ml. of acetonitrile under the same conditions gave no material boiling in the neighborhood of 0°, and *ca.* 25 g. distillate, b.p. −24 to −16°, presumably unreacted HFP, was obtained.

In another experiment, 26 g. of COF_2 and 30 g. of HFP under the same conditions likewise gave 25 g. of distillate, b.p. −27 to −24°, presumably recovered HFP. There was no product boiling near 0°.

[Contribution from the Pioneering Research Division, Textile Fibers Department, the Jackson Laboratory, Organic Chemicals Department, and the Elastomers Department, E. I. du Pont de Nemours and Company, Inc.]

Carbodiimides. II. Mechanism of the Catalytic Formation from Isocyanates

By John J. Monagle,[1a] Tod W. Campbell[1b] and Herbert F. McShane, Jr.

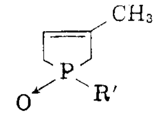
Received May 10, 1962

Isocyanates are smoothly and cleanly converted to carbodiimides by certain phospholene oxides. The kinetics of evolution of carbon dioxide from a variety of isocyanates has been studied, and the rate constants correlated by a Hammett equation. The data indicate that two consecutive reactions are involved with regeneration of the catalyst in the second (fast) step (shown in equations 5 and 6). The reaction is reversible and has a low energy of activation. Although phosphine oxides in general serve as catalysts, the cyclic phospholene oxides are by far the most effective.

Introduction

The formation of dimers and trimers from isocyanates in the presence of catalytic amounts of tertiary phosphines is well known.[2] More recently, it has been shown that certain phosphine oxides[3] have an entirely different catalytic effect on isocyanates.

$$2\mathrm{RNCO} \xrightarrow{\text{I or II}} \underset{\text{III}}{\mathrm{RN{=}C{=}N{-}R}} + \mathrm{CO_2} \qquad (1)$$



I, R′ = C_2H_5
II, R′ = C_6H_5

The formation of carbodiimides (III) from isocyanates by the catalytic action of the phosphine oxides I and II represents a decided improvement in ease of preparation and purity of product over methods formerly used.[4] The reaction proceeds rapidly and in most cases isolation is simple and yields are high. The unusual nature of the reaction and its potential synthetic applications prompted a study of its mechanism.

Discussion

Examination of the literature did not disclose any reactions of phosphine oxides with isocyanates. Several similar reactions were found, however, in the work of Staudinger on phosphinimides (IV).[5] These compounds were prepared by reaction of aromatic azides with tertiary phosphines.

$$\mathrm{R_3P + R'N_3 \longrightarrow R_3P{=}NR' + N_2} \qquad (2)$$

Both the aliphatic and aromatic phosphinimides were extremely reactive compounds; however, the derivatives of the aromatic phosphines such as triphenylphosphine phenylimide were less reactive than the aliphatic derivatives. Reaction of the molten imide with carbon dioxide yielded phenyl isocyanate and triphenylphosphine oxide. The reaction of *molar* amounts of the imide and phenyl isocyanate with slight warming produced diphenylcarbodiimide and triphenylphosphine oxide exothermically.

$$\mathrm{C_6H_5N{=}P(C_6H_5)_3 + CO_2 \longrightarrow C_6H_5NCO + (C_6H_5)_3PO} \qquad (3)$$

$$\mathrm{C_6H_5N{=}P(C_6H_5)_3 + C_6H_5NCO \longrightarrow C_6H_5N{=}C{=}NC_6H_5 + (C_6H_5)_3PO} \qquad (4)$$

The aromatic carbodiimides were also formed in an exothermic reaction between triethylphosphine phenylimide and carbon dioxide. Both reactions were considered to go through the initial formation of the isocyanate.

The over-all reaction obtained by a combination of reaction 4 with the reverse of reaction 3 represented a possible mechanism for the formation of carbodiimides from isocyanates.

$$\mathrm{RNCO + R'_3PO \rightleftarrows R\overset{-}{N}\overset{+}{P}R'_3 + CO_2} \qquad (5)$$

$$\mathrm{R\overset{-}{N}\overset{+}{P}R'_3 + RNCO \rightleftarrows RNCNR + R'_3PO} \qquad (6)$$

In the present case, considering the extreme reactivity of the phosphine oxides I and II, the intermediate phosphinimides would have to form and react very rapidly in order to account for the catalytic nature of the reaction. However, the high reactivity reported for triphenylphosphine phenylimide with phenyl isocyanate compared to the lack of further reaction between triphenylphosphine oxide and phenyl isocyanate (eq. 3) indicated that the formation of the imide should be rate determining. Therefore, one should be able to deduce kinetically the presence of the imides as true intermediates.

Formation of an intermediate phosphinimide in its simplest form would be expected to exhibit

---

(1) (a) New Mexico State University, University Park, N. Mex. (b) To whom inquiries should be directed.

(2) (a) J. S. Blair and G. E. P. Smith, *J. Am. Chem. Soc.*, **56**, 907 (1934); (b) W. J. Balon and O. Stallman, U. S. Patent 2,683,144, July 6, 1954 (*C. A.*, **48**, 12465C (1954)); (c) L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, **8**, 230 (1940); (d) H. L. Snape, *J. Chem. Soc.*, **49**, 254 (1886); (e) A. W. Hoffmann, *Jahrb. Fortsch. Chem.*, 335 (1862); (f) K. H. Slotta and R. Tschesche, *Chem. Ber.*, **60B**, 295 (1927).

(3) (a) T. W. Campbell and J. J. Monagle, *J. Am. Chem. Soc.*, **84**, 3673 (1962); (b) T. W. Campbell and J. J. Verbane, U. S. Patent 2,853,473 to du Pont (9/23/58).

(4) (a) H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953); (b) G. Amiard and R. Heymes, *Bull. soc. chim. France*, 1360 (1956); (c) H. Eilingsfeld, M. Seefelder and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960); (d) S. Hunig, H. Leamann and G. Grimmer, *Liebig's Ann.*, **579**, 87 (1953); (e) E. Schmidt, M. Seefelder, R. Jennen, W. Striewsky and H. von Martius, *Ann.*, **571**, 83 (1951); (f) E. Schmidt, E. Kammerl, D. Ross and F. Zaller, *ibid.*, **594**, 233 (1954).

(5) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 636 (1919).

second-order kinetics, first order in isocyanate and in catalyst. In addition, it would be expected that the reaction would be reversible in accord with Staudinger's observation of the reaction of CO_2 with phosphinimides. Accordingly, the kinetic dependence of the rate of the reaction on the concentration of catalyst and isocyanate was sought using catalyst I. To define further the mechanism, the rates of reaction of several substituted phenyl isocyanates and the effect of changes of solvent were also determined.

Experimental Part

Materials.—The isocyanates were all redistilled before use. Xylene solvent was Fisher reagent grade and was dried by distillation from $LiAlH_4$ or CaH_2. Catalyst I was prepared by a modification[3] of the procedure of McCormack.[6] Catalyst II was prepared without modification.[6]

The catalysts were extremely hygroscopic and had to be carefully dried before good analyses and reproducible kinetic data could be obtained.

Purification of Catalyst I.—Traces of phosphine and water were removed as follows: Hydrogen peroxide (3%), 150 ml., was added dropwise with stirring to the phosphine oxide I, 103.7 g., at a rate which kept the temperature below 50°. After the addition was complete the solution was stirred at 50° for 6 hours. The water solution was extracted continuously with chloroform and dried over sodium carbonate. The chloroform was removed at atmospheric pressure and the residue was distilled to yield 95.1 g. of I, b.p. 115–119° (1.2–1.3 mm.), $n^{25}D$ 1.5056. Calcd. for $C_7H_{13}OP$: C, 58.3; H, 9.0; P, 21.5. Found: C, 58.3; H, 8.8; P, 21.6.

Procedure.—Three methods were used for measuring the CO_2 evolved. In the first (method A), the gas was collected in a gas buret maintaining the CO_2 in contact with the reaction system, thus allowing equilibration. In the second method (method B), CO_2 was measured by absorption. Nitrogen was passed through the reaction flask at a constant rate to ensure a constant flow of CO_2. In the third method (method C), the CO_2 was expelled from the reaction mixture by boiling. The level of the refluxing solvent was adjusted to the point at which the condenser became water cooled, and the gas was collected in a gas buret. This latter system was quite stable, as judged by the steady level of the liquid in the buret.

The reaction flask for the kinetic runs consisted of a 125-ml. or 250-ml. cylindrical flask with two standard taper joints and a gas outlet tube fitted with a stopcock and ball joint. In all cases, the reaction mixture was stirred by means of a glass stirrer which was completely enclosed in a glass chamber and equipped with a bar magnet sealed to the upper end. The stirrer assembly was inserted through the center joint and turned by a magnet attached to the stirring shaft of a constant speed motor, thus furnishing a gas-tight seal. The remaining joint was sealed with a self-sealing rubber stopper. A water condenser was attached to the gas outlet. For measurement of the volume of CO_2, the gas outlet was attached to two 100-ml. gas burets in parallel. The burets were filled with mercury and maintained at constant temperature by water jackets. A stopcock arrangement was used to switch burets during the run. A 3-way stopcock connected the burets to a dimethyl phthalate leveling tube which was used to take the readings at atmospheric pressure. The runs at 0° were made in a bath containing a large quantity of ice (variation ±0.05°). Those made at elevated temperatures were run either at the boiling point of the solvent or in a constant temperature bath (variation ±0.1°). Since gas evolution was so rapid at elevated temperatures, it was necessary to use dilute solutions of isocyanate and catalyst or to measure CO_2 evolved by absorption in Ascarite. In the latter measurements, the absorption bulb was suspended on a sensitive beam balance enclosed in a box to avoid errors caused by air currents.

Variation in rate with catalyst concentration was determined by maintaining the concentration of isocyanate essentially constant by using it as solvent.[7] Reaction in bulk isocyanate with catalyst I at room temperature was too rapid for accurate measurement. The rates were therefore determined at 0°.

At 0°, variation in rate with isocyanate concentration was determined in xylene solvent (because of its low freezing point and vapor pressure), holding the catalyst concentration constant. In these latter experiments, to minimize the large influence of small errors in concentration on the reaction rate, a stock solution of catalyst was prepared and aliquots taken. For reactions at higher temperatures, rates could be determined conveniently by suitable modification of the procedure.

Kinetic Runs.—The catalyst I was freshly distilled under vacuum and stored in a carefully dried flask fitted with a self-sealing rubber stopper. Catalyst portions were withdrawn with a hypodermic syringe fitted with a metal stopcock. Catalyst II was distilled under vacuum into a pear-shaped receiver containing inverted, weighed, thin-walled ampoules with long necks. When the level of the liquid was judged high enough to fill the ampoules to the desired level, nitrogen was bled into the receiver forcing the catalyst into the ampoules. The ampoules were then removed, quickly sealed in a flame and reweighed.

All equipment including the hypodermic syringe was thoroughly dried before each run. For the runs using isocyanate without solvent, the assembled reaction flask containing the known volume (50.0 ml.) and weight of isocyanate was immersed in the constant temperature bath and allowed to reach equilibrium by stirring for 10–15 minutes. The flask was flushed with dried, prepurified nitrogen during this period. For runs with catalyst I, the catalyst was withdrawn from the storage flask, the stopcock closed and the needle removed and replaced by a dry previously weighed 4″ needle. The sample was weighed and the catalyst delivered to the reaction flask through the self-sealing stopper. This time was taken as t_0. The syringe was withdrawn, the needle point inserted into a weighed rubber stopper to prevent catalyst loss and the amount delivered was determined by reweighing.

For the runs with catalyst II, the ampoule was dropped into the reaction flask through the stirrer joint and crushed with a glass stirring rod. The stirrer was then quickly inserted and started. The time at which the ampoule was crushed was taken as t_0. (The catalyst was very soluble in the isocyanate.)

The isocyanate concentration in these runs was calculated using the average weight of several 50.0-ml. samples. The concentration of catalyst was calculated using the volume of isocyanate delivered from the pipet at room temperature. No correction was made for the change in density of the solution with temperature.

The CO_2 evolved was measured at 0° by creating a partial vacuum in the system by lowering the mercury leveling bulb and noting the time and volume of gas when the levels in the phthalate manometer were equal. At elevated temperatures (method B), the readings were taken at 0.1-g. intervals by noting the time of zero deflection of the balance.

For the runs in xylene solvent at 0°, the isocyanate solutions were prepared at room temperature by pipetting the isocyanate into a dried volumetric flask containing a weighed amount of xylene. The flask was reweighed and the contents diluted to volume. The concentration was checked by reaction with a known amount of butylamine followed by back titration with hydrochloric acid.[8]

For runs at elevated temperatures, catalyst solutions were prepared by adding an accurately weighed quantity of catalyst to solvent in a volumetric flask and diluting to volume. The procedure for the kinetic runs was the same as that used for pure isocyanate except that the catalyst solution, previously thermostated, was pipetted into the flask, t_0 being taken as the time when the last drop of catalyst solution was added.

Treatment of Data.—For the volumetric runs, the barometric pressure and the temperature of the water in the jackets of the gas burets were noted (the water temperature was maintained at either 0–1° or approximately 25°). The volume of gas evolved at time t was corrected to S.T.P.,

---

(6) W. B. McCormack, U. S. Patent 2,663,737 (Dec. 22, 1953); *C. A.*, **49**, 7601a (1955).

(7) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co. Inc., New York, N. Y., 1950, p. 16.

(8) (a) H. E. Stagg, *Analyst*, **71**, 557 (1946); (b) J. H. Saunders and R. J. Slocombe, *Chem. Revs.*, **43**, 203 (1948).

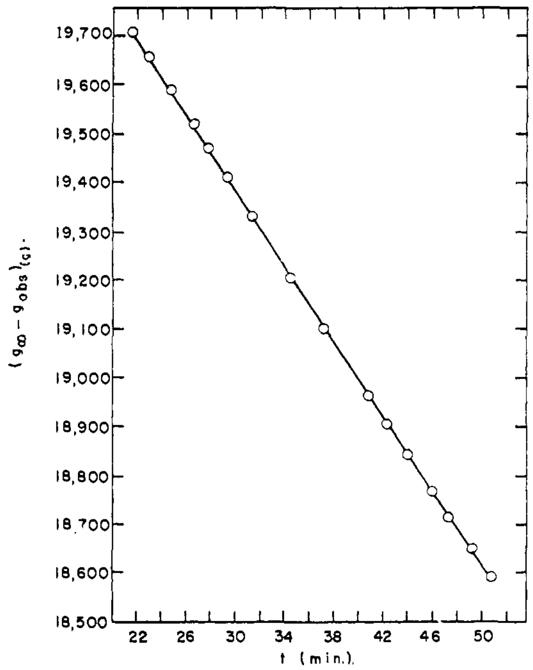


Fig. 1.—$g\ CO_{2\infty} - gCO_{obs}$ *vs.* time (min.) for catalyst I + phenyl isocyanate.

including a correction for the vapor pressure of solvents.[9] This volume was either used directly or converted to the corresponding weight of CO_2. In all cases, g_∞ or V_∞ was calculated from the weight of isocyanate used. The values obtained were plotted according to the kinetic relationships which gave the best straight lines. The rate constants were determined from the slope of the plots or by calculation from the half-life.

The data were plotted, $(V_\infty - V)$ *versus t*, using a semi-log scale, and pseudo-first-order reaction constants were calculated. In other cases, the rate constants were determined from the straight line portion of the plot of log $(g_\infty - g_{obs})$ *versus t*, using the theoretical g_∞.

In order to use the half-life method in the "closed system" to determine constants, it was necessary to determine V_∞ experimentally, it being taken as the volume of CO_2 evolved at equilibrium. In the case of slow reactions, this value may be rather uncertain.

Energies of activation were obtained from the slope of the plot of ln K *versus* $1/T$. Entropies of activation (at 50°) were calculated from the equation

$$S^{\mp} = -1.987[2.3 \log 2.12 \times 10^{12}\, T - \frac{\Delta E^{\mp}}{1.987T} - \ln K] \qquad (7)$$

Results

Kinetic Dependence on Catalyst Concentration.—With catalyst I, phenyl isocyanate in bulk exhibited pseudo-zero-order kinetics as shown by a plot of $(g_\infty - g_{obs})$ *versus t* (Fig. 1). A plot of log $(g_\infty - g_{obs})$ *versus t* showed continuous curvature. An induction period was observed which was much shorter (*ca.* 4% of reaction) than that observed when the catalyst was not carefully dried. Rate constants obtained from the slopes and first- and second-order rate constants obtained by dividing the slope by the catalyst and isocyanate concentration are given in Table I. The reaction did not exhibit dependence on the initial amount of catalyst as do reactions of isocyanates with alcohols and amines.[10]

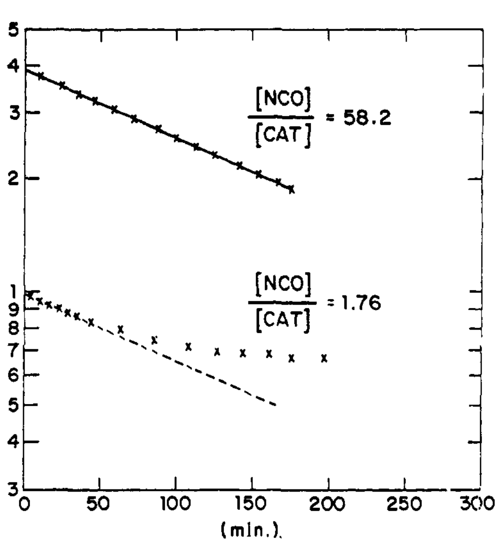


Fig. 2.—Log $(g_\infty - g_{obs.})$ *vs. T*; phenyl isocyanate in xylene; [cat] = 0.0503 m./l., T = 0°.

Experiments were also carried out in boiling benzene in which the *initial* concentration of isocyanate was held constant while the concentration of the catalyst was varied. The reaction showed first-order dependence. Measurement of half-lives and calculation of the order of the reaction[11] using successive increments of catalyst and half-lives gave an average value of about 1.8 (see Table II). The deviation probably arose from the rather high concentrations of catalyst, compared to isocyanate (Fig. 2).

Table I

Rate Constants[a] for $2C_6H_5NCO \rightarrow C_6H_5N{=}C{=}NC_6H_5$

Method	$k \times 10$, l. mole^{-1} sec.$^{-1}$	Solvent	T, °C.	[NCO], m./l.	[Cat.], m./l.
A	0.020	....	0	9.15	0.0197
A	.018	....	0	9.15	.0197
A	.018	....	0	9.15	.0373
A	.018	....	0	9.15	.0383
A	.014	Xylene	0	0.089	.0503
A	.018	Xylene	0	0.150	.0503
A	.014	Xylene	0	1.23	.0503
A	.015	Xylene	0	2.24	.0503
A	.014	Xylene	0	2.93	.0503
A[b]	1.3	Xylene	63.3	0.161	.0020
A[b]	2.5	Xylene	83.3	0.161	.0020
B	0.376	Xylene	50	1.33	.0159
B	0.380	Xylene	50	1.57	.0145
C[b]	5.5	Benzene	80	0.161	.0020
C[b]	16.5	Toluene	110	0.161	.0020
C[b]	34.5	Xylene	140	0.161	.0020

[a] Catalyst I. [b] Average of three duplicate runs.

Kinetic Dependence on Isocyanate Concentration.—With phenyl isocyanate xylene at 0°, holding the catalyst concentration constant, the reaction showed pseudo-first-order kinetics by plotting log $(g_\infty - g_{obs})$ *versus t*. Good straight line plots were obtained over approximately 75% reaction after a short induction period (Fig. 2). Carbon dioxide evolution was followed to 90% com-

---

[9] T. E. Jordan, "Vapor Pressures of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1954, p. 8.

[10] R. G. Arnold, J. A. Nelson and J. J. Verbanc, *Chem. Revs.*, **57**, 47 (1957), and earlier references.

[11] Reference 7, p. 14.

TABLE II

EFFECT OF CHANGES IN CATALYST CONCENTRATION

$[NCO]_{init.} = 0.165$ m/l

[Cat.], m./l. × 10^3	Rel. concn.	$t_{1/2}$, sec.	k, l. mole^{-1} sec.$^{-1}$	M^a
1.0	1	1350	0.50	1.84
2.0	2	750	.46	1.82
4.0	4	426	.41	1.76
8.0	8	252	.34	1.78
16.0	16	150	.29	1.64
32.0	32	96	.23	
			Av.	1.76

^{a} $M = 1 + \frac{\log(\tau_1/\tau_2)}{\log(a_2/a_1)}$ where $\tau = t_{1/2}$; $a = [NCO]_{init.}$

pletion in several cases. Second-order constants obtained by dividing the slopes by the catalyst concentration are given in Table I.

In boiling benzene (80°) in the open system, holding the catalyst concentration constant, the reaction was also clearly first order in a series of four experiments over a fifty-fold increase in isocyanate concentration (see Table I and Fig. 3) and as much as 95% of reaction. Within experimental error, these runs all gave a half-life of 10.5 minutes. No induction period was observed in these reactions. Other isocyanates were also clearly first order over greater than 90% conversion (Fig. 4).

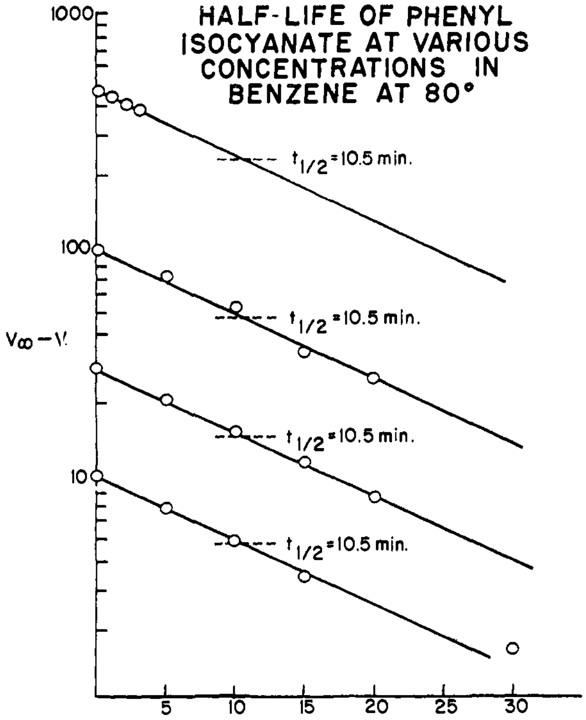


Fig. 3.

In the "closed" system where the reactants and products remained in contact, and at low concentrations of phenyl isocyanate and catalyst where the molar ratio of isocyanate to catalyst was low, the plots deviated very quickly from a straight line and gradually reached a constant value (Figs. 2 and 5) with from 40–60% of isocyanate converted to carbodiimide (see Table III).

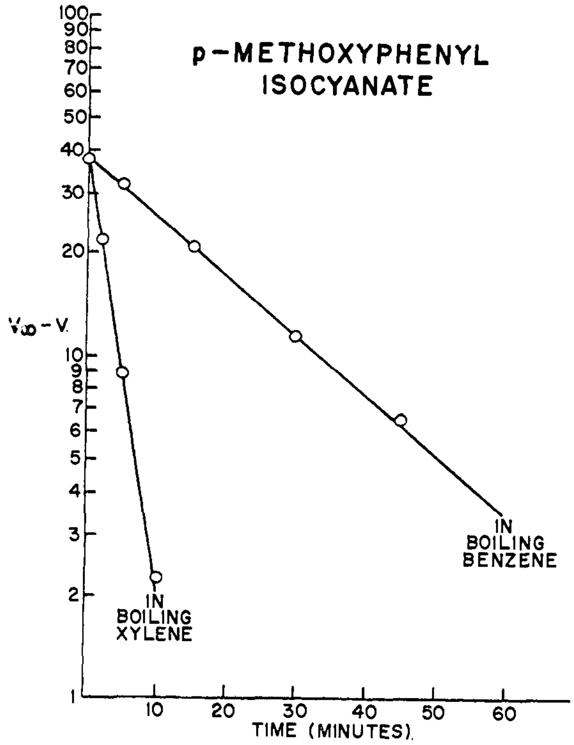


Fig. 4.

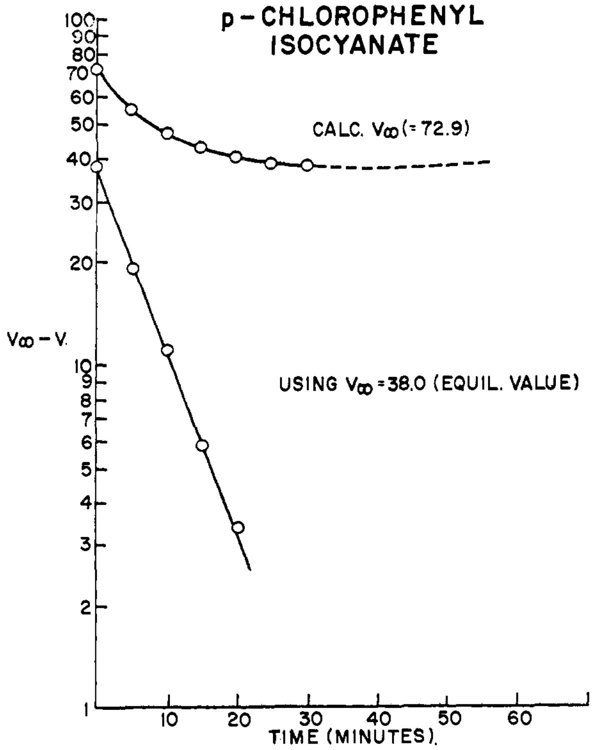


Fig. 5.

The position of the equilibrium was governed by the substituents on the aromatic ring, and the concentration. Electron-withdrawing groups favored

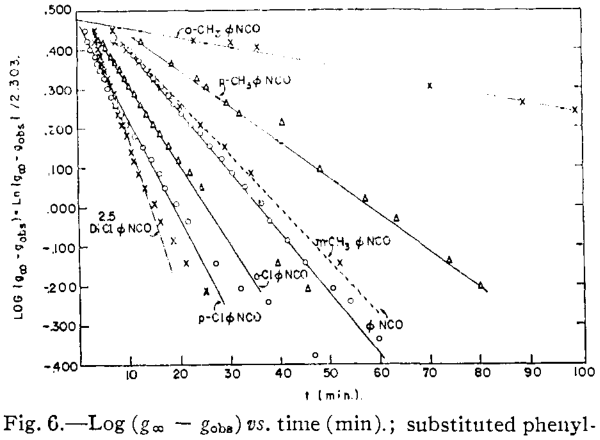


Fig. 6.—Log ($g_\infty - g_{obs}$) *vs.* time (min).; substituted phenylisocyanates + catalyst I.

carbodiimide, while electrondonating groups favored isocyanates. When the equilibrium value of CO_2 evolved was used as V_∞, it was found that the forward reaction was first order in isocyanate. Rate constants calculated from the half-life were essentially the same as those obtained in the open system (Table I). However, statistical analysis of the rates of reaction of phenyl isocyanate in xylene at a series of temperatures in both the "open" and "closed" systems showed that the rates were independent of the system used (see following).

TABLE III

EQUILIBRIUM EVOLUTION OF CO_2 IN CLOSED SYSTEMS

$$2\ RC_6H_4NCO \rightleftharpoons RC_6H_4N{=}C{=}NC_6H_4R + CO_2 \quad (8)$$

R	V_{obs}/V_{calc}	T, °C.	R	V_{obs}/V_{calc}	T, °C.
p-Cl	0.466	63.3	*m*-CH_3	0.449	83.3
p-Cl	.520	83.3	*m*-Cl	.575	83.3
p-CH_3	.368	83.3	*m*-NO_2	.461	63.3
H	.392	63.3	*m*-NO_2	.554	83.3
H	.498	83.3	*p*-NO_2	.552	83.3

In addition to the indirect evidence for the reversibility of the reaction shown by establishment of equilibrium, direct evidence for the reversibility was obtained by demonstrating that CO_2 reacted with carbodiimide in the presence of I to give isocyanate. Off-gases from the passage of CO_2 through hot ditolylcarbodiimide containing a trace of I were run into benzene. The presence of tolyl isocyanate was demonstrated by infrared spectra and by conversion to *t*-butyl-di-*p*-tolylurea.

Effect of Substituents in the Isocyanate.—Introduction of electron-donating groups decreased (Fig. 6 and Table IV) the rate with the most pronounced effect being shown by the *ortho*isomers, indicating a pronounced steric effect. Electron-withdrawing groups increased the rate very strongly with a pronounced dependence on the inductive effect being evident. For example, the *o*-chloro isomer is about 7 times as fast as the *o*-methyl, though by resonance both would be electron donating and should be sterically similar. In addition, the *o*-chloro isomer reacts more rapidly than phenyl isocyanate. The influence of the inductive effect is further shown by the high rate of reaction of the 2,5-dichlorophenyl isocyanate.

Effect of Catalyst Structure.—A few kinetic runs were made using catalyst II. Replacement of the ethyl group of catalyst I by phenyl led to a fivefold decrease in rate. In this case also, good pseudo-first-order rates were found.

Some rough kinetic measurements with triphenylphosphine oxide in bulk isocyanate were made at 100°. The reaction followed pseudo-zero-order kinetics with an approximate rate constant of 4×10^{-3} l. mole^{-1} sec.$^{-1}$. Comparison of this constant with that for catalyst I calculated for 100° showed the latter to be about 2×10^4 times as active as triphenylphosphine oxide.

Effect of Solvents.—Kinetic runs were carried out in a large number of solvents of widely different structures and polarity at their boiling points. Results are shown in Table V and in a plot of ln *K* *versus* 1/*T* (Fig. 7). The results were analyzed statistically: (1) as a complete group, (2) all runs except those in acetonitrile and nitrobenzene, (3) runs in xylene only, and (4) all experiments except those in xylene, acetonitrile and nitrobenzene. From the analysis it was concluded that with the exception of acetonitrile and nitrobenzene there was no significant effect of solvent or experimental method on the reaction rate (at the 95% confidence level). The plot (Fig. 7) is best expressed by the equation

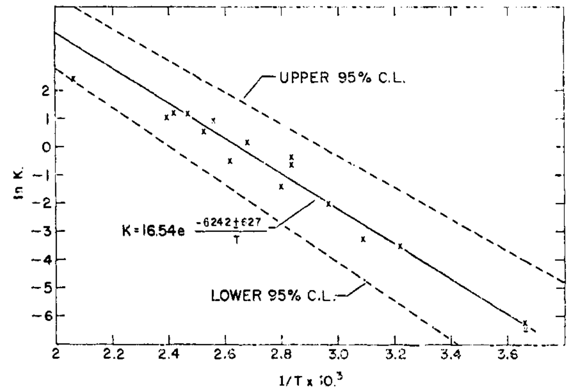


Fig. 7.—Activation energy of phenyl isocyanate with phosphine oxides in different solvents.

$$K = 16.54\, e^{\frac{-6242 \pm 627}{T}} \qquad (9)$$

from which ΔE = 12,400 ± 1450 cal. per mole. Using data for phenyl isocyanate at 0°, an entropy of activation ΔS = 37.9 ± 3.9 e.u. was calculated.

The lack of variation in pure isocyanate as compared to xylene was also supported by a plot of the rate of CO_2 evolution *versus* isocyanate concentration (Fig. 8), where the rate extrapolates to a value obtained with bulk isocyanate at the same catalyst concentration. This apparent lack of solvent effect is not surprising since the dipole moments do not change significantly in going from phenyl isocyanate (2.23[12]–2.34 D.[13]) to xylene (2.25–2.58 D.[14a]; 2.37 for mixed xylenes[14b]). Other solvents which apparently had a large influence on the reaction were di-

---

(12) N. V. Sidgwick, L. E. Sutton and W. Thomas, *J. Chem. Soc.*, 406 (1933).

(13) A. E. Eide and D. Hassel, *Tidsskr. Kjemi Berg.*, **10**, 93 (1930); *C. A.*, **25**, 2698 (1931).

(14) (a) "International Critical Tables," Vol. 6, p. 92; (b) T. W. Richards and J. W. Shipley, *J. Am. Chem. Soc.*, **41**, 2002 (1919).

TABLE IV

RATE CONSTANTS[a] FOR $2RC_6H_4NCO \rightarrow RC_6H_4N{=}C{=}NC_6H_4R$

Method	R	1. mole^{-1} sec.$^{-1}$	Solvent	T, °C.	[NCO], m./l.	[Cat], m./l.
A	o-CH_3	0.001	...	0	7.95	0.0262
A	*o*-CH_3	.001	...	0	7.95	.0514
A	*o*-CH_3	.001	...	0	7.95	.0612
A	*o*-CH_3	.001	...	0	7.95	.1165
B	*o*-CH_3	.065	Xylene	50	1.33	.0159
B	*m*-CH_3	.325	Xylene	50	1.33	.0159
C	*m*-CH_3	12.0	Toluene	110	0.144	.0020
A	*p*-CH_3	0.006	...	0	7.94	.0327
A	*p*-CH_3	.006	...	0	7.94	.0420
A	*p*-CH_3	.006	...	0	7.94	.0492
A	*p*-CH_3	.005	...	0	7.94	.0727
B	*p*-CH_3	.203	Xylene	50	1.33	.0159
C	*p*-CH_3	4.0	Benzene	80	0.144	.0020
C	*p*-CH_3	26.5	Xylene	140	0.144	.0020
B	*o*-Cl	0.491	Xylene	50	1.33	.0159
A	*m*-Cl	17.0	Xylene	83.3	0.125	.0020
C	*m*-Cl	65.0	Toluene	110	0.125	.0020
B	*p*-Cl	0.619	Xylene	50	1.33	.0159
A	*p*-Cl	3.9	Xylene	63.3	0.125	.0020
A	*p*-Cl	10.5	Xylene	83.3	8.125	.0020
C	*p*-Cl	18.0	Benzene	80	.125	.0020
C	*p*-Cl	41.0	Toluene	110	.125	.0020
C	*p*-Cl	100.0	Xylene	140	.125	.0020
C	o-CH_3O	0.51	Xylene	140	.129	.0020
C	*p*-CH_3O	3.4	Benzene	80	.129	.0020
C	*p*-CH_3O	11.5	Toluene	110	.129	.0020
C	*p*-CH_3O	24.0	Xylene	140	.129	.0020
B	2,5-DiCl	0.935	Xylene	50	1.33	.0159
A	*m*-NO_2	18.0	Xylene	63.3	0.117	.0020
A	*m*-NO_2	39.0	Xylene	83.3	.117	.0020
C	*m*-NO_2	24.0	Benzene	80.0	.117	.0020
C	*m*-NO_2	115.0	Toluene	110	.117	.0020
A	*p*-NO_2	60.0	Xylene	83.3	.117	.0020

TABLE V

EFFECT OF SOLVENT ON REACTION RATES

Run	Solvent	ϵ^a (20°)	k, 1. mole^{-1} sec.$^{-1}$	$1/T$, $\times 10^3$
1	Perclene	..	3.5×10^{-3}	2.53
2	Methyl isobutyl ketone	13.1	5.0×10^{-3}	2.56
3	Cyclohexane	2.0	1.4×10^{-3}	2.84
4	Dioxane	2.3	1.7×10^{-3}	2.68
5	Nitrobenzene	20.0	2.3×10^{-3}	2.07
6	Styrene	..	5.8×10^{-3}	2.39
7	Chlorobenzene	5.7	6.3×10^{-3}	2.47
8	Acetonitrile	20.0	0.55×10^{-3}	2.82
9	Benzene	2.3	1.1×10^{-3}	2.84
10	Toluene	2.4	3.3×10^{-3}	2.62
11	Phenyl isocyanate	2.2^b	1.8×10^{-3}	3.66
12	Xylene	2.4^c	3.45	2.42
13	Xylene	2.4	0.13	2.97
14	Xylene	2.4	0.25	2.80
15	Xylene	2.4	37.6×10^{-3}	3.09
16	Xylene	2.4	1.6×10^{-3}	3.66

[a] "Landolt-Bornstein Tables," Springer Verlag, Berlin, 1959, Vol. 2, Pt. 6, p. 613. [b] Ref. 14 and 15. [c] Ref. 16b.

methylformamide and dimethyl sulfoxide. These solvents gave abnormal reaction rates and CO_2 evolution which was not first order and which gave only a fraction of the theoretical amount of gas. This behavior is probably a result of reaction of the isocyanate with these solvents.[15] Acetonitrile gave a rate about one-half that of benzene which boils at the same temperature. On the other hand, nitrobenzene gave an extremely rapid reaction at its boiling point which prevented an accurate measure of the rate constant.

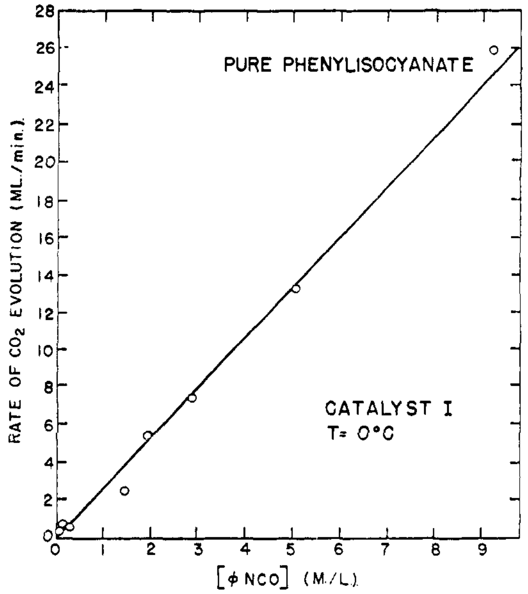


Fig. 8.—Rate of CO_2 evolution (ml./min.) *vs.* phenyl isocyanate concn. (moles/liter); xylene solvent.

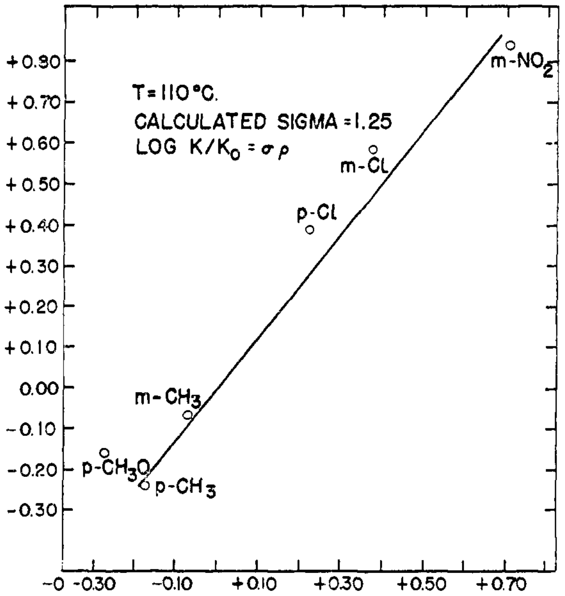


Fig. 9.—Rho–sigma plot.

A Hammett ρ- value[16] of 1.19 was obtained in xylene at 50° from a plot of σ-values[17] *versus* log k (Fig. 9). At 110° in toluene a ρ-value of 1.25 was obtained.

In the presence of a large excess of catalyst at room temperature (*i.e.*, when it was used as solvent), isocyanate was converted rapidly and completely to a mixture of carbodiimide and isocyanate trimer with carbodiimide predominating. There was no evidence for the storage of isocyanate as phosphinimide. Under these conditions, it appeared probable that isocyanate was "stored" to a certain ex-

---

[15] W. R. Sorenson, *J. Org. Chem.*, **24**, 978 (1959).

[16] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 71.

[17] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

tent as trimer during the course of the catalyzed reactions at higher temperature, since infrared examination of a reacting mixture showed that NCO appeared to disappear faster than carbodiimide and carbon dioxide formed (Table VI). However, in several preparations of diphenylcarbodiimide using catalytic amounts of the phosphine oxide, infrared analysis of the reaction mixture showed the presence of less than 1% of phenyl isocyanate trimer when the reaction was complete.

TABLE VI

COMPARISON OF RATE OF APPEARANCE OF CARBODIIMIDE *vs.* DISAPPEARANCE OF ISOCYANATE BY MEASUREMENT OF CO_2 EVOLVED, AND BY INFRARED ANALYSIS OF REACTION MIXTURE

Time	CO_2 $V_{evolv.}$, moles	Moles unreacted CH_3-C_6H_4NCO calcd. ex CO_2	Moles CH_3-$C_6H_4NCN-C_6H_5CH_3$ calcd. from moles of CO_2	$\frac{N{=}C{=}N}{N{=}C{=}O}$ calcd.	Ratio obsd. by infrared
0	0.0	108.8	0	0.	0
1	0.7	107.4	0.7	.0065	0.05
3	5.7	97.4	5.7	.06	.10
5	10.1	88.6	10.1	.114	.21
15	26.7	55.4	26.7	.48	.62
30	39.6	29.6	39.6	1.34	2.20
60	45.5	17.8	45.5	2.55	12.40
	54.5	0	54.4	—	—

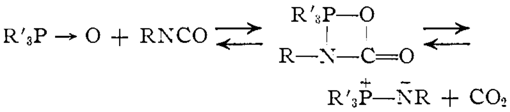
Discussion of Results

The stoichiometry of the reaction is expressed by the equation

$$2RNCO \longrightarrow RNCNR + CO_2$$

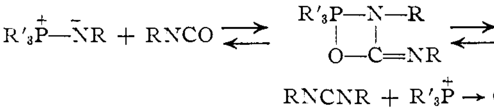
However, the reaction is clearly first order in isocyanate and catalyst over as much as 95% of the reaction.

The results of the kinetic study are consistent with the rate-determining formation of a phosphinimide followed by reaction with another molecule of isocyanate to yield the carbodiimide and regenerate the catalyst. The formation of the phosphinimide probably occurs by nucleophilic attack of the polarized oxygen of the phosphine oxide to form a four-membered ring transition state which can decompose readily, especially under the driving force of the elimination of CO_2. The formation of the carbodiimide is believed to proceed through the same type of transition state



$$R'_3P \rightarrow O + RNCO \rightleftarrows \begin{matrix} R'_3P-O \\ | \quad\;\; | \\ R-N-C{=}O \end{matrix} \rightleftarrows R'_3\overset{+}{P}-\overset{-}{N}R + CO_2 \qquad (10)$$

(10)



$$R'_3\overset{+}{P}-\overset{-}{N}R + RNCO \rightleftarrows \begin{matrix} R'_3P-N-R \\ | \quad\;\; | \\ O-C{=}NR \end{matrix} \rightleftarrows RNCNR + R'_3\overset{+}{P} \rightarrow \overset{-}{O} \qquad (11)$$

(11)

The reaction sequence is further supported by the reversibility of the reaction and the catalysis of the reaction by triethyl- and triphenylphosphine oxides. The choice of 11 as the fast reaction is supported by the kinetics, by the pseudo-zero-order dependence of the rate in bulk isocyanate which indicates that the concentration of the catalyst must be essentially unchanged and by the fact that in the presence of a gross molar excess of catalyst, isocyanate still goes predominantly to carbodiimide very rapidly. If 10 were slow, all of the isocyanate would be rapidly converted to phosphinimide; hence reaction 10 could not occur to any appreciable extent.

The addition of the oxygen atom to the isocyanate carbonyl is consistent with ρ-values which are close to the value obtained for the nucleophilic addition reactions of isocyanates.[18] The effect of substituents also supports this mechanism since electron-donating groups reduce the rate of reaction in accord with other addition reactions of isocyanates.[10,19] The formation of the four-membered ring transition state gains support from the high negative value for the entropy of activation, which indicates marked ordering in the transition state, by the large steric effect of an *ortho* substituent on the rate[10,19] and by the difference in activity between the cyclic phosphine oxides and triphenylphosphine oxide. This difference is probably largely a result of steric hindrance since by resonance the phenylphosphine derivatives should show enhanced polar character because of stabilization of the positive charge on phosphorus. However, the possibility of this type of resonance is uncertain, evidence having been cited for[20] and against[21] the interaction of unsaturated groups with the phosphorus atom.

The proposed reaction sequence for the reaction of the phosphinimide with isocyanates is the same as that proposed by Staudinger[22] and Horner[23] for this type of compound, and is quite similar to the accepted mechanism for the Wittig reaction.[24] The much higher activity of the phosphinimides is consistent with their much more polarized character.[23]

The nucleophilic activity of the phosphoryl group is not surprising in view of its basicity[25] and the examples of this type of reaction with amine oxides,[4,26] sulfoxides[27] and even the carbonyl group.[28] Evidence for nucleophilic activity by the phosphoryl group has also been found in the reaction of dimethyl phenylphosphonite with β-bromoethyl acetate.[29] One of the unusual aspects of this reaction is the dependence of the rate on the inductive effect of substituents. Considering the much reduced rate of the *o*-tolyl and *o*-methoxy derivative, the increased rates in the *o*-chloro and 2,5-dichloro compounds in which both steric *and* res-

---

[18] (a) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 743 (1947); (b) D. W. Browne and G. M. Dyson, *ibid.*, 3285 (1931); (c) private communication with F. W. Blodgett; (d) J. W. Baker and J. J. Gaunt, *J. Chem. Soc.*, 27 (1949).

[19] J. W. Baker and J. P. Holdsworth, *ibid.*, 713 (1947).

[20] V. Baliak and P. Subbarayan, *J. Org. Chem.*, **25**, 1833 (1960).

[21] R. G. Gillis, J. R. Horwood and G. C. White, *J. Am. Chem. Soc.*, **80**, 2999 (1958).

[22] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).

[23] L. Horner and H. Hofmann, *Angew. Chem.*, **68**, 473 (1956).

[24] A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

[25] J. Meisenheimer, J. Casper, M. Horning, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 224 (1926).

[26] (a) E. Ochai, M. Katada and T. Naito, *J. Pharm. Soc., Japan*, **62**, 210 (1942); *C. A.*, **45**, 5154 (1951); (b) V. J. Traynelis and R. F. Martello, *J. Am. Chem. Soc.*, **80**, 6590 (1958).

[27] S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[28] (a) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 687 (1956); (b) W. Lwowski, *Angew. Chem.*, **70**, 490 (1958).

[29] H. J. Harwood and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **82**, 423 (1960).

onance effects should operate to reduce the rate are unusual. Conversely, the steric effect is very powerful since the *o*-chloro compound which should show the maximum inductive effect is slower than the *p*-chloro compound.

One of the most important corollaries, and indeed evidence for the mechanism, is that the presence of a coördinate covalent bond to phosphorus seemed to be the only intrinsic requirement for catalytic activity in this reaction. On this basis, it could be predicted that other compounds of this type should also be catalytically active. This prediction has been verified.[30]

---

(30) J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO, BUFFALO 14, N. Y.]

The Wittig Rearrangement of the Benzyl Ethers of Cyclobutanol and Cyclopropylcarbinol[1]

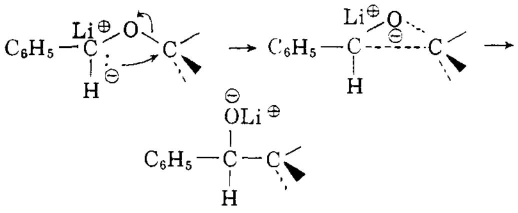
BY PETER T. LANSBURY AND VICTOR A. PATTISON

RECEIVED MAY 17, 1962

The rearrangements of cyclopropylcarbinyl benzyl ether and cyclobutyl benzyl ether in the presence of methyllithium in tetrahydrofuran lead to alcohols in which the migrating group is itself largely or completely unisomerized. The only instance of isomerization was that of the cyclopropylcarbinol anion, which in previous carbanion reactions had been found not to be a stable species. These findings are best rationalized in terms of a cleavage–recombination mechanism, involving the intermediacy of an aldehyde–organolithium ion pair.

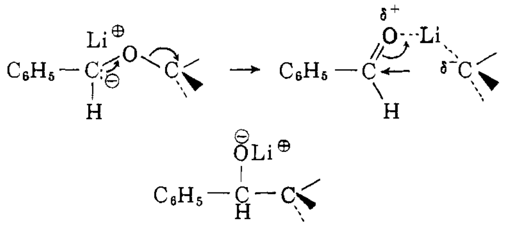
Introduction

The organolithium-induced isomerization of benzyl alkyl ethers to alcohols was considered for some time[2] to be an intramolecular nucleophilic substitution reaction in which a carbanion displaced an alkoxide, the net result being transfer of the migrating group without its bonding electrons.



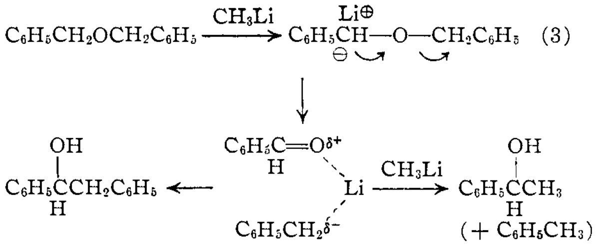
(1)

An alternative mechanism for the rearrangement involves the cleavage of the α-metalated ether into a carbonyl compound and organolithium reagent, followed by recombination of these fragments to give the alkoxide in the usual manner. The earlier workers[2] had rejected this latter mechanism because no evidence for "trapping" of the intermediate carbonyl component by excess metalating base could be obtained. Moreover, the intramolecular substitution mechanism (eq. 1) seemed to find analogy[2b] with the base-induced Stevens rearrangement.[3] The first mechanism predicts that an optically-active migrating group should retain its configuration and in fact a high degree of retention had been observed in an appropriate Stevens rearrangement.[4]



(2)

Recently, Schollkopf and Fabian[5] showed that optically-active *sec*-butyl benzyl ether rearranges when treated with *n*-butyllithium in a variety of solvents to give phenyl-*sec*-butylcarbinol in which the migrated group is largely racemized. This stereochemical evidence was interpreted as favoring the cleavage–recombination mechanism, wherein carbanion racemization could occur, rather than the intramolecular nucleophilic substitution path.[6] Although not an exact analogy, the SNi reaction of alcohols with thionyl chloride has been shown[7] to give variable stereochemical results and therefore one cannot exclude the SNi mechanism for the Wittig rearrangement wholly on this basis. We have, however, provided confirmation of Schollkopf's interpretation by the isolation of varying amounts of methylphenylcarbinol from the methyllithium-induced isomerization of benzyl ether in a series of solvent mixtures.[8] Polar solvents which are good cation solvators, such as tetrahydrofuran,



(3)

---

(1) Presented in part at the 141st Meeting of the American Chemical Society, March, 1962, Washington, D. C.

(2) (a) G. Wittig and E. Stahnecker, *Ann.*, **605**, 69 (1957), and earlier papers; (b) C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).

(3) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 55 (1932).

(4) J. H. Brewster and M. W. Kline, *J. Am. Chem. Soc.*, **74**, 5179 (1952).

(5) U. Schollkopf and W. Fabian, *Ann.*, **642**, 1 (1961).

(6) We hesitate to call this the "SNi" mechanism since this terminology has generally been applied to chlorosulfite decompositions which usually involve a two-step process with intermediate ion pair formation (ref. 7), analogous to SN1 reactions. One may speak, however, of a graded series of SNi reactions, in which the other extreme is an intramolecular substitution with concerted bond making and breaking, similar to the SN2 mechanism. Our use of the term "SNi" will be in this more general sense.

(7) C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953).

(8) P. T. Lansbury and V. A. Pattison, *J. Org. Chem.*, **27**, (1962).