

tane was used to develop the chromatogram and elute the *p*-nitroiodobenzene.

The positions of the iodobenzene and nitrated isomers could be observed under ultraviolet light. Iodobenzene (bluish-white fluorescence) was eluted first and was followed by *p*-, *m*- and *o*-iodobenzenes (purple fluorescence) in order. Although these were not developed into separate bands, the head of the band was a deeper purple than the latter portions of the band and was found to be nearly pure *p*-isomer.

Material recovered from the head of the purple band melted at 174.8–175.6° and was decomposed without further purification. The activity of the silver iodide counted (0.4999 g.) was 3650 c./min., after correction for decay, compared to an activity of 29,774 c./min. given by silver iodide from the original iodobenzene. From these data and the percentage of *p*-isomer determined above, it was found that the number of millimoles of iodobenzene nitrated was 4.8 ± 0.1 .

A similar analysis was carried out on the products of nitration in acetic anhydride. To 35.0 ml. (70%) of the glacial acetic acid solution of the products were added 3.1919 g. of inactive *p*-nitroiodobenzene and 0.07 g. and 1.4 g., respectively, of inactive *m*- and *o*-nitroiodobenzenes. From the acetic acid solution when chilled was recovered 3 g. of crystalline *p*-nitroiodobenzene. This material, 0.5 g. of inactive *o*-nitroiodobenzene and 5 ml. of inactive iodobenzene were dissolved in benzene and chromatographed on a 45-mm. $\times$ 70-cm. column of alumina. The *p*-nitroiodobenzene recovered (m.p. 174.8–175.6°) was converted to silver iodide which had an activity of 1076 c./min. The amount of iodobenzene nitrated in acetic anhydride was, therefore, 1.51 ± 0.01 millimoles. When used to calculate the reactivity toward acetyl nitrate of iodobenzene with respect to benzene this gave the values 0.22 ± 0.01 and 0.13 ± 0.01 for nitration in nitromethane and acetic anhydride, respectively.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Acid Catalysis in the Decomposition of Benzazide¹

BY RALPH A. COLEMAN, MELVIN S. NEWMAN AND A. B. GARRETT

RECEIVED APRIL 27, 1954

The rates of Lewis acid catalyzed decomposition of benzazide into phenyl isocyanate and nitrogen have been determined in benzene and nitrobenzene. When the acids were gallium chloride, aluminum bromide, aluminum chloride and ferric chloride, the kinetics of the nitrogen evolution indicates that an acid-benzazide complex formed rapidly, then decomposed slowly by first-order kinetics. Furthermore, the released catalyst does not complex with phenyl isocyanate but immediately recombines with unreacted azide. The decomposition in the presence of antimony pentachloride, titanium tetrachloride, stannic chloride and tellurium tetrachloride were first order with respect to azide and to halide. The rate measurements suggest that the order of decreasing acid strength is as follows: gallium chloride, aluminum bromide, aluminum chloride, ferric chloride, antimony pentachloride, titanium tetrachloride, stannic chloride, tellurium tetrachloride and antimony tetrachloride. Arsenic trichloride, arsenic tribromide, phosphorus trichloride and phosphorus pentachloride were without effect on the decomposition rate.

The decomposition of benzazide into nitrogen and phenyl isocyanate in non-aqueous solvents was found to be catalyzed by protonic acids and by boron fluoride in dioxane.² This suggested that the relative strengths of Lewis acids might be determined by measuring their catalytic effect on the rate of benzazide decomposition. In order that complicating factors such as the formation of carbon dioxide gas³ and products other than phenyl isocyanate be excluded, this study was confined to non-protonic acids in aprotic solvents. In benzene and nitrobenzene solutions, the rate of decomposition of benzazide is increased to varying degrees by soluble metallic halides and could be followed by measurements of the evolved nitrogen.

Experimental

Reagents.—The benzazide, prepared from recrystallized benzhydrazide and nitrous acid, was recrystallized from petroleum ether to a melting point of 27.1–27.2°. The melting point remained unchanged over a period of four months when stored near 0°.

The following C.P. or reagent quality chemicals were distilled in all-glass apparatus at atmospheric pressure (b.p.'s uncorrected): antimony tribromide, 279–281°; antimony trichloride, 217–218°; arsenic tribromide, 215–216°; stannic chloride, 110.5–111°; titanium tetrachloride, 131.5–132.5°; tellurium dichloride, 321.4°; antimony pentachloride 89° at 30 mm. Anhydrous aluminum chloride was

twice sublimed in a stream of dry nitrogen. Gallium trichloride, b.p. 195–196°, was prepared by chlorinating hot metallic gallium. Ferric chloride was prepared from the elements.⁴ Tellurium tetrachloride, formed by chlorinating tellurium dichloride, was distilled. Aluminum bromide (Westvaco) was redistilled, b.p. 349–351°. Boron tribromide, distilled from a mixture of aluminum bromide and sodium fluoroborate,⁵ was redistilled, b.p. 96–97°. Arsenic trichloride, mercuric bromide, phosphorus trichloride and phosphorus pentachloride (all C.P. grade) were used without further purification.

The benzene was C.P. "thiophene free," distilled over sodium. "Pure" grade nitrobenzene was partially crystallized and centrifuged; the crystals were then melted, the liquid dried over phosphorus pentoxide and distilled, b.p. 82–83° at 8 mm.

Apparatus.—A 125-ml. round-bottom reaction flask with a sealed-on water cooled condenser was immersed in a constant temperature bath. The top of the condenser was connected by Tygon tubing to a Hempel gas buret. Changes in atmospheric pressure and temperature were automatically corrected for by balancing a reference reaction flask containing only solvent against the reacting system through a glycol manometer. By doing this, the volume of gas collected was converted to standard conditions with but one conversion factor. During runs, the flask was subjected to pendulum-type agitation.

Procedure.—Twenty-five ml. of solvent was pipetted into a dried reaction flask, then one to three millimoles of the metallic halide was added. After allowing the solution to reach equilibrium temperature, a small tube containing approximately three millimoles of benzazide was placed in the top of the condenser on a movable iron support. The entire gas system was then closed off and balanced against the reference system; the azide was then allowed to drop into the solvent by moving the iron support with a magnet.

(1) Taken from the Ph.D. thesis of R. A. C., The Ohio State University, 1951.

(2) M. S. Newman and H. L. Gildenhorn, *THIS JOURNAL*, **70**, 317 (1948).

(3) See M. S. Newman, S. H. Lee and A. B. Garrett, *ibid.*, **69**, 113 (1947), for references.

(4) L. F. Audrieth, *et al.*, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, Vol. III, p. 29.

(5) Reference 4, p. 191.

The nitrogen evolved was collected over mercury in a Hempel gas buret; the volumes were corrected for the vapor pressure of solvent and converted to milliliters of nitrogen at 760 mm. and 0°. At least ten measurements were made during the first half-life of the reaction. The reaction temperatures were 54.9° and 10.5°.

Treatment of Data.—The rate of decomposition of benzazide in organic solvents has been shown to follow first-order kinetics,³ the rate constant, k_1 , being calculated from the data through equation 1

$$\log(V_\infty - V) = \frac{k_1 t}{2.303} + \log V_\infty \quad (1)$$

where V is the volume of nitrogen collected in milliliters at time t in minutes, and V_∞ is the total gas collected (usually very close to the theoretical). The decomposition of benzazide in benzene and nitrobenzene followed first-order kinetics for about 70% of the reaction.

When antimony pentachloride, titanium, stannic and tellurium tetrachlorides were used the rate of nitrogen evolution for each kinetic run followed the first-order rate law, equation 1, but the experimental rate constant, k_1 , varied with concentration of the added metallic halide (Fig. 1). This experimental rate constant was resolved into two rate constants by the relationship

$$k^1 = k_1 + k_c(A) \quad (2)$$

where k_1 is the rate constant in the pure solvent, k_c is a catalytic rate constant characteristic of the metallic halide, and (A) is the concentration of the metallic halide (calculated as monomer).

The value of k_c was obtained by plotting k^1 versus concentration of catalyst (A) , the slope of the line being k_c and the intercept when $(A) = 0$ being k_1 (Fig. 1). Data for a typical run treated by equation 2 are shown in Table I. However, for antimony trichloride and antimony tribromide it was necessary to use equation 3 to get constant value for k^1 presumably because antimony trichloride exists chiefly as non-catalytic dimer in solution. The rate constants for all of these cases are listed in Table II.

$$k^1 = k_1 + k_c(A)^{1/2} \quad (3)$$

TABLE I

DECOMPOSITION OF BENZAZIDE ACCORDING TO EQUATION 2, RUN 61

0.403 g. of benzazide, 0.526 g. (0.077 M) of stannic chloride, 25.6 ml. of nitrobenzene, temperature 54.9°, $(A) = 0.0774$; $k_1 = 0.00098$

$$k_c = \frac{1}{(A)} \left(\frac{2.3}{t} \log \frac{V}{V_\infty - V} - k_1 \right)$$

Time, min.	Vol. N ₂	k_c	Time, min.	Vol. N ₂	k_c
0	0	...	39	37.3	0.280
4	5.5	0.284	47	41.7	.280
8	10.7	.284	61	47.7	.282
11	14.0	.379	69	50.4	.282
14	17.2	.280	77	52.6	.282
20	23.1	.279	89	55.2	.282
26	28.3	.280	107	57.9	.279
32	32.8	.280		63.6 (V_∞)	...

The data obtained when gallium chloride, aluminum bromide, aluminum chloride and ferric chloride were present always followed *over-all* first-order kinetics. When benzazide was in excess the reaction

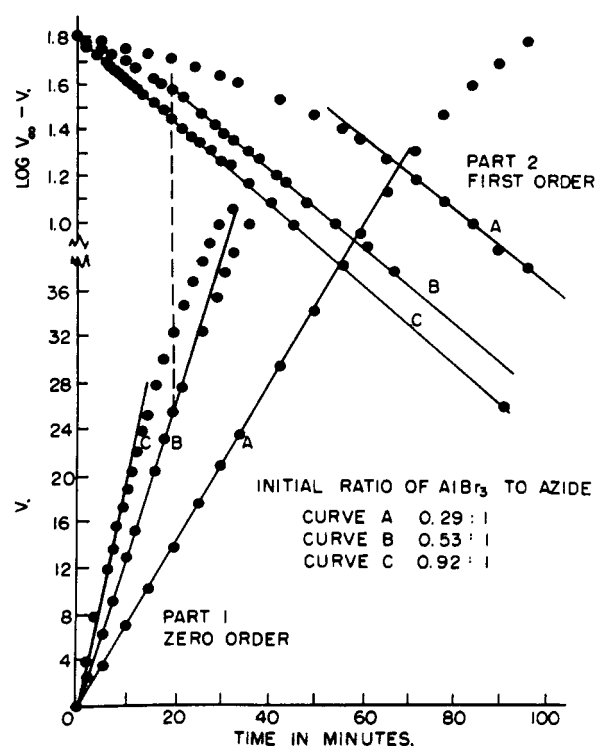


Fig. 1.—Rates of decomposition of benzazide in nitrobenzene in the presence of aluminum bromide at 10.5°. Part I shows zero order when benzazide is in excess at beginning of experiment thus giving constant concentration of active complex; Part 2 shows first-order kinetics of same runs as soon as excess benzazide has decomposed and the concentration of the active complex is changing with time.

TABLE II
CATALYTIC RATE CONSTANT FOR BENZAZIDE DECOMPOSITION

Catalyst	Temp., °C.	Benzene k_1^a	Nitrobenzene k_1^a
None	54.9	6.16×10^{-4}	9.8×10^{-4}
Class I, rate = $k_2(AZ)^b$			
		k_2	k_2
FeCl ₃	10.5		0.0111
AlCl ₃	10.5		.0340
AlBr ₃	10.5	0.0301	.0376 ^c
GaCl ₃	10.5		.0473
Class II, rate = $k_1(Z) + k_c(A)(Z)^b$			
		k_1	k_c
TeCl ₄	54.9	0.0232	0.0184
SnCl ₄	54.9	0.0107	.274 ^d
TiCl ₄	54.9	2.34	
TiCl ₄	10.5		.0370
SbCl ₅	10.5		.547
Class III, rate = $k_1(Z) + k_c(A)^{1/2}(Z)^b$			
SbBr ₃	54.9	0.00088	
SbCl ₃	54.9	.00118	0.0113

^a Time in minutes. ^b Where (Z) is concentration of benzazide, (A) is concentration of catalyst (calculated as the monomer), (AZ) is concentration of complex. ^c The same rate constant was obtained in an identical experiment except that one equivalent of phenyl isocyanate was added. ^d In a duplicate experiment an added equivalent of phenyl isocyanate the rate constant was 0.231.

was zero order with respect to benzazide and first order with respect to metallic halide, the data fitting equation 4⁶

$$V = 22,400k_2(A)t \quad (4)$$

Thus in Fig. 2 a plot of V versus t gives a straight line (zero order in azide) with a slope that varied directly with the amount of catalyst present (first order in catalyst). However, when the reaction had proceeded sufficiently so that benzazide was no longer in excess, the reaction became first order with respect to benzazide and zero order with respect to the catalyst. This is shown in Fig. 2 in

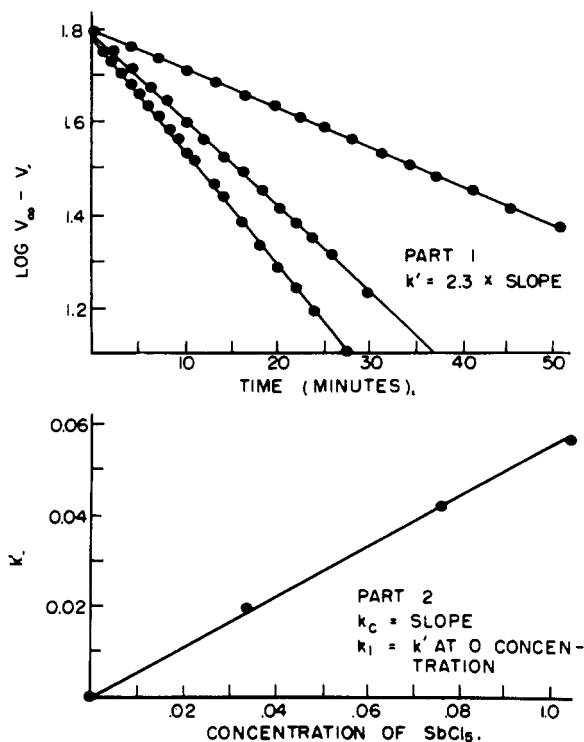


Fig. 2.—The rates of decomposition of benzazide in nitrobenzene in the presence of SbCl_5 at 10.5° showing first-order kinetics (Part 1) and method of evaluating k' , k_c and k_1 (Part 1 and 2).

the plot of $\log (V_\infty - V)$ versus time t , which does not become a straight line (first order) until the excess benzazide has been decomposed. The kinetic equation for this case was shown to be

$$\log (V_\infty - V) = -\frac{k_2}{2.3} (t - n) + \log (V_\infty - V_n) \quad (5)$$

where " n " is the time at which the reaction becomes first order in azide and V_n is the volume of nitrogen collected at time n . Data for a typical run treated by equations 4 and 5 are shown in Table III. The rate constants for these several catalysts are listed in Table II.

Arsenic trichloride and tribromide and phosphorus trichloride and pentachloride did not affect the rate of decomposition of benzazide.

(6) Equation 4 is derived from the expression $d(\text{azide})/dt = k_2(A)$ by substituting for (azide) its equivalent, $V_\infty - V/22,400$ (when V_∞ and V have the same significance as before) and for (A) its equivalent (A/v) where A is the number of moles and v is volume of the solution.

TABLE III
DECOMPOSITION OF BENZAZIDE ACCORDING TO EQUATIONS 4 AND 5, RUN 74

0.399 g. of benzazide, 0.257 g. (0.00192 mole) of aluminum chloride and 24.7 ml. of nitrobenzene, temperature 10.5° , $(A) = 0.00192$, $k_2 = V/22,400(A)t$

Time, min.	Vol. N_2	k_2
0	0	...
3	4.2	0.0326
6	9.0	0.0349
8	11.9	0.0346
10	14.9	0.0346
12	17.9	0.0346

$$k_2 = \frac{2.3}{t - n} \log \frac{V_\infty - V_n}{V_\infty - V}$$

(Pseudo zero-order changes to first order)

14(n)	20.7(V_n)	
18	25.9	0.0334
22	30.7	0.0346
26	34.8	0.0347
31	39.0	0.0343
37	43.4	0.0345
45	47.9	0.0346
50	50.2	0.0346
63	54.5	0.0346
81	58.0	0.0345
92	59.3	0.0345
	62.1	...

The following substances are insoluble in nitrobenzene and benzene and therefore could not be studied: lithium chloride, sodium bromide, sodium chloride, cupric chloride, magnesium bromide, mercuric chloride, tellurium dichloride, zinc bromide, bismuth chloride and chromium trichloride.

Boron tribromide was an extremely active catalyst but only 50 to 75% of the expected nitrogen was collected. From the very rapid rate of nitrogen evolution, its rate constant, k_2 , is estimated to be about eighteen times larger than that for gallium chloride.

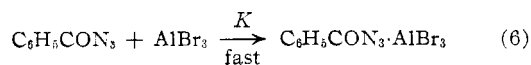
Discussion

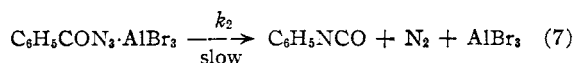
Originally our intention was to classify Lewis acids according to their relative strengths as demonstrated by their ability to catalyze the decomposition of benzazide. However, since more than one kind of kinetics was encountered it is not possible to place all the catalysts in a single strength scale without making some assumptions. Accordingly we have grouped the halides into three classes or series based on the kinetic equation involved. In each case the halides are listed in the order of their relative acid strengths.

- Class I $\text{GaCl}_3 > \text{AlBr}_3 > \text{AlCl}_3 > \text{FeCl}_3$
- Class II $\text{SbCl}_5 > \text{TiCl}_4 > \text{TeCl}_4$
- Class III $\text{SbCl}_3 > \text{SbBr}_3$

These classes are also listed in the order of decreasing acid strength.

Class I: In this class the rate of formation of the complex with the catalyst is very rapid and the rate-determining step is the decomposition of the complex. This is represented by equations 6 and 7.

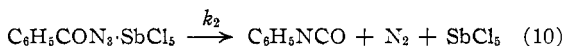
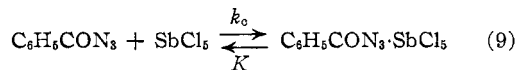




The results of a typical run which fits this scheme are illustrated in Fig. 1. The equilibrium (eq. 6) is attained rapidly and the constant K is large. Hence as long as benzazide is in excess the concentration of the complex remains constant and equal to the concentration of halide introduced at the start of the reaction. The rate for this stage of the reaction is zero order with respect to benzazide and first order with respect to metallic halide. In keeping with this explanation is the fact that the addition of an equivalent of phenyl isocyanate in an experiment at 10° with aluminum bromide in nitrobenzene did not affect the rate constant obtained (0.0376—see Table II). In another experiment in which one millimole of sodium bromide was added to a reaction mixture catalyzed by three millimoles of aluminum bromide in nitrobenzene at 10° , the rate constant was the same as that obtained in a similar experiment involving only two millimoles of aluminum bromide. This result indicates that the millimole of added sodium bromide neutralized one millimole of aluminum bromide according to equation 8.



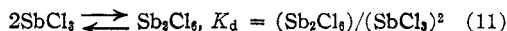
Class II: In this class the rate of formation of the complex may be slow and the rate of decomposition of the complex fast; or the equilibrium between the reactants and the complex may be attained rapidly but the decomposition of the complex may be slow. This is represented by equation 9 and 10.



The results of a typical run which fits this scheme are illustrated in Fig. 2. The kinetics data obtained are consistent with either of the two explanations but are insufficient to decide between the two. If k_0 is small and k_2 large, the experimental rate constant would be equal to k_0 . On the other hand the equilibrium (eq. 9) may be obtained rapidly and k_2 may be small but K would have to be small to give second-order kinetics. Then the experimental rate constant would be Kk_2 . By either kinetic path the halides comprising this class would appear to be less acidic than those in Class I: either the equilibrium constant is small (implying less coordinating power for the halide); or the rate of formation of the complex is slow (also slower than Class I).

In two comparable experiments in nitrobenzene at 54.9° using stannic chloride, that in which an equimolar amount of phenyl isocyanate was added had a rate constant of 0.231 (compared to 0.274—see Table II). Other experiments, however, showed that the rate constant did not decrease near the end as would be expected if phenyl isocyanate were complexing with catalyst. More work is needed here to clarify the picture.

Class III: In this class, which may be similar to Class I, the question of dimerization of the catalyst must be considered. This involves the additional equation 11



$$\text{catalyzed rate} = k(\text{azide})(\text{SbCl}_3) = \frac{k}{K_d^{1/2}} (\text{azide})(\text{Sb}_2\text{Cl}_6)^{1/2} \quad (12)$$

The rates of the reactions in which antimony trichloride is the catalyst can be interpreted readily if the $\text{Sb}_2\text{Cl}_6/(\text{SbCl}_3)_2$ factor is introduced and is assumed to be large; a similar situation obtains with antimony tribromide.

However, it would seem reasonable to expect a similar factor to be required in all cases where dimerization occurs (FeCl_3 , AlCl_3 , AlBr_3 ,⁷ GaCl_3). Van Dyke has shown that aluminum bromide in benzene probably exists as $\text{Al}_2\text{Br}_7 \cdot 2\text{C}_6\text{H}_6$. Carlett and Gregory⁸ have shown that two of the halogens (probably of the two bridging halogens) in solid aluminum bromide are only slowly replaced by other halogens.

The idea that antimony trichloride exists in solution as a dimer is not unreasonable as aluminum bromide and chloride have been reported to exist as dimers in solution. That aluminum bromide does not require a square root term in its rate equation can be explained if we assume that it reacts so fast and completely to form the complex, that its rate of dissociation need not appear in the rate-determining step, the decomposition of the complex. On the other hand, it appears that the equilibrium for the dimerization of antimony trichloride is largely in favor of the dimer, so that the concentration of monomer is kept low. This will explain the square root term in equation 12.

However, antimony bromide is reported to be monomeric in benzene.⁹ No data are reported on the chloride.

It is interesting to note that while the rate of the uncatalyzed decomposition of benzazide is greater in nitrobenzene than in benzene, this differential is not maintained for all the catalyzed reactions (see Table II).

TABLE IV
DECREASING ORDER OF ACID STRENGTHS

Acid catalyst	Bond energies	Acid catalyst	Bond energies
GaCl_3	AlI_3	TiCl_4	SnCl_4
AlBr_3	AlBr_3	SnCl_4	ZrCl_4
AlCl_3	AlCl_3	TeCl_4	SbCl_3
FeCl_3	SbCl_3	SbCl_3	
SbCl_5	TiCl_4		

The order of acid strengths of metallic halides found in this work agrees in general with that for their relative effectiveness as catalysts for Friedel-Crafts reactions^{10,11} for the polymerization of isobutene,¹² for the Gattermann-Koch reaction,¹³ and for the dissolution of metals in thionyl chloride.¹⁴ Agreement was found with other methods of meas-

(7) Ross E. Van Dyke, *THIS JOURNAL*, **72**, 3619 (1950).

(8) John D. Carlett and N. W. Gregory, *ibid.*, **75**, 5238 (1953).

(9) R. Wright, *J. Chem. Soc.*, **109**, 1134 (1916).

(10) O. C. Dermer, D. M. Wilson, F. M. Johnson and V. H. Dermer, *THIS JOURNAL*, **63**, 2881 (1941).

(11) O. C. Dermer and R. A. Billmeier, *ibid.*, **64**, 464 (1942).

(12) P. H. Plesch, N. Polanyi and H. A. Skinner, *J. Chem. Soc.*, 257 (1947).

(13) M. H. Dilke and D. D. Eley, *ibid.*, 2613 (1949).

(14) R. A. Hubbard, 2nd, and W. F. Luder, *THIS JOURNAL*, **73**, 1327 (1951).

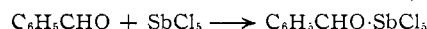
uring acid strength such as titration curves,¹⁵ polarization measurements,¹⁶ and bond energy calculations of benzaldehyde-metallic halide complexes.¹⁷ The bond energies of Dilke and Eley were calcu-

(15) W. S. Peterson, C. J. Heimerzheim and G. B. L. Smith, *THIS JOURNAL*, **65**, 2403 (1943).

(16) F. Fairbrother, *J. Chem. Soc.*, 503 (1945).

(17) M. H. Dilke and D. D. Eley, *ibid.*, 2601 (1949).

lated from the measured heats of reactions; e.g.,



The comparison of the relative acid strengths from the benzazide decomposition rates (kinetic method) and the bond energy calculations (thermodynamic method), as shown in Table IV is striking.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE AGRICULTURAL AND INDUSTRIAL STATE UNIVERSITY]

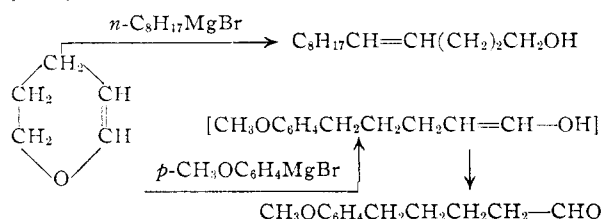
Grignard Reagents and Unsaturated Ethers. III.¹ Reaction of Grignard Reagents with Cyclic Unsaturated Ethers²

BY CARL M. HILL, GILBERT W. SENTER, LONNIE HAYNES AND MARY E. HILL

RECEIVED FEBRUARY 12, 1954

The reactivity of cyclic unsaturated ethers with Grignard reagents has been investigated. Results of this study indicate that alkyl and aryl Grignard reagents cleave 2,3-dihydropyran and 4-methyl-3,4-dihydro-2H-pyran at the ether linkage to form unsaturated alcohols and saturated aldehydes. *n*-Hexylmagnesium bromide reacts with 2-methyl- and 2,5-dimethylfuran to yield β,γ -unsaturated methyl ketones.

Previous papers^{1,3} in this series have illustrated that both aryl and alkyl Grignard reagents cleave aryl substituted vinyl ethyl and allyl alkyl ethers with the formation of aryl and alkyl substituted olefins and alcohols. In the present paper, we have extended these studies to two α,β -unsaturated cyclic ether systems, namely, the furan and dihydropyran. It was postulated that by structural comparison with the open chain vinyl analogs α,β -unsaturated cyclic ethers should be susceptible to reaction with Grignard reagents. The results of the present investigation have fulfilled this prediction. For example, reaction of 2,3-dihydropyran with *n*-octylmagnesium bromide (25% excess) gave as reaction product 4-tridecen-1-ol (36%); while reaction of 2,3-dihydropyran with *p*-anisylmagnesium bromide (25% excess) yielded 5-(*p*-methoxyphenyl)-pentanal (30%).



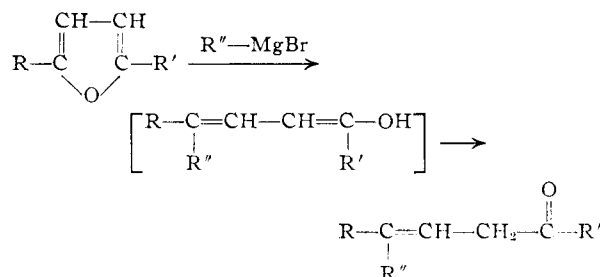
However, when 4-methyl-3,4-dihydro-2H-pyran is allowed to react with *n*-hexyl- and *p*-anisylmagnesium bromides (25% excess), 3-methyl-4-hendecen-1-ol (31%) and 3-methyl-5-(*p*-anisyl)-4-penten-1-ol (40%) are formed, respectively.

Our studies were extended to furans by an investigation of the reaction of 2-methyl- and 2,5-dimethylfuran with *n*-hexylmagnesium bromide which yielded 4-hendecen-2-one (36%) and 5-methyl-4-hendecen-2-one (30%), respectively

(1) The second paper in this series was published by C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, *THIS JOURNAL*, **75**, 5408 (1953).

(2) This research was supported in part by the United States Air Force under Contract AF 16(600)-466 monitored by the Office of Scientific Research, H. G. Air Research and Development Command.

(3) C. M. Hill, R. A. Walker and M. E. Hill, *THIS JOURNAL*, **75**, 1663 (1951).



where R = H or CH₃, R' = CH₃ and R'' = *n*-C₆H₁₃. Recent investigations of Fuson and Wallingford⁴ have shown that mesitylmagnesium bromide cleaves 2-mesitylfuran to yield 1-mesityl-4-mesityl-1-hydroxy-1,3-butadiene.

Reaction products were identified through their benzoates or hydrazones and by characterization of their ozonization products. In addition, 4-tridecen-1-ol and 5-methyl-4-hendecen-2-one were converted to the corresponding saturated alcohols.

Acknowledgment.—The authors express thanks to George Canty, who gave valuable assistance in the development of this investigation.

Experimental⁵

Cyclic Unsaturated Ethers.—The 2,3-dihydropyran used in this investigation was purchased from Matheson, Coleman and Bell, Inc., and 2-methyl- and 2,5-dimethylfuran from Eastman Kodak. The 4-methyl-3,4-dihydro-2H-pyran was synthesized according to the procedure reported by Parham and Holmquist.⁶

Reaction of 2,3-Dihydropyran with *n*-Octylmagnesium Bromide.—*n*-Octylmagnesium bromide (1 mole) was prepared under dry nitrogen in the usual manner, and treated with 69 g. (0.8 mole) of freshly distilled 2,3-dihydropyran in an equal volume of absolute ether added during 5 hours. The reaction mixture was refluxed 40 hours and then hydrolyzed with saturated ammonium chloride. The ether layer was separated and the aqueous layer extracted continuously with ether for 36 hours. The ether extracts were combined, dried and concentrated to give a dark residue which was distilled through a Poddelniak column. Fifty-

(4) R. C. Fuson and H. P. Wallingford, *ibid.*, **75**, 5950 (1953).

(5) All melting points are corrected.

(6) W. E. Parham and H. E. Holmquist, *THIS JOURNAL*, **73**, 913 (1951).