204. *A New Mechanism for the Beckmann Rearrangement of Ketoximes.*

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Based on experimental observations, a new mechanism is proposed for the Beckmann rearrangement involving the formation of a ketoxime anhydride by dehydration of two molecules of the ketoxime. The anhydride rearranges to give the ketoxime imidate which further rearranges forming the imidoyl anhydride which in the presence of hydrogen chloride gives an imidoyl chloride and an amide in equimolecular proportions.

IT is generally accepted that if a ketoxime is treated with certain acidic reagents such as thionyl chloride,[1] phosphorus pentachloride,[2] phosphorus oxychloride,[2] or benzenesulphonyl chloride,[3] and the product treated with water, a substituted amide is obtained. It has now been established that the substituted amide is produced during the rearrangement in the complete absence of water, and the present investigation has further shown that any of the above reagents (1 mol.) rearranges a ketoxime (2 mols.) to yield the corresponding amide and imidoyl chloride in approximately equimolecular amounts. It is of interest that in the rearrangement of the oximes of acetophenone and 2-acetylnaphthalene the isomeric amides separate as hydrochlorides (37%) from the chloroform solutions, the imidoyl chlorides (37%) remaining in solution. With these exceptions, the proportions of reactants stated above gave equimolar mixtures of the products in solution; these were identified, and their respective yields ascertained, by converting the imidoyl chlorides into (*a*) amidines by treatment with gaseous ammonia, and (*b*) 2 : 3-disubstituted quinazol-4-ones by condensation with methyl anthranilate,[4] and separation of the bases in each case from the amide by treatment with acid. The 3-substituent in the quinazolone is that radical of the ketoxime which has migrated during the rearrangement. Phosphorus pentachloride differs from the other reagents in that, if more than $\frac{1}{2}$ mol. is used per mol. of ketoxime, the excess reacts with the amide to form more imidoyl chloride: $R{\cdot}CO{\cdot}NHR + PCl_5 \longrightarrow R{\cdot}CCl{:}NR + POCl_3 + HCl$; with 1 mol. each of benzophenone oxime with phosphorus pentachloride, the amount of imidoyl chloride formed is sufficient to yield 80% of 2 : 3-diphenylquinazol-4-one, whereas only 40% of it is obtained with $\frac{1}{2}$ mol. of phosphorus pentachloride. It is now clear why Beckmann [1] and Coleman and Pyle,[5] who used equimolecular proportions, obtained only *N*-phenylbenzimidoyl chloride as the penultimate product, and benzanilide after treatment with water. It is worth noting that the action of phosphorus pentachloride (1 mol.) on a ketoxime (1 mol.) in anhydrous chloroform is useful for the preparation of imidoyl chlorides which can be used *in situ* for the preparation of amidines and quinazol-4-ones in good yields.

[1] Stephen and Bleloch, *J.*, 1931, 886.
[2] Beckmann, *Ber.*, 1886, **19**, 988.
[3] Kuhara, *Mem. Coll. Sci., Kyoto Univ.*, 1917, **3**, 1.
[4] Levy and Stephen, following paper.
[5] Coleman and Pyle, *J. Amer. Chem. Soc.*, 1946, **68**, 2007.

During the rearrangement of ketoximes a characteristic yellow colour develops, and it is suggested that this is associated with the presence of a ketoxime benzimidate (III) such as the yellow compound (III; R = Ph) prepared by Chapman.[6] Alkyl aryl ketoximes undergo a further colour change, to deep red, which appears to be due to the action of excess of the reagent on amides of the type R·NH·COMe, usually resulting in a tar.

Chapman [6] observed that *N*-phenylbenzimidoyl chloride (0·002 mol.) in the presence of hydrogen chloride rearranges benzophenone oxime almost quantitatively, but that in the absence of hydrogen chloride only 10% conversion takes place. The efficacy of the chloride in rearranging benzophenone oxime is shown (p. 985) when 2 c.c. of a rearranged solution of benzophenone oxime containing the chloride (0·005 g.) and no thionyl chloride is added to a solution of benzophenone oxime (2 g.) in chloroform saturated with hydrogen chloride; this effects 15% rearrangement of the oxime to benzanilide. Similarly when a trace (0·06 mol.) of various other reagents (Table 3) is used, the imidoyl chloride first formed continues the rearrangement in the presence of hydrogen chloride after the reagent has been exhausted. As the rearrangement proceeds the amount of amide produced becomes greater and the ratio of imidoyl chloride to amide decreases as long as unchanged oxime is present. It therefore becomes possible to produce amide as the chief product of rearrangement. Although hydrogen chloride is essential during the rearrangement, there is no rearrangement when an oxime hydrochloride is refluxed in chloroform solution. During the rearrangement of ketoximes in chloroform with traces of reagent, the only hydrogen chloride available is that produced by the reaction between the reagent and the ketoxime, but this is insufficient for the maximum rearrangement of certain ketoximes (see Table 1). Maximum rearrangement can be attained by saturating the chloroform solution of the ketoxime and a trace of reagent with dry hydrogen chloride (see Table 3).

The mechanism now proposed for the Beckmann rearrangement of ketoximes is an attempt to explain (*a*) the formation of equimolecular amounts of imidoyl chloride and amide during from 2 : 1 molecular proportions of ketoxime and reagent, and (*b*) the almost quantitative conversion of ketoximes into amides by traces of reagent in presence of hydrogen chloride. The first stage is dehydration of the ketoxime to ketoxime anhydride (I), which is symmetrical and would not be expected to rearrange spontaneously. Addition of hydrogen chloride disturbs the symmetry, forming the salt (II). The electromeric effect arising from the attachment of a proton to one of the nitrogen atoms causes the cation of (II) to rearrange to the ketoxime imidate (III) in a manner similar to the rearrangement of the picryl ethers and benzenesulphonyl esters of ketoximes. Chapman [6] showed that benzophenone oxime *N*-phenylbenzimidate (III; R = H) rearranges in presence of hydrogen chloride in anhydrous ether to *N*-phenylbenzimidoyl chloride and benzanilide in approximately equimolecular proportions and suggested that the ester was formed by the reaction :

$$Ph_2C{:}N{\cdot}OH + Ph{\cdot}CCl{:}NPh \longrightarrow Ph_2C{:}N{\cdot}O{\cdot}CPh{:}NPh$$

However, since the ester is readily decomposed by hydrogen chloride at room temperature it is not likely to be produced by the condensation of the oxime and the imidoyl chloride. The present authors are of the opinion that the formation of the ester (III) is, nevertheless, an essential part of the Beckmann rearrangement and that it is produced by rearrangement of the ketoxime anhydride in presence of hydrogen chloride. The ester then rearranges to the imidoyl anhydride (IV), which decomposes in the presence of hydrogen chloride to give equimolecular amounts of imidoyl chloride and amide :

$$R_2C{:}N{\cdot}OH \xrightarrow{\text{Reagent}} \underset{\text{(I)}}{(R_2C{:}N{\cdot})_2O} \xrightarrow{HCl} \underset{\text{(II)}}{[R_2C{:}NH^+{\cdot}O{\cdot}N{:}CR_2]Cl^-} \longrightarrow$$

$$R{\cdot}N{:}CR{\cdot}O{\cdot}N{:}CR_2 \longrightarrow \underset{\text{(IV)}}{(R{\cdot}N{:}CR{\cdot})_2O} \xrightarrow{HCl} R{\cdot}CCl{:}NR + R{\cdot}CO{\cdot}NHR$$

$$\underset{\text{(III)}}{}$$

This mechanism can be applied when traces of the reagent are used, provided that in the initial stage there is sufficient to form a trace of the ketoxime anhydride (I) in presence of

[6] Chapman, *J.*, 1935, 1223.

hydrogen chloride. The rearrangment of anhydride will take place as above with formation of the imidoyl chloride which can then dehydrate the ketoxime to (I), forming the amide at the same time :

$$2R_2C{:}N{\cdot}OH + R{\cdot}CCl{:}NR \longrightarrow (R_2C{:}N{\cdot})_2O + R{\cdot}CO{\cdot}NHR + HCl$$

The yield of amide thus increases at the expense of the chloride.

The formation of amidines during the rearrangement of ketoximes was first demonstrated by Stephen and Bleloch,[1] and the mechanism for their formation as suggested by Chapman [6] is from the imidoyl anhydride (IV) which can undergo an intramolecular

$$\underset{\text{(IV)}}{(R{\cdot}N{:}CR{\cdot})_2O} \longrightarrow \underset{\text{(V)}}{R{\cdot}CO{\cdot}NH{\cdot}CR{:}NR} \longrightarrow R{\cdot}CO_2H + R{\cdot}NH{\cdot}CR{:}NR$$

$$\text{(VI)}\quad HN{:}CR{\cdot}O{\cdot}COR \longrightarrow (R{\cdot}CO)_2NH \quad \text{(VII)}$$

change to the acylamidine (V). The change of (IV) ⟶ (V) is analgous to the change of the imidoyl anhydride (VI) to the diacylamine (VII) investigated by Mumm, Hesse, and Volquartz.[7]

Other reagents used for the Beckmann rearrangement of ketoximes, such as zinc chloride, ferric chloride, or aluminium chloride,[8] may function as dehydrating agents for the formation of the anhydride (I).

Experimental

Apparatus and reagents were carefully dried. The oximes were stored over phosphoric oxide. The chloroform was heated with phosphoric oxide for 1 hr. and then distilled.

Rearrangement of Acetophenone Oxime (1 *mol.*) *by Reagent* (1 *mol.*).—To this oxime (2·7 g.) in anhydrous chloroform (40 c.c.), thionyl chloride (1·5 c.c.) in anhydrous chloroform (5 c.c.) was added. The solution warmed to 35°, sulphur dioxide and hydrogen chloride being evolved. Dry hydrogen chloride was passed into the solution until it acquired a deep yellow colour (1—2 hr.) and acetanilide hydrochloride separated. On cooling in ice for a further 1—2 hr., the colour changed from yellow to deep red. Acetanilide hydrochloride was filtered off, washed with dry chloroform (5—10 c.c.), and dried (P_2O_5) (yield, 1·3 g., 38%). The filtrate and washings were distilled under reduced pressure; the residue was extracted with N-sodium hydroxide to remove unchanged oxime, and then with N-hydrochloric acid. The residue of crude acetanilide was crystallised from the minimum volume of boiling water, leaving a small quantity of tar. The acid extract, on being made ammoniacal, deposited diphenylacetamidine (0·2 g.) which after crystallisation from methanol had m. p. and mixed m. p. 131—132°. Unchanged oxime (0·45 g.), m. p. 52—56°, was recovered on acidification of the sodium hydroxide extract. The yield of acetanilide (0·98 g.), m. p. and mixed m. p. 112—113°, was 36%.

When a solution of acetanilide (2·7 g.) in dry chloroform (40 c.c.) was warmed with thionyl chloride (1·5 c.c.) its colour changed to deep red and acetanilide hydrochloride was deposited. After removal of chloroform the residue yielded acetanilide and a tar.

β-Acetonaphthalide behaved similarly with thionyl chloride in chloroform.

The product, which crystallised during the rearrangement of acetophenone oxime, was practically colourless and when freshly prepared and dry had m. p. 120—125° (decomp.). On storage it lost hydrogen chloride and yielded acetanilide. On treatment with water it yielded acetanilide, m. p. 112—113°, and hydrochloric acid. Two unstable hydrochlorides, $(NHPhAc)_2,HCl$ and NHPhAc,HCl, are known.[9,10] Titration of the aqueous filtrate with 0·1N-sodium hydroxide indicates that the 1 : 1 salt was obtained during the rearrangement, though, owing to instability, the experimental values for chloride are low (Found : HCl, 20·3. Calc. for C_8H_9ON,HCl : HCl, 21·3%).

2-Methyl-3-phenylquinazol-4-one.—Acetophenone oxime (2·7 g.) was rearranged as above and acetanilide hydrochloride (1·3 g., 38%) removed. To the chloroform filtrate and washings, methyl anthranilate (12 c.c.) was added and the mixture kept at room temperature for 12 hr., made alkaline with aqueous ammonia, and steam-distilled, leaving crude quinazolone, m. p. 137—142° (1·46 g., 31%). Recrystallisation from methanol gave colourless crystals, m. p. and mixed m. p. 144—146°.

[7] Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379.
[8] Beckmann and Bark, *J. prakt. Chem.*, 1923, **105**, 327.
[9] Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 1904.
[10] Ephraim and Hochuli, *Ber.*, 1915, **48**, 634.

To acetophenone oxime (2·7 g.) in dry chloroform, powdered phosphorus pentachloride (2·08 g.) was added with shaking till all the reagent had dissolved (5 min.). The clear yellow solution was kept at room temperature for 3—4 hr. but no acetanilide hydrochloride separated. Methyl anthranilate (20 c.c.) was added and after a further 12 hr. the mixture was treated as above, yielding 2-methyl-3-phenylquinazol-4-one (3·45 g., 71%), m. p. 140—145°.

Rearrangement of 2-Acetylnaphthalene Oxime.—The oxime (3·7 g.), suspended in dry chloroform (60 c.c.), was rearranged with thionyl chloride (1·5 c.c.) as described above. β-Acetonaphthalide hydrochloride was deposited (1·7 g., 39·2%) (Found: HCl, 15·5. Calc. for $C_{12}H_{11}ON,HCl$: HCl, 16·5%); with water it gave β-acetonaphthalide, m. p. and mixed m. p. 131—132°. The chloroform filtrate and washings, after steam-distillation, yielded material (2·15 g.), m. p. 115—124°. Fractional crystallisation from methanol separated unchanged oxime (0·5 g.) from β-acetonaphthalide (1·5 g., 40%), leaving a small quantity of tar. The acid filtrate on being made ammoniacal did not deposit amidine.

To the oxime (1·32 g.) in chloroform (30 c.c.) phosphorus oxychloride (0·7 c.c., 1 mol.) was added without cooling. After 12 hr. the clear yellow solution was saturated with hydrogen chloride; it deposited β-acetonaphthalide hydrochloride (0·56 g.), which with water gave β-acetonaphthalide, m. p. 130—131° (0·5 g., 38%).

2-*Methyl*-3-β-*naphthylquinazol*-4-*one.*—2-Acetylnaphthalene oxime (3·7 g.) was rearranged with thionyl chloride as above. β-Acetonaphthalide hydrochloride (1·7 g., 39%) was filtered off and the filtrate treated with excess of methyl anthranilate (12 c.c.) and allowed to remain for 12 hr. 2-Methyl-3-β-naphthylquinazol-4-one (1·9 g., 32%), m. p. and mixed m. p. 174—175°, was obtained as above.

The best yield (71%) of the quinazolone was obtained by shaking a cold suspension of the oxime (1·85 g.) in dry chloroform with phosphorus pentachloride (2·08 g.) for 5 min. and allowing the yellow solution to remain at room temperature for 2 hr. The solution, cooled in ice, was then treated with methyl anthranilate (15 c.c.) and kept for 12 hr. and worked up as above, yielding the quinazol-4-one (2·03 g.), m. p. 174—175°.

Rearrangement of Benzophenone Oxime.—To a solution of the oxime (1·97 g.) in dry chloroform (40 c.c.), thionyl chloride (0·8 c.c.) in dry chloroform (10 c.c.) was added. Hydrogen chloride and sulphur dioxide were evolved from the clear solution, the temperature rising to 20°, and the solution rapidly became yellow. After 12 hr. the solution was saturated with dry ammonia and kept for 1 hr. Ammonium chloride formed was filtered off and the chloroform filtrate distilled under reduced pressure, leaving a yellow residue (1·9 g.). This product was warmed with N-hydrochloric acid to dissolve phenylbenzamidine. The insoluble benzanilide (0·95 g., 48%), after crystallisation, had m. p. and mixed m. p. 161—162°. The acid filtrate, on being made ammoniacal, deposited phenylbenzamidine (0·9 g., 45%), recrystallisation giving the pure product, m. p. and mixed m. p. 111—113°.

2 : 3-*Diphenylquinazol*-4-*one.*—To a solution of benzophenone oxime (1·97 g.) rearranged with thionyl chloride (0·8 c.c.), methyl anthranilate (10 c.c.) was added and the mixture left at room temperature for 12 hr. The residue, after treatment with ammonium hydroxide and steam-distillation, was warmed with N-hydrochloric acid (40 c.c.) and filtered. Benzanilide (0·9 g., 45%), m. p. 161—162°, was obtained from the insoluble residue, and the acidic filtrate, when made ammoniacal, deposited the quinazolone (1·8 g., 40%). After crystallisation from methanol, this had m. p. and mixed m. p. 158—159°.

To a solution of benzophenone oxime (1·97 g.) in chloroform (50 c.c.) phosphorus pentachloride (2·08 g.) was added. After 2 hr. methyl anthranilate (15 c.c.) was added and the mixture treated as above. The quinazol-4-one (2·3 g., 80%) and a trace of benzanilide (0·2 g.) were obtained.

2-*Methyl*-3-p-*tolylquinazol*-4-*one.*—To a cold solution of 4-methylacetophenone oxime (1·49 g.), dissolved in dry chloroform (50 c.c.), phosphorus pentachloride (2·08 g.) was added rapidly. The yellow solution was cooled in ice and methyl anthranilate (15 c.c.) added. After 12 hr. at room temperature aqueous ammonia was added, and the mixture steam-distilled. The residue was treated with concentrated hydrochloric acid and filtered and the filtrate made alkaline to liberate the base which crystallised from methanol as pale yellow needles, m. p. and mixed m. p. 148—150° (1·73 g., 69%).

Rearrangement of Ketoximes (2 *mol.*) *with Reagent* (1 *mol.*).—(*a*) Acetophenone oxime (2·7 g.) was rearranged with thionyl chloride (0·8 c.c.) as above. Acetanilide (1·0 g., 37%) separated as the hydrochloride; and a further 1 g. (37%) was obtained from the chloroform filtrate together with unchanged oxime (0·4 g.) and diphenylacetamidine (0·05 g.). No tar was produced.

(*b*) 2-Acetylnaphthalene oxime (1·85 g.) was rearranged with phosphorus pentachloride

(1·04 g.). β-Acetonaphthalide hydrochloride (0·88 g., 40%) separated and the chloroform filtrate yielded β-acetonaphthalide (0·76 g., 40%) and unchanged oxime (0·45 g.).

(*c*) A solution of benzophenone oxime (1·97 g.), rearranged with thionyl chloride (0·4 c.c.), was treated with methyl anthranilate (10 c.c.), yielding the previous products in the same proportions.

A solution of benzophenone oxime (1·97 g.) in dry chloroform (50 c.c.) was rearranged with phosphorus pentachloride (1·04 g.) and saturated with dry ammonia. The product yielded benzanilide (0·9 g., 45%), and phenylbenzamidine (0·9 g., 45%).

Rearrangement of Ketoximes with Traces of Reagent.—(*a*) When a solution of the hydrochloride of acetophenone oxime, 2-acetylnaphthalene oxime, or benzophenone oxime in dry chloroform was refluxed, hydrogen chloride was evolved. The solutions remained clear and colourless, and, after removal of the chloroform, the residue in each case yielded only unchanged oxime.

(*b*) When a ketoxime (1 mol.) in dry chloroform (40 c.c.) was refluxed with thionyl chloride (0·06 mol.) for ½ hr. a characteristic yellow colour developed, but with acetophenone oxime very gradually. After removal of the chloroform, the amides were obtained as reported in Table 1.

(*c*) The rearrangements of ketoxime hydrochlorides (1 mol.) with thionyl chloride (0·06 mol.) carried out as described above are recorded in Table 2.

(*d*) When a solution of ketoxime (1 mol.) in dry chloroform (40 c.c.) was saturated with dry hydrogen chloride, treated with thionyl chloride (0·06—0·11 mol.), and left at room-temperature, the yields of amides were as given in Table 3.

(*e*) Table 4 gives results obtained when benzophenone oxime hydrochloride (2·34 g.) in dry chloroform (40 c.c.) was rearranged with traces of various reagents (0·06 mol.) on refluxing the solution for ½ hr. After removal of the chloroform, any unchanged oxime was separated from the benzanilide by the method given by Chapman.[6]

(*f*) Acetophenone oxime hydrochloride (2 g.) in dry chloroform (60 c.c.) was rearranged with a trace of reagent (0·06 mol.). The mixtures were saturated with hydrogen chloride and left for 48 hr. Acetanilide hydrochloride was filtered off and dried. The chloroform filtrates were treated as usual, and acetanilide in solution was separated from unchanged oxime. The results are given in Table 5.

(*g*) To 2-acetylnaphthalene oxime (1·85 g.) in dry chloroform (40 c.c.) thionyl chloride (0·06 mol.) was added, and the mixture saturated with dry hydrogen chloride and left for 48 hr. β-Acetonaphthalide hydrochloride (1·8 g., 80%) separated and the chloroform filtrate yielded β-acetonaphthalide (0·1 g., 5%) and a small amount of unchanged oxime.

(*h*) A rearranged solution of benzophenone oxime hydrochloride (2·34 g.) in dry chloroform (40 c.c.) with thionyl chloride (3 drops) (cf. *b*) was saturated with dry ammonia and left for

TABLE 1.

Ketoxime	Amide	M. p.	Yield (%)
$Ph_2C{:}N{\cdot}OH$	NHPhBz	160°	97
$(p\text{-}C_6H_4Cl)_2C{:}N{\cdot}OH$	$C_6H_4Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4Cl$	210	29
$p\text{-}C_6H_4Cl{\cdot}CPh{:}N{\cdot}OH$	Ar·NH·COAr (mixed)	—	56
$PhMeC{:}N{\cdot}OH$	NHPhAc	112	7

TABLE 2.

Ketoxime	Amide	M. p.	Yield (%)
$Ph_2C{:}N{\cdot}OH$	NHPhBz	160°	97
$(p\text{-}C_6H_4Me)_2C{:}N{\cdot}OH$	NHAr·COAr	159	96
$(p\text{-}C_6H_4Cl)_2C{:}N{\cdot}OH$	,,	210	35
$p\text{-}C_6H_4Cl{\cdot}CPh{:}N{\cdot}OH$	Mixed	—	90
$(CH_2Ph)_2C{:}N{\cdot}OH$	$CH_2Ph{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$	—	Trace
$PhMeC{:}N{\cdot}OH$	NHPhAc	112	13
$2\text{-}C_{10}H_7{\cdot}CMe{:}N{\cdot}OH$	$2\text{-}C_{10}H_7{\cdot}NHAc$	130	6

TABLE 3.

Ketoxime	$SOCl_2$ (mol.)	Time (hr.)	Yield of amide (%)	Ketoxime	$SOCl_2$ (mol.)	Time (hr.)	Yield of amide (%)
$CPh_2{:}N{\cdot}OH$	0·06	0·25	75	$(CH_2Ph)_2C{:}N{\cdot}OH$	0·11	96	32
	—	3·0	97	$2\text{-}C_{10}H_7{\cdot}CMe{:}N{\cdot}OH$ ...	0·11	72	82
$PhMeC{:}N{\cdot}OH$ ...	0·06	24	59	$p\text{-}C_6H_4Me{\cdot}CMe{:}N{\cdot}OH$	0·09	24	83
	0·09	48	90	$(p\text{-}C_6H_4Me)_2C{:}N{\cdot}OH$	0·06	1	97

TABLE 4.

Reagent	Yield of NHPhBz (%)	Oxime recovered (%)	Reagent	Yield of NHPhBz (%)	Oxime recovered (%)
$SOCl_2$ *	95	0	CCl_3·CHO	0	89
PCl_5 *	97	0	CPh_3Cl	0	86
$POCl_3$ *	91	0	P_2O_5	4	89
Ph·SO_2Cl	67	27·5	H_2SO_4	0	87
AcCl	0	91	$AlCl_3$	0	78
Ac_2O	0	87			

* Yellow colour developed on refluxing.

TABLE 5.

Reagent	Yield (%) of NHPhAc,HCl	Yield (%) of R·CCl:NR	Unchanged oxime (g.)	Reagent	Yield (%) of NHPhAc,HCl	Yield (%) of R·CCl:NR	Unchanged oxime (g.)
$SOCl_2$ ...	80	8	0·75	Ph·SO_2Cl	... 65	13	0·5
PCl_5	75	10	0·5				

12 hr. The product yielded phenylbenzamidine (0·1 g.), corresponding to the *N*-phenylbenzimidoyl chloride in solution, and benzanilide (1·8 g.). The rearranged solution, therefore, contained no more than 0·0025 g. of imidoyl chloride, and 0·045 g. of benzanilide per c.c., and no thionyl chloride.

(*i*) A similarly rearranged solution (2 c.c.) was added to benzophenone oxime hydrochloride (2·34 g.) in dry chloroform (40 c.c.), and the mixture saturated with dry hydrogen chloride and refluxed for 1 hr. Benzanilide (0·41 g.) and unchanged oxime (1·62 g.) were obtained. Since the 2 c.c. of the rearranged solution added contained about 0·1 g. of benzanilide, rearrangement was approx. 15% complete.

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