mined by the double titration method.[21] Solvents were dried over sodium and distilled immediately before use.

Preparation of Organolithium Compounds.—The organometallic compounds were prepared by a general method.[22] Methyllithium was prepared from iodomethane and phenyllithium from bromobenzene. Lithium was made into ribbon, cut, and dropped directly into anhydrous ether in the reaction vessel. The halide was then added in the prescribed manner. The organometallic solution was forced through a glass wool plug into a graduated flask with helium. Phenyllithium prepared in this manner and commercial phenyllithium gave the same results in the rearrangement reactions.

Lithium Ethoxide.—Lithium ethoxide in ethanol was prepared by the slow addition of 40 mmoles of *sec*-butyllithium in hexane to 50 ml. of absolute ethanol. The hexane–ethanol mixture was decanted from the solid lithium ethoxide. Absolute ethanol (100 ml.) was added to the solid and the mixture was used in the rearrangement reaction.

General Procedures for Rearrangement.—Data presented in Tables I–III were taken using procedures B or C. The results with method A were comparable with those with method B.

Method A.—Anhydrous ether (100 ml.) was placed in a 200 ml. three-neck, round-bottomed flask equipped with dry nitrogen inlet on an equallizing dropping funnel, reflux condenser, and wide flexible connector to the salt-containing erlenmeyer. A glass-encapsulated magnetic stirring bar was used for mixing the reactants. One-third of the organometallic compound (20 or 40 mmoles total) in hexane or ether was added to the solution and the remainder was added at about 1 drop/min. Five per cent of the benzyltrimethylammonum halide (total 20 mmoles) was added initially and approximately 10% of the total salt every 15 min. thereafter. The addition of all reactants required 3 hr. Slow nitrogen flow (4 cc./min.), gentle reflux, and rapid stirring were maintained during the entire period of reaction. Reaction was allowed to proceed for no less than 4 nor more than 24 hr. Termination of the reaction was accomplished by the cautious addition of 15 ml. of of water. Dilute hydrochloric acid (50 ml. of 6 *F*) was then added. Extraction to obtain basic, neutral, and acidic fractions was as previously described.[1a] The amines obtained were analyzed by gas chromatography.

Method B.—The solution of organometallic reagent (20 or 40 mmoles) was placed in a 200-ml. indented, three-necked flask equipped with nitrogen inlet and reflux condenser, and containing the stirring bar. The solution was brought to 100 ml. with appropriate dry solvent (diethyl ether or *n*-pentane). The dry salt I (5.4 g. of the iodide) was finely powdered in a drybox and rapidly introduced into the reaction vessel. Reaction was allowed to proceed for the prescribed period and then quenched by the addition of crushed ice. The reaction mixture was worked up as in method A.

Method C. Kinetic Conditions.—The reaction was carried on in a sealed 200-ml. indented flask with magnetic stirring. Temperature was controlled by submersion in a constant-temperature water bath at 26.0 ± 0.2°. Stirring in both the bath and reaction flask was by individual magnetic stirrers. *n*-Butyllithium in pentane or phenyllithium in ether (40 mmoles) was diluted to 100 ml. with anhydrous ether. Finely powdered dry iodide of I (5.4 g., 20 mmoles) was rapidly added to the constant-temperature solution under an atmosphere of dry nitrogen. The flask was sealed with a silicone rubber port. At intervals 1-ml. samples were drawn with a hypodermic syringe. These samples were added to 1 ml. of a known solution of benzyldimethylamine in ether and 1 ml. of water. After vigorous mixing, the solution was allowed to stand at least 4 hr. A sample was drawn off the top layer and analyzed in the gas chromatograph. A control run to show the absence of other compounds which might interfere with the quantitative analyses was also carried out. No additional components were detected in the region of interest.

Acknowledgment.—This investigation was supported by Public Health Service Research Grant GM-09136, from the National Institute of General Medical Sciences.

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1,5-Hydrogen Transfer during Diazonium Ion Decomposition. III. Kinetic Studies[1-3]

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Received May 7, 1965

The rates of thermally induced nitrogen evolution of N,N-dicyclohexylbenzamide-*o*-diazonium fluoroborate in methanol and acetic acid solutions containing sulfuric acid have been found to be first order over more than 3 half-lives. The rates were of the same order of magnitude in both solvent systems and they were not appreciably affected by carrying out the decomposition in the presence of a variety of radical-chain inhibitors. The results of this kinetic study, in conjunction with previous product studies, are considered to be compatible with an ionic mechanism involving a 1,5-hydride ion transfer, in which the product composition is determined by the state of ion association of the salt.

In previous work[3,4] it has been shown that thermal decomposition of diazonium salts (I) derived from *o*-amino-N,N-dialkylbenzamides, yields, after aqueous work-up, a variety of products among which are V and the usual products of diazonium salt decomposition, IV (X = OH, OCH_3, F, etc.). Arguments for an ionic mechanism involving a hydride ion transfer have been presented.[3,4]

In the previous discussion,[3] it was pointed out that, of the available radical mechanisms involving hydrogen atom transfers, a radical-chain mechanism could most reasonably explain the product composition, although one involving geminate recombination of a radical pair could not be definitely excluded.[5] The chain mechanism was, however, ruled out for the decomposition of I (R = C_6H_5) in acetic–sulfuric acid since the product composition is not significantly changed by the addition of the radical traps *m*-dinitrobenzene and thiophenol. In the case of thiophenol, no reduction product, N,N-dibenzylbenzamide, is formed. The later[4b] detection of the intermediate III (R = C_6H_5) when the decomposition was carried out in ethylene chloride also

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(1) This investigation was supported by Grant NSF G-23705 from the National Science Foundation.

(2) Based on the Ph.D. Thesis of J. Lipowitz, University of Pittsburgh, July 1964.

(3) Part II: T. Cohen, A. H. Dinwoodie, and L. D. McKeever, *J. Org. Chem.*, **27**, 3385 (1962).

(4) (a) Part I: T. Cohen, R. M. Moran, and G. Sowinski, *ibid.*, **26**, 1 (1961); (b) T. Cohen and J. Lipowitz, *J. Am. Chem. Soc.*, **86**, 2514 (1964); (c) T. Cohen and J. Lipowitz, *Tetrahedron Letters*, 3721 (1964).

(5) See ref. 3, footnote 8.

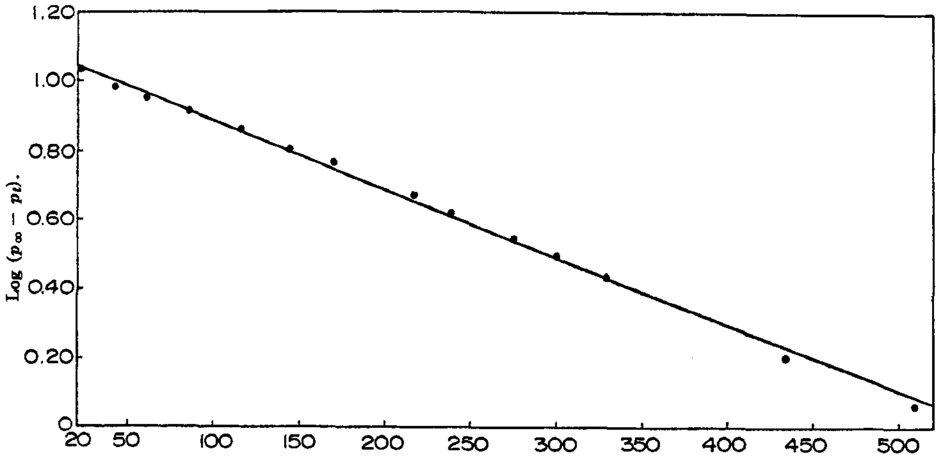
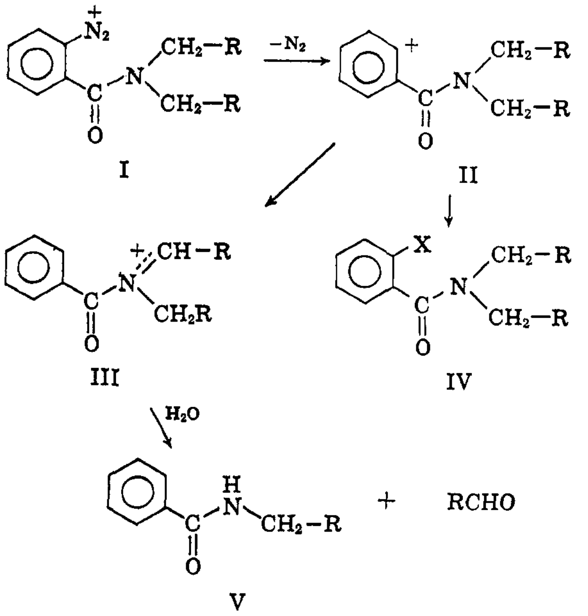
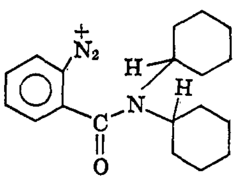


Figure 1.—The first-order kinetic plot of the thermal decomposition of N,N-dicyclohexylbenzamide-*o*-diazonium fluoroborate (5.16 × 10^{-3} *M*) in methanol, 1 *M* in sulfuric acid, at 29.97°.

rules out the radical-pair mechanism, at least in this medium.



The analogous products arising from the decomposition of the dicyclohexyl compound VI have been



VI

recently discussed.[4c] The ratio of dealkylation products to substitution products increases sharply in going from acetic acid to aqueous acetic acid and from acetic acid to methanol to aqueous methanol–sulfuric acid. This has been attributed to a decrease in the state of ion pairing as the polarity of the solvent increases. It also appeared possible, however, that the change in product composition could be due to a change of mechanism from hydride ion transfer to hydrogen atom transfer[3,6] in going from the more acidic solvents (acetic acid) to the more basic solvents (aqueous acetic acid, methanol). Evidence that radical mechanisms are favored in more basic solvents is available.[7] Furthermore, studies[8] of the copper-catalyzed diazonium decompositions in this series indicate that hydrogen transfer is by far the major reaction and that free radicals are intermediates. That is, a hydrogen *atom* transfer is involved.

In order to detect a possible change from an ionic to a radical-chain mechanism in going to more basic solvents, a study of the rates of decomposition of the diazonium ion VI in acetic–sulfuric acid and in methanol–sulfuric acid, both in the presence and absence of radical-chain inhibitors, was initiated. It might be expected that such a change in mechanism would probably be accompanied by a significant change in rate and that the latter would be sensitive to the presence of chain inhibitors in that medium in which the radical mechanism prevails. Another goal of this study was the confirmation of the conclusion reached previously[3] on the basis of the insensitivity of product composition to radical traps that a radical-chain mechanism is not important in the acetic–sulfuric acid medium.

Results and Discussion

The manometric rate of nitrogen evolution of N,N-dicyclohexylbenzamide-*o*-diazonium fluoroborate (VI) in acetic acid, 1.0 *M* in sulfuric acid (solvent A) and in methanol, 1.0 *M* in sulfuric acid (solvent B), was found to follow first-order kinetics over more than 3 half-lives. Slight curvature in plots (Figure 1) of log ($p_\infty - p_t$) *vs.* *t* appears to be due to slow leakage in the apparatus since the pressure during a run was found to reach a maximum (p_∞) and then to decrease slowly. To eliminate errors due to the inaccuracy of the p_∞ value, the Guggenheim[9] procedure was used to obtain rate constants at 39.98 ± 0.02°. This proce-

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[6] D. N. Brown, D. H. Hey, and C. W. Rees, *J. Chem. Soc.*, 3873 (1961).

[7] D. F. DeTar and M. N. Turetzky, *J. Am. Chem. Soc.*, **77**, 1745 (1955); **78**, 3925, 3928 (1956); D. F. DeTar and T. Kosuge, *ibid.*, **80**, 6072 (1958); L. Horner and H. Stohr, *Ber.*, **85**, 993 (1952).

[8] A. H. Lewin and T. Cohen, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p. 54S.

[9] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926); A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 49.

TABLE I
RATE OF NITROGEN EVOLUTION OF N,N-DICYCLOHEXYLBENZAMIDE-*o*-DIAZONIUM FLUOROBORATE AT 39.98 ± 0.02°[a]

Solvent[b]	Additive ($M \times 10^3$)	$k \times 10^4$, sec.$^{-1}$
A	Collodion wrapper	1.20 ± 0.08[c]
A	...	1.11 ± 0.06
A	...	1.15 ± 0.02
A	Thiophenol (15.7)	1.36 ± 0.06
A	Thiophenol (15.7)	1.43 ± 0.07
A	Iodine (15.0)	*d*
B	...	2.66 ± 0.20
B	...	4.09 ± 0.08
B	...	3.52 ± 0.39
B	Iodine (7.52)	*e*
B	Nitric oxide[f]	2.58 ± 0.09
B	Nitric oxide[f]	2.39 ± 0.16
B	Thiophenol (15.7)	*e*
B	*p*-Benzoquinone (15.2)	3.29 ± 0.15
B	*p*-Benzoquinone (15.2)	3.16 ± 0.12
B	*p*-Benzoquinone (15.2)	3.17 ± 0.12
B	Hydroquinone (7.62)	3.88 ± 0.18
B	Chloranil (15.0)	2.60 ± 0.16
B	No oxygen	2.40 ± 0.31

[a] Initial diazonium fluoroborate concentration was 7.52×10^{-3} *M* unless otherwise noted. [b] A = acetic acid, 1.0 *M* in sulfuric acid; B = methanol, 1.0 *M* in sulfuric acid. [c] Initial diazonium fluoroborate concentration, 5.02×10^{-3} *M*. [d] Fast, not a first-order reaction. [e] Very fast. [f] Saturated solution.

dure proved quite satisfactory. A typical plot is shown in Figure 2.

The results are summarized in Table I. The rate in solvent A appears to be unaffected (within experimental error) by the presence of collodion, which was used to encapsulate the diazonium salt in some preliminary runs. (This method was later abandoned.) The rate constants for three runs (one containing collodion) are quite reproducible [$k = (1.15 \pm 0.03) \times 10^{-4}$ sec.$^{-1}$].

The rate of decomposition in solvent B is not reproducible but the spread in rate constants [$k = (2.66$ to $4.09) \times 10^{-4}$ sec.$^{-1}$] is fairly modest. Nonreproducibility of some diazonium decompositions has been noted previously.[10] The increase in rate in proceeding from acetic acid to methanol is no more than might be expected of a very moderate solvent effect.

The average rate [$k = (1.40 \pm 0.04) \times 10^{-4}$ sec.$^{-1}$] in solvent A in the presence of more than a twofold ratio of thiophenol to diazonium salt shows an enhancement of approximately 20%. This enhancement may be due to a small contribution to the "ionic" rate by a radical reaction, involving homolytic cleavage of a diazothio ether. In the less acidic solvent B, reaction

$$\mathrm{Ar{-}N{=}N{-}S{-}C_6H_5} \longrightarrow \mathrm{Ar}\cdot + \mathrm{N_2} + \cdot\mathrm{S{-}C_6H_5}$$

in the presence of thiophenol is too fast to measure. The equilibrium concentration of diazothio ether is expected to increase in a less acidic solution.

$$\mathrm{ArN_2^+ + C_6H_5SH} \rightleftarrows \mathrm{Ar{-}N{=}N{-}S{-}C_6H_5 + H^+}$$

Reaction in solvent A in the presence of a twofold ratio of iodine to diazonium salt is a fast reaction which does not follow first-order kinetics. The reaction appears to exhibit an induction period of several minutes. Reaction in solvent B containing an equimolar amount of iodine is very fast and does not appear to be preceded by an induction period. These reactions may occur by a radical mechanism requiring the formation of iodide ion for initiation. The formation of an aryl radical by reduction of a diazonium ion with iodide ion has been proposed.[11] However, the increase in reaction rate may be the result of formation of a diazonium triiodide, requiring prior formation of iodide ion. Diazonium triiodides are known to be highly reactive.[12]

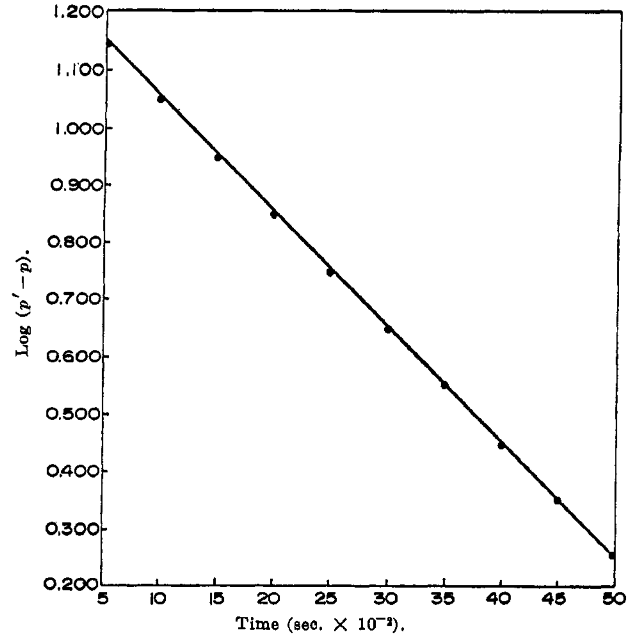

Figure 2.—The Guggenheim plot of the thermal decomposition of N,N-dicyclohexylbenzamido-*o*-diazonium fluoroborate (7.52×10^{-3} *M*) in methanol, 1 *M* in sulfuric acid, at 39.98°.

The decomposition rate [$k = (2.60$ to $3.88) \times 10^{-4}$ sec.$^{-1}$] in solvent B in the presence of equimolar or larger amounts of the radical inhibitors *p*-benzoquinone, hydroquinone, and chloranil is essentially the same as the rate in the absence of inhibitors. The rate in a solution saturated with nitric oxide is slightly lower [$k = (2.49 \pm 0.10) \times 10^{-4}$ sec.$^{-1}$], although this is probably not significant. In the absence of oxygen, the rate [$k = (2.40 \pm 0.31) \times 10^{-4}$ sec.$^{-1}$] is the same, within experimental error, as the rates of the reactions in air.

The absence of a substantial difference between the rates of decomposition in the two reaction media and the insensitivity of the rates in the more basic medium to the presence of *p*-benzoquinone, hydroquinone, chloranil, nitric oxide, and oxygen confirm the previous conclusion[3,4b,c] that these reactions are not radical chain in character and strongly suggest that a *hydride* ion transfer process is indeed occurring in the thermal decomposition. The large differences in product composition obtained in different solvents are therefore not satisfactorily explained by postulating a change from an ionic to a radical mechanism in proceeding from acidic to less acidic solvents. The explanation[4c] based on differing states of ion association in the different solvents still appears valid.

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(10) E. S. Lewis and W. H. Hinds, *J. Am. Chem. Soc.*, **74**, 304 (1952); E. S. Lewis and J. E. Cooper, *ibid.*, **84**, 3847 (1962).

(11) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1946, Chapter VIII.

(12) J. G. Carey, G. Jones, and I. T. Millar, *Chem. Ind.* (London), 1018 (1959).

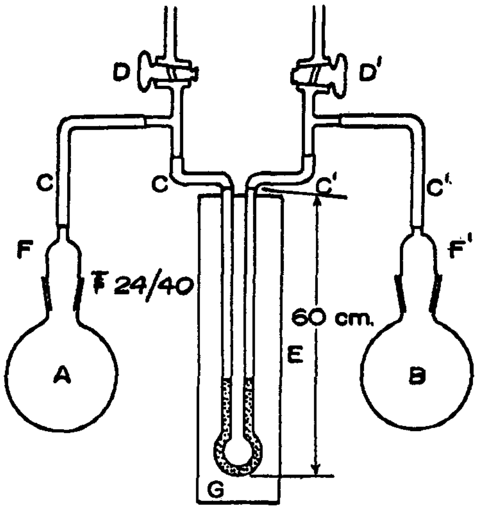

Figure 3.—Apparatus: A, reaction flask (500 cc.); B, ballast flask (500 cc.); C, red rubber vacuum tubing ($^3/_8$-in. i.d.); D, oblique-bore stopcock; E, capillary tubing (4-mm. i.d.) filled to a height of 20 cm. with distilled xylene; F, connecting joint; and G, section of a meter scale.

Experimental Section[13]

Solvent Preparation.—A solution of acetic acid, 1.0 *M* in sulfuric acid, was prepared by diluting 49.0 g. of concentrated sulfuric acid to a volume of 500.0 ml. with glacial acetic acid. Methanol, 1.0 *M* sulfuric acid, was prepared in a similar way using Fisher Certified reagent grade methanol.

Preparation and Purification of Additives.—In one run, noted in Table I, the diazonium salt was wrapped in a collodion sheet which was sealed with collodion solution. The pellet was allowed to dry for 10 min. before use. A similar blank pellet was added to the ballast flask.

Nitric oxide[14] was passed through a drying tube containing phosphorus pentoxide and was allowed to bubble through a solution of methanol, 1.0 *M* in sulfuric acid.

Iodine and *p*-benzoquinone were sublimed twice. Chloranil was recrystallized from benzene. Thiophenol was freshly distilled (b.p. 168–170°) before use. Hydroquinone was used without purification.

N,N-Dicyclohexylbenzamide-*o*-diazonium Fluoroborate.—A solution of *o*-amino-N,N-dicyclohexylbenzamide[15] (3.0 g., 0.010 mole) and 48–50% fluoroboric acid (5.4 g., 0.03 mole) in 50 ml. of alcohol was cooled below 0° and treated with small portions of freshly distilled isoamyl nitrite[16] (1.30 g., 0.011 mole). After 30 min., 200 ml. of cold ether was added to the solution, which was allowed to remain in the cold for an additional 30 min. Filtration and washings with cold ether afforded a light yellow (light pink in some preparations) solid (3.2 g., 80%) m.p. 100–102° dec. The solid gradually became pink on standing at room temperature, but could be stored for about 1 week under ether at 0° without discoloration. Its infrared spectrum in chloroform exhibited the following characteristic peaks: 2275 (w), 1631 (s), and 1065 cm.$^{-1}$ (s, broad).

Description of the Apparatus.—The manometric apparatus used to measure the rate of gas evolution consisted of a reaction flask and ballast flask attached to a differential manometer similar to that described by Moelwyn-Hughes and Johnson.[17] Some of the improvements on this apparatus suggested by DeTar[18] were incorporated into the final design (Figure 3).

The volume of the reaction flask (A) and connecting joint (F) was within 1 cc. of the volume of the ballast flask (B) and its connecting joint (F′). The total length of rubber tubing (C) was the same as the total length of rubber tubing (C′) and therefore the reaction and ballast volumes were approximately equal. During a rate run the reaction and ballast flasks were immersed in a constant-temperature bath so that the water level was within 1 cm. of the rubber tubing connections on the connecting joints (F, F′). The whole apparatus, including the constant-temperature bath, was enclosed in a plywood box fitted with a Plexiglas window so that temperature and manometer readings could be obtained without introducing air temperature fluctuations within the box. The plywood enclosure also served to reduce greatly the intensity of light during a diazonium decomposition. A fan blade was attached to the shaft of the bath stirrer in order to circulate air within the box and prevent air-temperature gradients. The contents of the reaction and ballast flasks were vigorously stirred during a run by the use of heavy-duty magnetic stirrers placed below the elevated apparatus.

Operational Procedure.—A typical rate run was conducted as follows. The diazonium fluoroborate (stored under ether at 0°) was filtered from the ether by vacuum filtration and was spread out, exposed to the air, to dry for several minutes. The stopcocks (D, D′) were opened and a weighed amount of diazonium salt was placed in the reaction flask (A) containing 50 ml. of solvent and additive (if any). The freshly greased joint F (Dow-Corning high-vacuum grease) was firmly attached to the reaction flask by means of three springs. The ballast flask (B), containing 50 ml. of solvent and additive (if any), was attached to its joint F′ in the same way. The two flasks were simultaneously lowered into the constant temperature bath and the contents were vigorously stirred. Stopcocks D and D′ were simultaneously closed 1000 sec. later for reactions conducted in acetic–sulfuric acid. The stopcocks were closed 500 sec. later for reactions conducted in methanol–sulfuric acid. Directly after the stopcocks were closed, the first manometer reading was taken. Subsequent readings were taken at equal time intervals.

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[13] Unless otherwise noted, melting points were taken on a Kofler block and are corrected.

[14] W. C. Fernelius, *Inorg. Syn.*, **2**, 126 (1946).

[15] T. Cohen and J. Lipowitz, *J. Am. Chem. Soc.*, **86**, 5611 (1964).

[16] W. A. Noyes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 108.

[17] E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

[18] D. F. DeTar, *J. Am. Chem. Soc.*, **78**, 3911 (1956).