576.

[7] It is possible that a considerable SAHR effect is operating in *o*-Ie since the rate depression, in the absence of this effect, would have been very large; a rate constant 1/200 of that for If would not have been unreasonable.[8]

[8] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 72 (1963) [entry no. 1 in Table 12: partial rate factors for *ortho* and *para* substitution in *t*-butylbenzene (*ortho*/*para* = 4.97:806)].

[9] J. W. Schulenberg and S. Archer, *J. Amer. Chem. Soc.*, **82**, 2035 (1960).

[10] J. von Braun and W. Pinkernelle, *Ber.*, **67**, 1218 (1934).

Infrared bands were present for the C–N vibration[11] (1670 cm^{-1}) and for the aryl ether vibration[11] (1263 cm^{-1}). The nmr spectrum consisted of a complex multiplet for the aromatic protons (τ 2.32–3.57; integral 12.4) and a single sharp peak for the *t*-butyl protons (8.56; integral 18.4).

Anal. Calcd for $C_{27}H_{31}NO$: C, 84.11; H, 8.11; N, 3.63. Found: C, 84.5; H, 7.8; N, 3.5.

N-(2,6-Di-*t*-butylphenyl)benzanilide (VII).—A 1.00-g sample of III was sealed in a glass tube in air and heated at 305° for 30 min. The resulting cooled mass was sampled (removed 0.10 g) and examined by nmr spectroscopy (CCl_4). Besides complicated changes that had occurred in the aromatic region, two new single peaks appeared at τ 8.88 and 8.67, and the *t*-butyl-proton peak of III at 8.56 had diminished proportionately. The nmr integration indicated that 55% of the starting material (III) was still present. Vapor phase chromatography (vpc) (2 ft, 10% polyphenyl ether; helium flow = 72 cc/min; 275°, isothermal) indicated that III (retention time = 10.0 min) and one other compound (retention time = 18.0 min) were present in the approximate ratio of 53:47.

The remaining 0.90 g of the reaction mixture was sealed in the glass tube again and heated at *ca.* 310° for 6 hr more and then cooled to room temperature. The nmr spectrum (CCl_4) of this material showed only a trace of III, two major peaks at τ 8.88 and 8.68, and a minor peak at 8.52. Vpc showed that the previously observed long retention time peak now accounted for greater than 90% of the reaction mixture while less than 5% was residual III. Two impurities were also observed in the vpc.

The infrared spectrum of the crude reaction mixture showed strong absorptions at 1640 and 1345 cm^{-1}, typical of carbonyl and tertiary phenyl amine bands, respectively, of the other tertiary amides reported herein.

When III was heated at 258 or 275° in diphenyl ether (c = 0.303 *M* or 0.5 *M*, respectively), only the τ 8.88 and 8.68 peaks appeared, besides complex changes in the aromatic region. The ratio of these two peaks (*ca.* 2.2) remained constant as the peak for the *t*-butyl protons of III (τ 8.56) diminished with time. This was the same ratio as observed previously for these two peaks which arose when III was heated at 310° without solvent.

The nmr spectrum of a diphenyl ether solution of III (originally 0.5 *M*) that had been heated at 275° for 11.75 hr (only 27% of III left) was recorded at various temperatures, ranging from 29 to 166°. On heating, the τ 8.88 and 8.68 peaks (w_h = 1.3 and 1.4 cps, respectively, at 29°) gradually broadened and overlapped. Coalescence occurred at 138°; the single peak became sharper as the temperature was raised; and, at 166°, the width at half-height was 1.9 cps. On cooling to room temperature, the original spectrum was regenerated. Thus, it appears that the expected product (VII) is obtained and it exists at room temperature as two rotational isomers which interconvert slowly enough to be distinguished by nmr spectroscopy.

The crude product, obtained by heating 0.90 g of III at 310° (see above), was chromatographed on activity I Woelm alumina. After eluting with pentane (nothing obtained) and 95:5 pentane–diethyl ether (recovered less than 5% of III), 60:40 pentane–diethyl ether afforded 0.71 g (79% isolated yield) of a colorless, viscous oil which was homogeneous by vpc. The nmr spectrum (CCl_4) showed aromatic protons (τ 2.2–3.4; integral 12.6) and two *t*-butyl peaks at 8.68 and 8.89 for the two different rotamers (total integral 18.0).

After several days, the viscous oil had completely crystallized; the broad melting point, 129–133.5°, was not unexpected for a mixture of isomers. The infrared spectrum of this product showed 1640- and 1343-cm^{-1} bands to be expected from the carbonyl and tertiary phenyl amine bands of VII.

Anal. Calcd for $C_{27}H_{31}NO$: C, 84.11; H, 8.11; N, 3.63. Found: C, 83.9; H, 8.0; N, 3.4.

2-Methyl-6-phenylphenyl N-Phenylbenzimidate (IV).—To 70 ml of 0.76 *M* sodium ethoxide in ethanol was added 9.203 g (0.0500 mol) of 2-methyl-6-phenylphenol. After the phenol had dissolved, 10.775 g (0.0500 mol) of N-phenylbenzimidoyl chloride in 45 ml of ethyl ether was added with continuous stirring. A precipitate formed and the system warmed slightly. After 15 hr of stirring at room temperature, the entire system was added to 250 ml of ether, extracted with water, and dried with anhydrous sodium sulfate. Removal of the ether gave 18.082 g of a solid material which was subsequently recrystallized three times from hexane to give 8.14 g (45%) of IV, mp 90–92.5°. The infrared spectrum ($CHCl_3$) showed C=N absorption[11] (1670 cm^{-1}) and aryl ether absorption[11] (1253 cm^{-1}). The nmr spectrum consisted of a complex aromatic proton multiplet (τ 2.17–3.82; integral 18.0) and a single sharp peak for the methyl protons (7.63; integral 2.9). One more recrystallization from ethanol gave an analytical sample, mp 95–97°.

Anal. Calcd for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.86. Found: C, 85.6; H, 5.8; N, 3.8.

N-(2-Methyl-6-phenylphenyl)benzanilide (VIII).—A sample of IV (1.045 g, 0.00288 mol) was sealed in a nitrogen atmosphere in a Carius tube and heated at 300° for 30 min. The nmr spectrum ($CDCl_3$) of the solid product was then recorded. This spectrum showed a broad single peak for the methyl protons (τ 7.59; integral 2.6) and a complex multiplet, entirely different in complexity from that of IV, for the aromatic protons (2.21–3.86; integral 18.0). The infrared spectrum of this unpurified product displayed a tertiary amide carbonyl absorption[11] (1635 cm^{-1}) and a tertiary phenyl amine absorption[11] (1345 cm^{-1}) and indicated that IV was completely absent.

Identical results were obtained when IV was heated at 300° for 30 min in air in a sealed tube.

The products from both the nitrogen and the air runs (see above) were combined (total 1.66 g) and recrystallized from ethanol to afford 1.44 g (87%) of pure amide (VIII), mp 187–189°.

Anal. Calcd for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.86. Found: C, 85.5; H, 5.6; N, 3.7.

The nmr spectrum of VIII was found to be temperature dependent. At 60°, there was one peak for the methyl protons having a width at half-height of 2 cps; at 38°, this single peak had a width at half-height of 3.6 cps; at 18°, two broad peaks began to appear; and at −39°, two sharp peaks, both having a width at half-height of 1.5 cps, were present. (The ratio of the low-field and high-field peaks was 85:15.)

Again, as in the cases of VI and VII, hindered rotation around the C—N amide bond seems evident.

2,6-Diphenylphenyl N-Phenylbenzimidate (V).—A solution of 12.301 g (0.0500 mol) of 2,6-diphenylphenol in 70 ml of 0.76 *M* sodium ethoxide in ethanol was prepared. While this solution was stirred, 10.774 g (0.0500 mol) of N-phenylbenzimidoyl chloride in 45 ml of ethyl ether was added, whereupon heat was evolved and a precipitate appeared. Stirring was continued for 15 hr at room temperature. Then the reaction mixture was poured into ether, extracted with water, and dried with anhydrous sodium sulfate. Removal of the solvent gave 19.90 g of a viscous residue which crystallized when stirred with a little hexane. Attempted recrystallization from hexane gave two distinct types of crystals, irregularly shaped white ones and orange prisms. All of the solvent was removed from the recrystallization systems, the residue was dissolved in a minimum of chloroform, and the chloroform solution was placed on a column of 760 g of alumina in hexane. Elution with 50:50 (v/v) hexane–ether gave 15.86 g of a white solid. Recrystallization from hexane gave 12.88 g (61%) of V, mp 117.5–120.5°. The infrared spectrum ($CHCl_3$) showed a C=N absorption[11] (1670 cm^{-1}) and an aryl ether absorption[11] (1249 cm^{-1}). The nmr spectrum ($CDCl_3$) showed only aromatic protons as a complex multiplet (τ 2.19–3.97).

Anal. Calcd for $C_{31}H_{23}NO$: C, 87.50; H, 5.45; N, 3.29. Found: C, 87.3; H, 5.5; N, 3.2.

N-(2,6-Diphenylphenyl)benzanilide (IX).—An amount of V (1.23 g) was heated in air in a sealed Carius tube at 300° for 30 min. The product was recrystallized from ethanol to give 0.89 g (72%) of IX, mp 159–160.5°. The infrared spectrum showed a tertiary amide carbonyl absorption[11] (1645 cm^{-1}) and a tertiary phenyl amine band[11] (1350 cm^{-1}). The nmr spectrum showed only a complex aromatic proton multiplet, entirely different in complexity from that of V, between τ 2.45 and 4.12. The use of an internal standard indicated that this product (IX) contained the required number of aromatic protons (*i.e.*, 23) per molecule.

Anal. Calcd for $C_{31}H_{23}NO$: C, 87.50; H, 5.45; N, 3.29. Found: C, 87.8; H, 5.6; N, 3.1.

Kinetic Runs.—Approximately 0.3 *M* solutions of II, III, IV, and V in diphenyl ether were prepared. Samples of II, III, and IV were sealed in nmr tubes and heated in a refluxing diphenyl ether bath at 258.0°. The samples were withdrawn periodically and cooled to room temperature, and the diminution in the amount of starting material was determined by nmr spectros-

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[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 115, 205, 249, and 263.

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.

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

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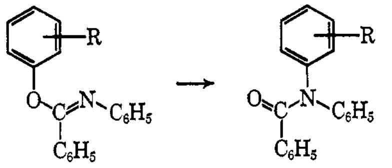
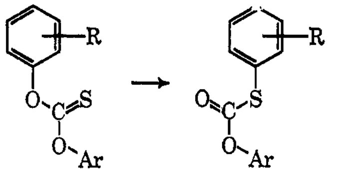
A series of O-aryl dimethylthiocarbamates have been prepared and their rates of rearrangement to the corresponding S-aryl dimethylthiocarbamates have been determined. Steric acceleration of rates due to hindered rotation (as found also in the Chapman rearrangement) appeared to be present in the *ortho*-substituted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

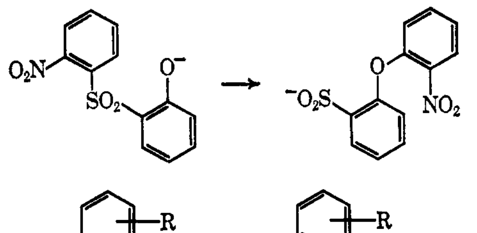
Intramolecular migration of aryl groups between adjacent atoms occurs quite commonly in organic chemistry. Much less common, however, are intramolecular migrations between nonadjacent atoms. Some examples of this latter type of reaction are the Chapman rearrangement[1] (reaction 1), the Schönberg rearrangement[2]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



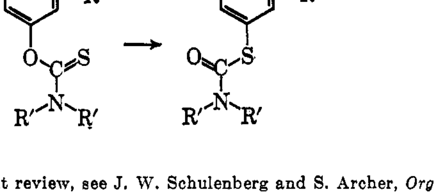
(1)



(2)



(3)

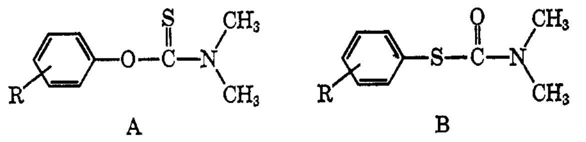


(4)

It has been reported[5] that the Chapman rearrangement is an intramolecular nucleophilic–aromatic substitution reaction and that *ortho* substituents in the migrating aromatic ring enhance the rate[5–7] (steric acceleration due to hindered rotation (SAHR) effect[6]). 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.



A B

1, R = 4-OCH$_3$
2, R = 4-CH$_3$
3, R = 4-t-C$_4$H$_9$
4, R = H
5, R = 4-Br
6, R = 4-C$_6$H$_5$
7, R = 2-CH$_3$
8, R = 2,6-(CH$_3$)$_2$
9, R = 2-t-C$_4$H$_9$
10, R = 2-t-C$_4$H$_9$-4-CH$_3$
11, R = 2,6-(t-C$_4$H$_9$)$_2$-4-CH$_3$
12, R = 2-C$_6$H$_5$
13, R = 2,6-(C$_6$H$_5$)$_2$
14, R = 4-NO$_2$

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

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[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 *inter*molecular nucleophilic–aromatic substitution reactions, *ortho* substituents sterically cause rate depressions (absence of SAHR effect). See, for example, (a) A. M. Porto, L. Altiere, 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).