where.[27] The values of $[\alpha]$ in various solvents are as follows[4]: methanol, $-3{,}100°$; ethanol, $-3{,}700°$; dioxane, $-4{,}100°$; carbon tetrachloride, $-10{,}440°$; octane, $-12{,}500°$.

Equilibration experiments. A 1.0-g. sample of *trans*-2-bromo-5-methylcyclohexanone (I t)[4] was dissolved in a solution prepared from 0.32 g. of anhydrous hydrogen bromide and 40 ml. of carbon tetrachloride. The mixture was allowed to stand at room temperature for 2 hr., after which time it was washed with water, dilute sodium bicarbonate solution and water. After drying, the infrared spectrum was obtained directly on the solution.

A similar isomerization was carried out in benzene solution. To show the absence of bromine migration under these conditions, 97 mg. of the bromoketone I t was dissolved in 1 ml. of carbon tetrachloride which had been saturated with dry hydrogen bromide. The solution was allowed to stand overnight at room temperature, after which time 108 mg. of 2,4-dinitrophenylhydrazine in 5 ml. of acetic acid was added. The solution was warmed under nitrogen for 10 min. and was diluted with benzene. After washing with water, the benzene concentrate was poured through a column of Fisher alumina. The benzene was removed from the eluate by distillation and the crude solid residue had $[\alpha]^{25}_{D}$ $-200°$ (chloroform; c, 0.369). The pure 2,4-dinitrophenylhydrazone[4] of 5-methylcyclohex-2-en-1-one has $[\alpha]^{25}_{D}$ $-219°$ (chloroform; c, 0.06).

Dipole moments. The apparatus used for the dielectric constant measurements has been described.[28] The benzene and heptane solvents were purified by refluxing reagent grade solvents with sodium followed by distillation from sodium. The dioxane was purified according to Fieser.[29] The dielectric constant and density were measured with solutions of various mole fractions as indicated in Table IV. The calculations were made following the general procedure of Halverstadt and Kumler[30] as described earlier.[31] The molar refractivity was calculated from standard values[32] of atomic refractivities and had the value 65.929 c.c. Atomic polarization was neglected. Experimental error is about 0.02 D.

Acknowledgment. The authors would like to thank Dr. Max T. Rogers, Michigan State University, for kindly making available to them his apparatus for the measurement of dipole moments, and Miss P. Burcar for the spectral measurements. This work was supported in part by a grant from the Sloan Foundation and in part by the National Cancer Institute (grant CY-2919) of the National Institutes of Health, U.S. Public Health Service.

DETROIT, MICH.

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[27] C. Djerassi, E. W. Foltz, and A. E. Lippman, *J. Am. Chem. Soc.*, **77**, 4354 (1955); C. Djerassi "Optical Rotatory Dispersion: Applications to Organic Chemistry," New York, McGraw-Hill, Chapter 3.

[28] M. T. Rogers, *J. Am. Chem. Soc.*, **77**, 3681 (1955).

[29] L. F. Fieser "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.

[30] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[31] N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

[32] J. A. Leermakers and A. Weissberger, in H. Gilman "Organic Chemistry", Vol. II, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE WESTVACO CHLOR-ALKALI DIVISION AND THE CENTRAL RESEARCH LABORATORY OF THE FOOD MACHINERY AND CHEMICAL CORP.]

α-Oximino Ketones. IV. The "Normal" and "Abnormal" Beckmann Rearrangements[1]

ARTHUR F. FERRIS

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The Beckmann rearrangement of α-oximino ketones possessing the *anti* configuration, whether brought about by acid chlorides like phosphorus pentachloride or thionyl chloride, by strong acids like sulfuric or trifluoroacetic, or by acylating agent and base, has been shown to proceed "abnormally", that is by cleavage to a nitrile and a carboxylic acid. If an amide product is obtained, it is always that which arises from hydrolysis of the nitrile initially formed. It is proposed that the term "second order" be retained to describe this type of Beckmann rearrangement, which is characterized by shift of an electron pair only.

It was observed a long time ago that α-oximino ketones possessing the *anti* or α-configuration behaved differently from simple ketoximes when treated with an acylating agent and base, in that they were cleaved to a carboxylic acid and a nitrile instead of giving the normal amide product of the Beckmann rearrangement.[2–4] This cleavage reaction has been called a Beckmann rearrangement of the second order[2,4] or an "abnormal" rearrangement. In contrast, it is generally stated or implied that rearrangement of α-oximino ketones with acids or acid chlorides such as phosphorus pentachloride proceeds "normally," that is, through an amide intermediate.[3,5,6] It was postulated originally that the rearrangement of α-oximino ketones in polyphosphoric acid proceeded *via* the "normal" route,[7] but more recent studies have shown that actually the "abnormal" or second order route is

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[1] A preliminary account of this work has been presented in *J. Org. Chem.*, **24**, 580 (1959).

[2] A. Werner and A. Piguet, *Ber.*, **37**, 4295 (1904).

[3] A. H. Blatt, *Chem. Revs.*, **12**, 215 (1933).

[4] A. H. Blatt and R. P. Barnes, *J. Am. Chem. Soc.*, **56**, 1148 (1934).

[5] N. V. Sidgwick, *The Organic Chemistry of Nitrogen*, (revised and rewritten by T. W. J. Taylor and W. Baker), Oxford University Press, 1942, p. 182.

[6] V. Migrdichian, *Org. Syntheses*, **Vol. 1**, 376 (1957).

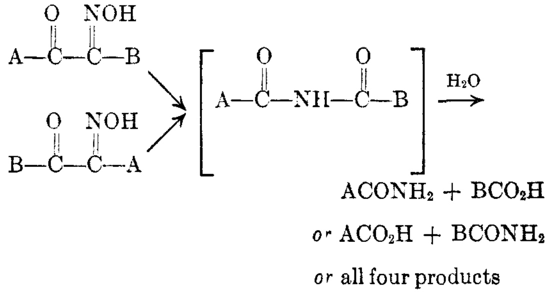
[7] E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.*, **74**, 5153 (1952).

followed, the nitrile originally formed frequently being hydrolyzed to the amide if the reaction is carried out at an elevated temperature.[8,9]

In this laboratory suspicion that the "normal" course of acid-catalyzed Beckmann rearrangements had not been correctly interpreted was aroused in the course of a study aimed at finding the best method for obtaining high yields in the rearrangement ("normal" or "abnormal") of α-oximino ketones. Because of the ease with which it is prepared and purified, 3-oximino-2-heptanone was used as a model compound. Treatment with a variety of acylating agents and base gave *n*-valeronitrile in 70–80% yield; sulfuric acid gave valeric acid (79%) when reaction conditions were vigorous and valeramide (59%) when they were milder; and polyphosphoric acid gave a mixture of valeric acid (28%) and valeramide (24%). In addition to these expected results, it was found most unexpectedly that phosphorus pentachloride, the classic reagent for carrying out the "normal" rearrangement, gave valeronitrile in 70% yield.

This discovery led to an investigation of both the supposedly "normal" and "abnormal" reactions, using a variety of unsymmetrical α-oximino ketones. In particular, two pairs of α-oximino ketones were chosen so that if an amide intermediate were involved in the so-called "normal" reaction the same one would be formed from both starting materials, and hence the same final products should be obtained, the nature of these being dependent only on the direction of hydrolysis of the intermediate secondary amide (route I). On the other hand, if the reaction were first a cleavage to nitrile and acid and then hydrolysis of the nitrile, different products would be formed (route II). This experimental concept is shown in generalized schematic form below:

(I)



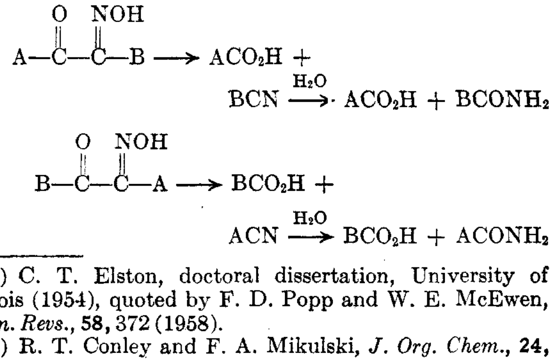
$$\left.\begin{array}{l}\mathrm{A{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}B}\\ \mathrm{B{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}A}\end{array}\right\} \rightarrow \left[\mathrm{A{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}B}\right] \xrightarrow{\mathrm{H_2O}}$$

$$\mathrm{ACONH_2 + BCO_2H}$$

$$or\ \mathrm{ACO_2H + BCONH_2}$$

$$or\ \text{all four products}$$

(II)



$$\mathrm{A{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}B \longrightarrow ACO_2H +}$$

$$\mathrm{BCN \xrightarrow{H_2O} ACO_2H + BCONH_2}$$

$$\mathrm{B{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}A \longrightarrow BCO_2H +}$$

$$\mathrm{ACN \xrightarrow{H_2O} BCO_2H + ACONH_2}$$

The two pairs of α-oximino ketones chosen to test this concept were 2-oximino-1-phenyl-1-propanone and 1-oximino-1-phenyl-2-propanone, both of which should have given *N*-acetylbenzamide or the same hydrolysis products therefrom in the "normal" rearrangement, and 1,3-diphenyl-2-oximino-1-propanone and 1,3-diphenyl-1-oximino-2-propanone, both of which should have given *N*-benzoylphenylacetamide or the same hydrolysis products.

In these experiments 85% sulfuric acid at about 120° was used to bring about the "normal" reaction, and benzenesulfonyl chloride and aqueous sodium hydroxide at about 25° were used for the "abnormal" reaction. No attempt was made to isolate two carbon fragments (acetonitrile, acetamide, or acetic acid). Table I summarizes the results obtained with the two pairs of α-oximino ketones mentioned above, and with several other unsymmetrical α-oximino ketones for which pairing was inconvenient from a preparative standpoint. Although yields in some cases were lowered by isolation difficulties, evidence was obtained for the alternative products to be expected from route I in only two cases, and in both of these the relative yields made it seem almost certain that the carboxylic acid not predicted by route II was obtained by partial hydrolysis of the amide which was the major product. All solid products were identified by melting points and mixed melting points with authentic samples, and by infrared spectra identical with those of authentic samples. All liquid products were identified by boiling points and indices of refraction, and by infrared spectra identical with those of authentic samples.

The results obtained in the second order or "abnormal" reaction were those expected from the work of previous investigators of this reaction,[4,10–12] that is, in all cases the nitrile product contained the radical originally attached to the carbon bearing the oxime group, and the carboxylic acid product contained the radical originally attached to the carbonyl group. In contrast to what would have been predicted from the conventional view of the "normal" rearrangement, precisely the same relationship was noted in the products of the acid-catalyzed reaction. The amide products all contained the radical originally attached to the carbon bearing the oxime group, and the carboxylic acids all contained that originally attached to the carbonyl group. The conclusion seems inescapable that both the "normal" and "abnormal" reactions actually proceeded by the same route (II, above), and that the only difference between them was that the nitrile originally formed in the acid-

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(8) C. T. Elston, doctoral dissertation, University of Illinois (1954), quoted by F. D. Popp and W. E. McEwen, *Chem. Revs.*, **58**, 372 (1958).

(9) R. T. Conley and F. A. Mikulski, *J. Org. Chem.*, **24**, 97 (1959).

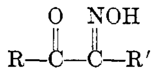
(10) J. Meisenheimer, P. Zimmermann, and U. v. Kummer, *Ann.*, **446**, 205 (1926).

(11) G. Darzens and R. Mentzer, *Compt. rend.*, **213**, 268 (1941).

(12) A. L. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956).

TABLE I

BECKMANN REARRANGEMENTS OF α-OXIMINO KETONES



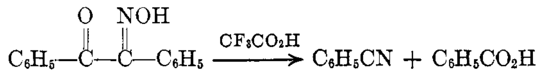
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle NOH}{\|}}{C}-R'$$

α-Oximino Ketone		Products and Yields from	
R	R′	85% H_2SO_4	$C_6H_5SO_2Cl$ + NaOH
C_6H_5	CH_3	$C_6H_5CO_2H$ (84%)	$C_6H_5CO_2H$ (91%)
CH_3	C_6H_5	$C_6H_5CONH_2$ (92%)	C_6H_5CN (87%)
C_6H_5	$CH_2C_6H_5$	$C_6H_5CH_2CONH_2$ (47%)	$C_6H_5CH_2CN$ (68%)[a]
		$C_6H_5CO_2H$ (86%)	$C_6H_5CO_2H$ (74%)
$C_6H_5CH_2$	C_6H_5	$C_6H_5CONH_2$ (61%)[b]	C_6H_5CN (77%)
		$C_6H_5CH_2CO_2H$ (68%)	$C_6H_5CH_2CO_2H$ (74%)
CH_3	$CH_3(CH_2)_3$	$CH_3(CH_2)_3CONH_2$ (59%)	$CH_3(CH_2)_3CN$ (70%)
CH_3	$CH_2C_6H_5$	$C_6H_5CH_2CONH_2$ (83%)[c]	$C_6H_5CH_2CN$ (87%)
$CH_3(CH_2)_2$	CH_3CH_2	$CH_3CH_2CONH_2$ (19%)	CH_3CH_2CN (45%)
		$CH_3(CH_2)_2CO_2H$ (78%)	$CH_3(CH_2)_2CO_2H$ (84%)

[a] A very small amount of 2-benzoyloximino-1,3-diphenyl-1-propanone was obtained also (see text). [b] An 8% yield of benzoic acid was obtained also. [c] A 12% yield of phenylacetic acid was obtained also.

catalyzed reaction was hydrolyzed to the amide and sometimes in part to the carboxylic acid by the hot aqueous sulfuric acid.

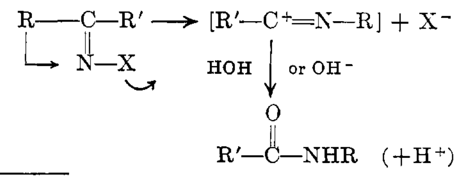
The rearrangement in 85% sulfuric acid is not initiated below about 100°, and 100% sulfuric acid tends to char most of the α-oximino ketones used in this study. It thus appeared useless to attempt to isolate the nitrile products from the sulfuric acid reaction. Nitrile products were obtained, however, with a number of other typical catalysts for the "normal" reaction. The use of phosphorus pentachloride to obtain *n*-valeronitrile from 3-oximino-2-heptanone has been mentioned; this reagent also gave an 86% yield of phenylacetonitrile from 2-oximino-1-phenyl-3-butanone. Similarly, thionyl chloride gave an 88% yield of benzonitrile from 1-oximino-1-phenyl-2-propanone, and phosphorus oxychloride gave a 37% yield in the same reaction. Finally, trifluoroacetic acid, which has been shown recently to give normal amide products with a variety of ketoximes,[13-15] gave valeronitrile (58%) from 3-oximino-2-heptanone and benzonitrile (94%) and benzoic acid (88%) from α-benzil monoxime.



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle NOH}{\|}}{C}-C_6H_5 \xrightarrow{CF_3CO_2H} C_6H_5CN + C_6H_5CO_2H$$

On the basis of all the evidence available on the Beckmann rearrangement of α-oximino ketones of the *anti* configuration, it seems reasonable to conclude that, however initiated, the reaction proceeds by only a single course, which results in cleavage of the molecule to a nitrile and a carboxylic acid. It is therefore suggested that the terms "normal" and "abnormal" as appiled to this reaction are superfluous and should be dropped. To do the least violence to accepted nomenclature it might be well to define two different types of Beckmann rearrangement; those of the *first order*, which are undergone by simple ketoximes and result in *N*-substituted amides as products, and those of the *second order*, which are undergone by *anti* α-oximino ketones or α-oximino alcohols[4] and result in cleavage to nitriles and carbonyl compounds, either carboxylic acids, aldehydes, or ketones. It should be noted also that some simple ketoximes rearrange by a "second order" path, giving a nitrile and another fragment whose exact nature depends on the structure of the oxime rearranged.[16] In some cases the rearrangement may follow a first or second order course depending on the nature of the reagent initiating it;[16b] in others the second order course appears to be followed regardless of the reagent.[16c] Such second order rearrangements of simple oximes have been called "abnormal,"[16c] and here the use of the term is logical. Because of the confusion in terminology which has existed in this area, it is suggested that such rearrangements be referred to as *abnormal Beckmann rearrangements of the second order.*

The two types of rearrangement also may be defined from a mechanistic point of view. It is commonly accepted[3,17,18] that the first order rearrangement of a simple ketoxime involves the con-



$$R-\underset{\underset{\displaystyle N-X}{\|}}{C}-R' \longrightarrow [R'-C^+=N-R] + X^- \xrightarrow[\text{or } OH^-]{HOH} R'-\overset{\overset{\displaystyle O}{\|}}{C}-NHR \quad (+H^+)$$

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(13) M. L. Huber, U. S. Patent **2,721,199,** Oct. 18, 1955.

(14) M. Hudlicky, *Chem. listy,* **51,** 470 (1957); *Collection Czechoslov. Chem. Communs.,* **23,** 462 (1958).

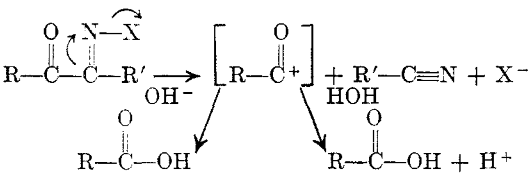
(15) W. D. Emmons, *J. Am. Chem. Soc.,* **79,** 6522 (1957).

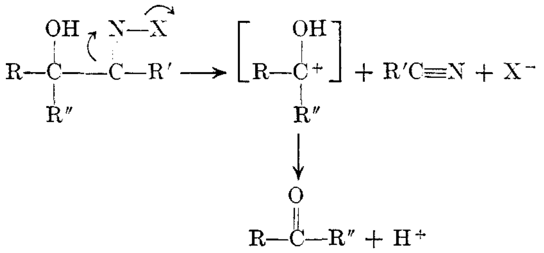
(16) (a) R. E. Lyle and G. G. Lyle, *J. Org. Chem.,* **18,** 1058 (1953). (b) R. F. Brown, N. M. van Gulick, and G. H. Schmid, *J. Am. Chem. Soc.,* **77,** 1094 (1955). (c) S. Wawzonek and J. V. Hallum, *J. Org. Chem.,* **24,** 364 (1959). References to earlier work are given in these papers.

(17) L. P. Hammett, *Physical Organic Chemistry,* McGraw-Hill Book Co., New York, 1940, p. 322.

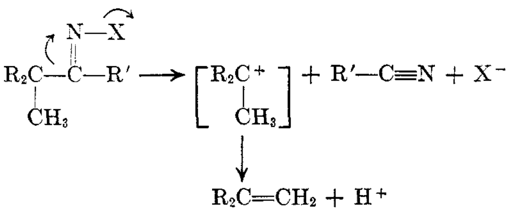
(18) J. Hine, *Physical Organic Chemistry,* McGraw-Hill Book Co., New York, 1956, p. 321.

current departure of the hydroxyl or acylated hydroxyl, X, with its bonding pair of electrons and the 1,2-shift of the group, R, originally *trans* to X, with its bonding pair. The intermediate cation then completes the reaction by combining with an hydroxide anion, water, or some other suitable species. The second order reaction may be pictured very similarly, except that the departure of X is accompanied by the shift of *an electron pair only*,[19] forming the carbon-nitrogen triple bond and hence the nitrile. The cation which is left then combines with an hydroxide anion, water, or other appropriate species. In the case of the α-oximino alcohols,[4] the intermediate cation expels a proton and forms an aldehyde or a ketone. Thus very simple definitions result if the first order rearrangement is defined as one which involves shift of an organic group with its pair of electrons, and the second order rearrangement as one which involves shift of an electron pair only.

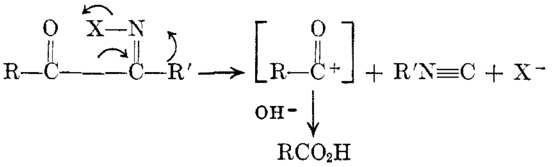


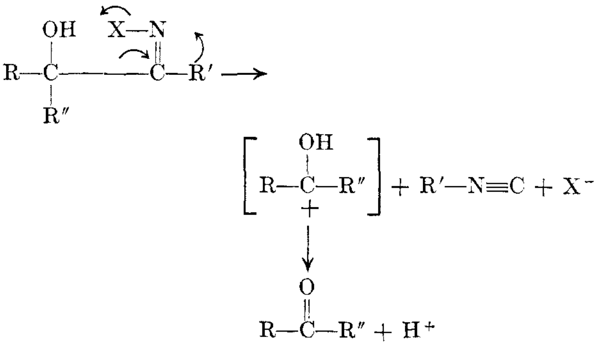


This mechanistic definition also applies to the abnormal second order rearrangement. In fact, mechanisms very similar to those presented above have been proposed[16] to explain the abnormal rearrangement. For example, the abnormal rearrangement of tertiary ketoximes may be pictured as involving departure of X and shift of the electron pair to give a nitrile and a tertiary carbonium ion. This ion then usually completes the reaction by expelling a proton and forming an olefin. The abnormal second order rearrangement of simple ketoximes is clearly related to the rearrangement of α-oximino ketones and alcohols, since in both cases the tendency of the *trans*-group to form a relatively stable cation is apparently what leads to shift of the electron pair only.



The considerations just presented suggest that possibly a "third order" Beckmann rearrangement also should be defined. Blatt and Barnes[4] found that α-oximino ketones or alcohols in the *syn* or β-configuration gave isonitriles and carbonyl compounds when treated with an acylating agent and base. These products can be accounted for by mechanisms analogous to those discussed, but wherein shifts of *both* an organic group with its electron pair and another electron pair take place.





A by-product obtained when 1,3-diphenyl-2-oximino-1-propanone was dissolved in base and treated with benzenesulfonyl chloride sheds some light on the mechanism of the second order reaction. As noted in Table I, the principal products of the reaction were phenylacetonitrile and benzoic acid, but there was obtained also a small amount of white solid which separated from the basic reaction medium as the reaction proceeded. Elemental analysis and infrared spectrum suggested that this was 2-benzoyloximino-1,3-diphenyl-1-propanone, and this was confirmed by synthesis of the compound from the α-oximino ketone and benzoyl chloride in the presence of pyridine. Although puzzling at first, the formation of this compound can be explained readily on the basis of the mechanism just discussed. Thus the first step in the rearrangement was almost certainly the formation of the benzenesulfonate of the oxime, and it may be hypothesized that this was followed by departure of the benzenesulfonate anion and shift of the electron pair as shown below to form phenylacetonitrile

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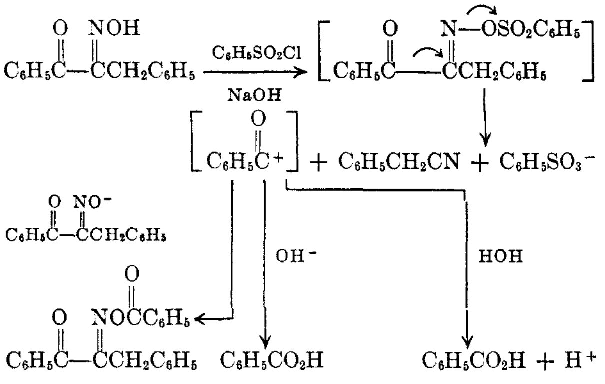
[19] In referring to the Beckmann rearrangement it is very common to speak of the "shift" of a group to the nitrogen atom. This convention has been used in this paper to correlate the discussion with most previous discussions of the reaction. However, the reaction may be regarded as the attack of the electron-deficient nitrogen atom on the electron pair of the *trans*-group. See P. T. Scott, D. E. Pearson, and L. J. Bircher, *J. Org. Chem.*, **19**, 1817 (1954); Footnote 4. It should be kept in mind that this is the probable course of the "shifts" discussed in this and other papers.

and the benzoyl oxocarbonium ion. Three principal modes of reaction were available to this carbonium ion: combination with water, with a hydroxide ion, or with the anion of 1,3-diphenyl-2-oximino-1-propanone. Either of the first two possibilities would give benzoic acid, the observed major product; the third would give 2-benzoyloximino-1,3-diphenyl-1-propanone, the observed minor product. Since this minor product is an acylated α-oximino ketone it would be expected that normally it would be cleaved in the presence of excess base just as shown for the benzenesulfonate, and indeed, no such by-product was found with any other α-oximino ketone studied. In this case, however, it appears that the extreme insolubility of the benzoyl derivative preserved enough of it from destruction so that it was found among the products.



EXPERIMENTAL[20]

α-Oximino ketones. 2-Oximino-1-phenyl-1-propanone was purchased from Distillation Products Industries, Rochester, N. Y. All the other α-oximino ketones were prepared by the method previously described.[21] Their properties are listed in Table II.

TABLE II

α-OXIMINO KETONES

RCOCR'NOH			Melting Point, °C.	
R	R'	Yield, %	Found	Lit.
CH_3	C_6H_5	86	162–163	164–165[a]
C_6H_5	$CH_2C_6H_5$	64	126–127.5	125–126[b]
$C_6H_5CH_2$	C_6H_5	57	114–114.5	——[c]
CH_3	$CH_3(CH_2)_3$	78	59–60	59–60[d]
CH_3	$CH_2C_6H_5$	75	80–81	80–81[e]
$CH_3(CH_2)_2$	CH_3CH_2	63	Liquid	——[f]

[a] H. Rheinboldt and O. Schmitz-Dumont, *Ann.*, **444**, 113 (1925). [b] W. Schneidewind, *Ber.*, **21**, 1323 (1888). [c] *Anal.* Calcd. for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.48; N, 5.85. Found: C, 75.46; H, 5.43; N, 5.81. [d] Ref. 21. [e] G. Ponzio, *Gazz. chim. ital.*, **35**, 394 (1905). [f] B.p. 62–63° (0.45 mm.), n_D^{35} 1.4548. *Anal.* Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.97; H, 9.30; N, 9.51.

Rearrangements. Details of typical experiments reported in Table I and in the text are given. Those rearrangements not described in detail were carried out exactly as reported for the particular rearranging reagent in the examples presented below. Isolation of products was accomplished by conventional methods which were identical or similar to the techniques described in the examples.

Action of phosphorus pentachloride on 3-oximino-2-heptanone. To a suspension of 68.8 g. (0.33 mol.) of phosphorus pentachloride in 300 ml. of ether was added a solution of 43.0 g. (0.30 mol.) of 3-oximino-2-heptanone in 250 ml. of ether. The temperature rose rapidly to 37° and was held there by refluxing ether. The addition required 18 min., and the solution was maintained at reflux for another 30 min. by the application of heat. The ether solution was then poured into 1 l. of ice water, the layers were mixed thoroughly, and the ether solution was separated. The aqueous solution was extracted with two 100-ml. portions of ether, then the combined ether solution was washed with three 100-ml. portions of 5% sodium bicarbonate solution. The ether solution was dried and the solvent evaporated. The residue was distilled under reduced pressure to give 17.5 g. (70%) of *n*-valeronitrile, b.p. 67–70° (60 mm.), n_D^{35} 1.3897.

Action of 85% sulfuric acid on 1,3-diphenyl-2-oximino-1-propanone. To 75 ml. of 85% sulfuric acid preheated to 115° was added during 15 min. 18.0 g. (0.075 mol.) of 1,3-diphenyl-2-oximino-1-propanone. Reaction temperature was maintained at 107–117° during the addition by heat of reaction. The mixture cooled to 30° over 90 min., then was poured with stirring into 500 ml. of ice water. The precipitate was recovered by filtration, and the aqueous filtrate was treated with solid sodium bicarbonate. Additional precipitate was recovered by filtration. After drying, the total solid recovered amounted to 14.7 g. This material was stirred with a solution of 16.8 g. (0.20 mol.) of sodium bicarbonate in 200 ml. of water for several hours. Part of the solid went into solution. The material which failed to dissolve was recovered by suction filtration, washed with a little water, and dried. There was thus obtained 4.8 g. (47%) of phenylacetamide, m.p. 152–155°. After recrystallization from benzene the material melted at 156–158°; mixed melting point with authentic phenylacetamide, 155–158°. The aqueous filtrate from the bicarbonate neutralization was acidified with concentrated hydrochloric acid, and a white precipitate formed. After recovery, washing with water and drying this amounted to 7.9 g. (86%) of benzoic acid, m.p. 116–121°. After recrystallization from water this melted at 121–122.5°; mixed m.p. with authentic benzoic acid, 121–123°.

Action of benzenesulfonyl chloride and base on 1,3-diphenyl-2-oximino-1-propanone. A sample, 18.0 g. (0.075 mol.), of 1,3-diphenyl-2-oximino-1-propanone was dissolved in a solution of 16.0 g. (0.40 mol.) of sodium hydroxide in 100 ml. of water. Benzenesulfonyl chloride, 17.7 g. (0.10 mol.), was added during 17 min., the temperature being held below 40° by external cooling. A white solid began to separate almost as soon as addition was begun. When addition was complete, the mixture was allowed to stand several hours, then was extracted with three 100-ml. portions of ether. The solid dissolved in the ether. The ether solution was dried over anhydrous magnesium sulfate. The aqueous solution was acidified with concentrated hydrochloric acid, and the heavy white precipitate was recovered, washed with water and dried. Benzoic acid 6.8 g. (74% yield), m.p. 120–122°, was recovered. After recrystallization from water this material melted at 121–122.5°; mixed m.p. with authentic benzoic acid, 120–122.5°.

Evaporation of the ether solution left 10.1 g. of a mixture of liquid and solid. This was treated with 35 ml. of ethanol, the solid failing to dissolve. The solid was recovered by filtration, washed with a little ether, and dried. It amounted to 1.7 g., m.p. 117–118.5°. The ethanol was evaporated from the filtrate, leaving 8.2 g. of yellow liquid. Distillation under reduced pressure gave 6.0 g. (68%) of phenylaceto-

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(20) All melting points and boiling points are uncorrected.

(21) A. F. Ferris, *J. Org. Chem.*, **24**, 1726 (1959).

nitrile, b.p. 52–53° (0.15 mm.), n_D^{25} 1.5208. Authentic phenylacetonitrile gave n_D^{25} 1.5210.

The solid from the ether extract was recrystallized from 95% ethanol to give material of m.p. 117–119°. The analysis of the material (below) and its infrared spectrum indicated that it was probably 2-benzoyloximino-1,3-diphenyl-1-propanone, and this was confirmed by independent synthesis (next experiment).

Anal. Calcd. for $C_{22}H_{17}O_3N$: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.20; H, 4.95; N, 4.22.

2-Benzoyloximino-1,3-diphenyl-1-propanone. To a solution of 2.8 g. (0.02 mol.) of benzoyl chloride and 1.2 g. (0.015 mol.) of pyridine in 10 ml. of benzene was added 1.0 g. (0.0042 mol.) of 1,3-diphenyl-2-oximino-1-propanone. The temperature rose from 25 to 32° and then began to fall. External heat was applied, and the temperature was held at 50–55° for 15 min. The mixture was cooled, and the solid which separated was removed by filtration. Solvent and excess benzoyl chloride were evaporated from the filtrate under reduced pressure. The residue crystallized on cooling and was recrystallized from 10 ml. of 95% ethanol. 2-Benzoyloximino-1,3-diphenyl-1-propanone, 0.4 g., m.p. 118–120°, was obtained. A mixture of this material and the minor product from the treatment of 1,3-diphenyl-2-oximino-1-propanone with benzenesulfonyl chloride and base melted at 117–119°. The infrared spectra of the two materials were identical.

Anal. Calcd. for $C_{22}H_{17}O_3N$: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.91; H, 5.25; N, 4.26.

Action of 85% sulfuric acid on 1,3-diphenyl-1-oximino-2-propanone. To 75 ml. of 85% sulfuric acid preheated to 110° was added over 8 min. 15.5 g. (0.065 mol.) of 1,3-diphenyl-1-oximino-2-propanone. The temperature was maintained at 109–114° during the addition by heat of reaction. The reaction mixture was allowed to cool to 35° over 45 min. and was added to 500 ml. of ice water. Organic material separated. The aqueous mixture was neutralized with solid sodium carbonate, then was made just acid with 5*N* hydrochloric acid and was extracted with five 100-ml. portions of chloroform. The chloroform solution was extracted with three 100-ml. portions of 10% aqueous sodium carbonate, and the combined carbonate solution was made acid with concentrated hydrochloric acid. A white solid separated and was recovered by filtration and dried. The aqueous filtrate was extracted with three 100-ml. portions of ether, and the ether solution was dried over anhydrous magnesium sulfate. The precipitated solid amounted to 2.2 g., m.p. 73–76°, and was shown to be phenylacetic acid by the fact that its infrared spectrum was identical with that of an authentic sample of phenylacetic acid, and by the fact that a mixture of the material and authentic phenylacetic acid melted at 73–77°. Evaporation of the ether solution gave another 3.8 g. of less pure phenylacetic acid, identified by infrared spectrum. The total yield of phenylacetic acid was thus 6.0 g. (68%).

The original chloroform solution was next extracted with three 50-ml. portions of 10% aqueous sodium hydroxide. The chloroform solution was then dried over anhydrous magnesium sulfate. The basic solution was acidified with concentrated hydrochloric acid, and the solid which separated was recovered, washed and dried. Benzoic acid, 0.6 g. (8%), m.p. 119–121°, was obtained. A mixture of this material and authentic benzoic acid melted at 120–122°.

Evaporation of the chloroform solution left 4.8 g. (61%) of benzamide, m.p. (after washing with ether) 124.5–127°. A mixture of this material and authentic benzamide melted at 124.5–127.5°.

Action of benzenesulfonyl chloride and base on 1,3-diphenyl-1-oximino-2-propanone. 1,3-Diphenyl-1-oximino-2-propanone, 23.9 g. (0.10 mol.), was dissolved in a solution of 16.0 g. (0.40 mol.) of sodium hydroxide in 100 ml. of water. To the resulting solution, was added during 17 min., 21.2 g. (0.12 mol.) of benzenesulfonyl chloride. The temperature was held below 36° by external cooling. After all the chloride had been added, the reaction mixture was stirred for 45 min., then extracted with four 75-ml. portions of ether. The ether solution was dried over anhydrous magnesium sulfate. The aqueous solution was acidified with concentrated hydrochloric acid, and the solid which separated was recovered by filtration, washed with cold water, and dried. The aqueous solution remaining was extracted with two 100-ml. portions of ether, and the ether solution was dried The total recovery of crude phenylacetic acid amounted to 14.1 g., 10.3 g. of precipitated solid and 3.8 g. from the ether extraction. The combined crude acid was recrystallized from 200 ml. of petroleum solvent (b.p. 65°) to give 10.1 g. (74%) of pure phenylacetic acid, m.p. 74.5–76.5°, mixed m.p. with authentic phenylacetic acid, 74.5–78°.

The ether solution from the original basic extraction was evaporated to leave 10.1 g. of brown oil. Distillation under reduced pressure gave 7.9 g. (77%) of benzonitrile, b.p. 67° (10 mm.), n_D^{35} 1.5207; authentic benzonitrile, n_D^{35} 1.5210.

Action of thionyl chloride on 1-oximino-1-phenyl-2-propanone. Thionyl chloride, 26.2 g. (0.22 mol.), was added during 15 min. to a suspension of 32.6 g. (0.20 mol.) of 1-oximino-1-phenyl-2-propanone in 150 ml. of ether. The temperature was maintained at 35–36° by refluxing ether, and vigorous evolution of hydrogen chloride took place. The reaction mixture was allowed to stand for several hours then was poured into 100 ml. of ice water. The layers were mixed thoroughly, then the ether layer was separated and the aqueous layer was extracted with 100 ml. of ether. The combined ether layer was washed with three 50-ml. portions of 5% sodium bicarbonate solution and dried. The ether was evaporated and the residue was distilled under reduced pressure to give 18.1 g. (88%) of benzonitrile, b.p. 68–70° (10 mm.), n_D^{35} 1.5210; authentic benzonitrile, n_D^{35} 1.5210.

Action of benzoyl chloride and base on 3-oximino-2-heptanone. 3-Oximino-2-heptanone, 35.8 g. (0.25 mol.), was dissolved in a solution of 40.0 g. (1.00 mol.) of sodium hydroxide in 250 ml. of water. Benzoyl chloride, 49.2 g. (0.35 mol.), was added during 25 min., the temperature being held at 30–35° by external cooling. The reaction mixture was extracted with three 100-ml. portions of ether and the solution was dried. The solvent was evaporated, and the residue was distilled under reduced pressure to give 17.1 g. (82%) of *n*-valeronitrile, b.p. 67–69° (60 mm.), n_D^{35} 1.3900; authentic *n*-valeronitrile, n_D^{35} 1.3901.

Action of polyphosphoric acid on 3-oximino-2-heptanone. To 125 ml. of polyphosphoric acid, preheated to 120°, was added 35.8 g. (0.25 mol.), 3-oximino-2-heptanone, during 18 min. Heat of reaction held the temperature at 120–135°. The mixture was allowed to cool to 54° over 25 min., then was poured into 750 ml. of ice water. The resulting mixture was extracted with three 100-ml. portions of ether. The aqueous solution was brought to *p*H 6 by the addition of solid sodium bicarbonate, and extracted with six 100-ml. portions of ether. Both ether solutions were dried over anhydrous magnesium sulfate. The ether was evaporated from the first extract to leave 16.1 g. of brown oil. Distillation under reduced pressure gave 7.1 g. (28%) of *n*-valeric acid, b.p. 80–84° (8 mm.), n_D^{35} 1.4027; authentic *n*-valeric acid, n_D^{35} 1.4024. The residue from this distillation was added to the second ether extract, and cautious evaporation of part of the ether led to the crystallization of 6.1 g. (24%) of *n*-valeramide, m.p. 102–104°. A mixture of this material and authentic *n*-valeramide melted at 102.5–105°.

Action of trifluoroacetic acid on α-benzil monoxime. To 150 g. of trifluoroacetic acid was added 45.1 g. (0.20 mol.) of α-benzil monoxime during 30 min. The temperature rose from 26 to 67° during the addition, then dropped to 30° during the next 30 min. To the clear solution was added 100 ml. of water at 15–30°, and a white solid separated. A solution of 65 g. of sodium hydroxide in 150 ml. of water was added, with cooling to hold the temperature below 25°. The solid dissolved, and an organic liquid separated. The liquid was extracted with four 100-ml. portions of ether. The ether solution was dried, the solvent was evaporated, and the residue was distilled under reduced pressure to give 19.4 g. (94%) of benzonitrile, b.p. 70–71° (10 mm.), n^{35}_{D} 1.5206. The aqueous solution was made strongly acid with concentrated hydrochloric acid, and the solid which separated was recovered by filtration, washed with water and dried. There was obtained 33.3 g. of solid, much more than the 24.4 g. of benzoic acid required by theory. It appeared that sodium trifluoroacetate or sodium chloride had coprecipitated with the benzoic acid. This was removed by treating the solid with 300 ml. of ether, filtering to remove undissolved solid, washing with two 50-ml. portions of water to remove any dissolved sodium trifluoroacetate, and drying. Evaporation of the ether left 21.4 g. (88%) of benzoic acid, m.p. 120.5–122°. A mixture of this material and authentic benzoic acid melted at 120.5–122°.

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Correlation of Polarographic Data with Structure. Use of the Hammett-Taft Relation

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The success which the Hammett polar substituent relation has had in correlating the polarographic half-wave potential data of certain series of organic compounds with their structure, prompted an examination of the applicability of the Taft elaboration on the Hammett relation for the same purpose. The Taft-Hammett equation very satisfactorily correlates data in the electrochemical reduction of a variety of functional groups in both aliphatic and aromatic compounds. In the case of aliphatic compounds, the equation is apparently not applicable for substituents larger than ethyl groups.

Considerable attention has been given in the polarographic literature to the search for consistent relationships between the half-wave potential, $E_{1/2}$, and the structural characteristics of electroreducible and electrooxidizable organic substances.[1] Generally, none of the various relationships developed has been widely applied. However, specific areas of good agreement between the observed behavior of a series of related compounds and a particular correlating equation are well known, especially in connection with the Hammett equation,[2]

$$\log (k/k_0) \text{ or } \log (K/K_0) = \sigma\rho \qquad (1)$$

where k is a rate constant, K an equilibrium constant, σ a polar substituent constant based on the structure of the reacting molecule, and ρ a reaction constant which measures the susceptibility of a given reaction series to polar substituents; the zero subscript refers to some member of a reaction series arbitrarily chosen as standard; k or K *sans* subscript refers to any other member of the same series.

Successful correlation of polarographic half-wave potentials with structure has been achieved through use of Equation 1 by assuming that $E_{1/2}$ is proportional to log K, the unknown proportionality constant being absorbed in the ρ factor, *e.g.*,

$$E_{1/2} - (E_{1/2})_0 = \sigma\rho \qquad (2)$$

As in the case of rates and equilibrium constants, this correlation fails for *ortho* benzene derivatives and aliphatic compounds.[3]

Taft[4] developed an equation analogous to that of Hammett but applicable to *ortho* derivatives and aliphatic compounds, and a further equation of great generality

$$P_\sigma = \sigma^*\rho^* \qquad (3)$$

where P_σ is any parameter proportional to energy and dependent upon the polar effect of substituent groups, *e.g.*, dipole moments, vibration frequencies and bond energies; dimensional consistency is maintained by assigning the proper dimensions to the empirical constant, ρ^*.

Taft[4] has applied his generalized form of the Hammett equation to predict successfully the outcome of the experimental determination of $E_{1/2}$ of an aliphatic compound studied by the

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[1] *E.g.*, R. L. Bent, J. C. Dessloch, F. C. Duennebier, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.*, **73**, 3100 (1951); P. Zuman, *Chem. Listy*, **48**, 94 (1954).

[2] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940.

[3] E. C. Bennett, Ph.D. Thesis, University of Michigan, 1954.

[4] (a) R. W. Taft, *J. Am. Chem. Soc.*, **74**, 2729 (1952); (b) *J. Am. Chem. Soc.*, **74**, 3120 (1952); (c) *J. Am. Chem. Soc.*, **75**, 4231 (1953).