[CONTRIBUTION FROM THE RESEARCH DIVISION OF ETHICON, INC.]

The Hydrolytic Rearrangement of 2-Acyloacetyl-2,5-dialkoxyhydrofuran Derivatives to 3-Acylcatechols

WERNER R. BOEHME AND WILLIAM G. SCHARPF

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A number of 2-acyloacetyl-2,5-dimethoxytetrahydrofurans (I) was synthesized by condensing methyl 2,5-dimethoxytetrahydro-2-furoate with the appropriate methyl ketones. Hydrolytic rearrangement of the diketones (I) in dilute aqueous hydrochloric acid gave the corresponding 3-acylcatechols (II. R′ = H). The condensation of methyl 2,5-dimethoxy-2,5-dihydro-2-furoate with acetone yielded 2-acetoacetyl-2,5-dimethoxy-2,5-dihydrofuran (III). Hydrolytic rearrangement of the latter gave 3,3′-diacetylbiphenyl-2,2′,4,4′,5,5′-hexol (IVA. R′ = H) and 2,3,6-trihydroxyacetophenone (IVB. R′ = H).

Certain furan derivatives are rearranged hydrolytically to polyhydric phenols with surprising ease. Vargha and co-workers,[1] for example, have shown that the easily hydrolyzed *p*-toluenesulfonyl-2-acetofuranoxime may be converted under very mild reaction conditions to catechol *via* 4,5-diketocaproic aldehyde, derived from the initially obtained 2-hexene-4,5-dione-1-al. Of particular value is the elegant method of Clauson-Kaas and his group who employed 2,5-dialkoxyhydrofuran derivatives.[2] These authors prepared catechol by refluxing 2-acetyl-2,5-dimethoxytetrahydrofuran dimethyl ketal with dilute hydrochloric acid and extended the method to the synthesis of several hydroxy- and carboxy-substituted catechols.[3] Hydrourushiol (3-pentadecylcatechol), one of the toxins of poison ivy, has been obtained recently by hydrolytic rearrangement of 2-heptadecanoyl-2,5-dimethoxytetrahydrofuran *via* the intermediate 4,5-diketoheneicosaldehyde.[4]

The need for some 3-acylcatechol derivatives in another investigation encouraged us to study the synthesis of these rather difficultly accessible isomers from 2,5-dialkoxyhydrofuran intermediates. 2-Acetoacetyl-2,5-dimethoxytetrahydrofuran (I. R = CH_3) was prepared by the Claisen condensation of methyl 2,5-dimethoxytetrahydro-2-furoate[5] with acetone in the presence of sodium hydride. Hydrolytic rearrangement of this diketone in the presence of 0.1*N* hydrochloric acid gave 2,3-dihydroxyacetophenone (II. R = CH_3, R′ = H) in good yields. In the same manner methyl 2,5-dimethoxytetrahydro-2-furoate was condensed with pinacolone, acetophenone, and 3-acetylpyridine to form the corresponding 2-acyloacetyl-2,5-dimethoxytetrahydrofurans (I. R = $(CH_3)_3C$, C_6H_5, and 3-C_5H_4N) which, upon hydrolytic rearrangement, yielded 2,3-dihydroxypivalophenone (II. R = $(CH_3)_3C$, R′ = H), 2 3-dihydroxybenzophenone (II. R = C_6H_5, R′ = H), and 3-(2,3-dihydroxybenzoyl)pyridine (II. R = 3-C_5H_4N, R′ = H), respectively. Thus, the hydrolytic rearrangement reaction of 2-acyloacetyl-2,5-dimethoxytetrafurans appears to be generally applicable to the synthesis of 3-acylcatechols.

The unsaturated analog, 2-acetoacetyl-2,5-dimethoxy-2,5-dihydrofuran (III), was obtained by condensing methyl 2,5-dimethoxy-2,5-dihydro-2-furoate[5] with acetone in the presence of sodium hydride. When this diketone was hydrolyzed at room temperature in the presence of 0.1*N* hydrochloric acid an olive-green solid precipitated which melted at 280–284° dec. From the filtrates a second product melting at 157.5–159° separated in the form of brilliant yellow crystals. Elementary analyses of the two hydrolysis products were practically identical. Their acetates (m.p. 156.5–158° and m.p. 97–98°, respectively) also gave almost identical analyses and the close chemical relationship of the two polyhydric phenols was shown by conversion of the lower melting compound to the higher melting material upon refluxing in aqueous solution.

The synthesis of 2,3,6-trihydroxyacetophenone has been recorded by several investigators. Nakazawa,[6] who subjected β-resorcaldehyde to oxidation with alkaline hydrogen peroxide, reported it to melt at 157° (triacetate, m.p. 96°). Almost simultaneously, Baker[7] oxidized 2,6-dihydroxyacetophenone with persulfate and obtained a substance (decomposing above 230° without melting; triacetate, m.p. 155°) to which he also assigned the 2,3,6-trihydroxyacetophenone structure. Because of the close coincidence of melting points with those reported by Nakazawa[6] and by Baker,[7] and the similarity of color reactions in ferric chloride and sodium hydroxide solutions reported by Baker,[7] it appeared probable that our products corresponded to both of the alleged 2,3,6-trihydroxyacetophenones. A sample of 2,3,6-trihydroxyacetophenone and its acetate prepared according

(1) L. Vargha, J. Ramonczai, and P. Bite, *J. Am. Chem. Soc.*, **70**, 371 (1948).

(2) J. T. Nielsen, N. Elming, and N. Clauson-Kaas, *Acta Chem. Scand.*, **9**, 9 (1955).

(3) N. Clauson-Kaas and P. Nedenskov, *Acta Chem. Scand.*, **9**, 27 (1955).

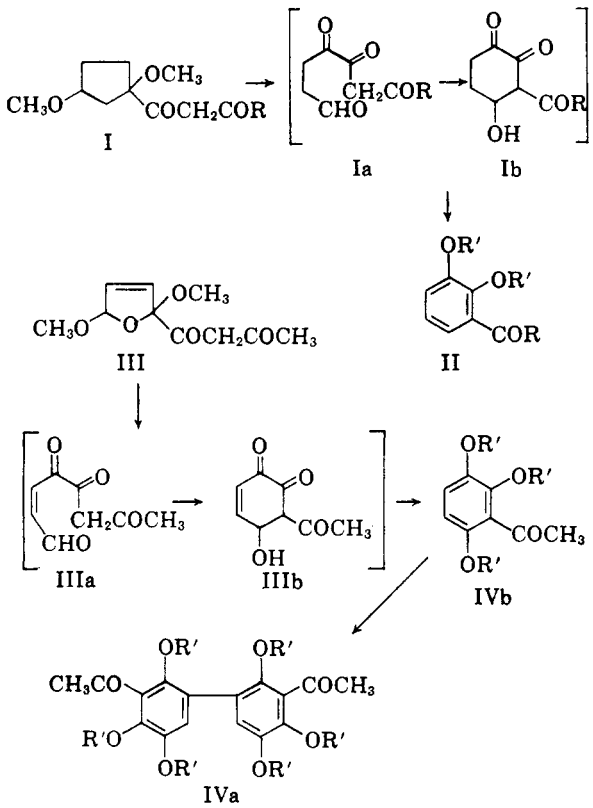
(4) W. R. Boehme, *J. Am. Chem. Soc.*, **82**, 498 (1960).

(5) N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **6**, 551 (1952).

(6) K. Nakazawa, *J. Pharm. Soc. Jap.*, **59**, 297 (1939).

(7) W. Baker, N. C. Brown, and J. A. Scott, *J. Chem. Soc.*, 1922 (1939).

to the directions of Baker[7] was shown by mixed melting points and a comparison of the infrared spectra to be identical[8] with our higher melting polyhydric phenol and its acetate. The low solubility in water and relatively high melting point suggested it to be a higher condensation product of 2,3,6-trihydroxyacetophenone. Oxidative dimerizations of certain polyhydric phenols are known to occur rather readily.[7,9] Cryoscopic molecular weight determinations showed the acetate melting at 97–98° to be monomeric 2,3,6-triacetoxyacetophenone and the acetate (m.p. 157.5–159°) to be a dimer. Both polyhydric phenols gave positive iodoform tests but only the lower melting one gave a positive (pink) color reaction with vanillin in 20% sulfuric acid and with the Ehrlich reagent.[10] The results indicate that oxidative coupling had taken place through the unsubstituted position *para* to the 2′-hydroxy group and that Baker's[7] alleged 2,3,6-trihydroxyacetophenone is, in fact, 3,3′-diacetylbiphenyl-2,2′,4,4′,5,5′-hexol (IVA, R′ = H).



It is evident that both tetrahydro- (I) and dihydro- (III) derivatives of 2-acetoacetyl-2,5-dimethoxyfuran are hydrolyzed initially to the saturated (IA) and unsaturated (IIIA) 4,5,7-triketoaldehydes which undergo intramolecular cyclization to form the aldols IB and IIIB, respectively. Enolization of the unsaturated aldol (IIIB) then leads to 2,3,6-trihydroxyacetophenone. 2,3-Dihydroxyacetophenone, however, must be formed through enolization of the saturated aldol (IB. R = CH_3) and subsequent aromatization by dehydration.

EXPERIMENTAL[11]

2-Acetoacetyl-2,5-dimethoxytetrahydrofuran, [1-(2,5-dimethoxytetrahydro-2-furyl)-1,3-butanedione (I), R = CH_3]. A solution of 16.0 g. (0.275 mole) of acetone in 25 ml. of anhydrous ether was added dropwise with gentle stirring during 0.5 hr. to a mixture of 26.1 g. (0.138 mole) of methyl 2,5-dimethoxytetrahydro-2-furoate,[5] 6.6 g. (0.275 mole) of sodium hydride and six ordinary glass marbles with occasional ice bath cooling to maintain the temperature at 30–40°. Stirring of the viscous, yellow paste was continued for 0.5 hr. longer and 100 ml. of anhydrous ether was added. The reaction mixture was allowed to stand overnight at room temperature and decomposed by careful addition of 15 ml. of ethanol followed by 100 ml. of water and 18.0 g. (0.30 mole) of acetic acid. The layers were separated and the ethereal phase was washed with sodium bicarbonate solution and saturated salt solution. Distillation after drying over anhydrous magnesium sulfate gave 18.7 g. (63%) of pale yellow liquid, b.p. 87–91°/0.5 mm., n_D^{25} 1.4819.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.75; H, 7.60.

2,3-Dihydroxyacetophenone [(II), R = CH_3, R′ = H]. A mixture of 7.4 g. of 2-acetoacetyl-2,5-dimethoxytetrahydrofuran [(I), R = CH_3] and 75 ml. of 0.1*N* hydrochloric acid was refluxed for 1 hr. The yellow solution was allowed to crystallize in the refrigerator and the pale yellow crystals (4.55 g., 88%, m.p. 94–97°) were recrystallized from benzene-hexane; yield 3.55 g., m.p. 98–98.5° (reported[12] m.p. 97°, 97–98°[13]).

The diacetate [(II), R = CH_3, R′ = CH_3CO] was prepared by dissolving 0.75 g. of 2,3-dihydroxyacetophenone in 3 ml. of pyridine, adding 10 ml. of acetic anhydride, and allowing the solution to stand overnight at room temperature. The precipitate (1.15 g., 99%, m.p. 110–111°), which separated upon stirring with 150 ml. of ice water, was recrystallized from methanol giving 1.00 g. of fine, colorless plates, m.p. 110–111° (reported[14] m.p. 109°).

2-Pivaloylacetyl-2,5-dimethoxytetrahydrofuran [(I), R = $(CH_3)_3C$]. A solution of 30.0 g. (0.30 mole) of pinacolone in 100 ml. of anhydrous ether was added dropwise with gentle stirring in 0.5 hr. to a suspension of 38.0 g. (0.20 mole) of methyl 2,5-dimethoxytetrahydro-2-furoate, 4.8 g. (0.20 mole) of sodium hydride and six glass marbles. A mild exothermic reaction with gentle refluxing took place during the addition. Anhydrous ether (100 ml.) was added to the viscous, light tan paste. Stirring was continued for 4 hr. longer and the mixture was allowed to stand at room temperature for 3 days. Fifteen milliliters of ethanol, 50 ml. of water, and 13.2 g. (0.22 mole) of acetic acid were added successively and the layers were separated. Isolation of the

(8) In our hands, 2,3,6-trihydroxyacetophenone and its triacetate prepared by the published method[7] melted at 280° dec. and 157°, respectively, when recrystallized from ethanol.

(9) B. C. Kar, *J. Ind. Chem. Soc.*, **14**, 291 (1937); M. Nierenstein and C. W. Webster, *Pharm. J.*, **154**, 14 (1945); S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 1726 (1951); A. Critchlow, R. D. Haworth, and P. A. Pauson, *J. Chem. Soc.*, 1318 (1951); R. G. R. Bacon, *Sci. Proc. Roy. Dublin Soc.*, **27**, 177 (1956).

(10) C. Steelink, *Nature*, **184**, 720 (1959).

(11) Melting points are uncorrected. Analyses were performed by Mr. E. R. Hoffmann and staff of these laboratories.

(12) W. Baker and A. R. Smith, *J. Chem. Soc.*, 346 (1936).

(13) V. K. Ahluwalia, D. S. Gupta, V. V. S. Murti, and T. R. Seshadri, *Proc. Ind. Acad. Sci.*, **38A**, 480 (1953).

(14) H. v. Krannichfeldt, *Ber.*, **46**, 4018 (1913).

product of the procedure described above gave 39.4 g. (76%) of almost colorless liquid, b.p. 102–109°/1.5 mm. For analysis a sample was redistilled (b.p. 106°/1.5 mm., n_D^{25} 1.4671).

Anal. Calcd. for $C_{12}H_{22}O_5$: C, 60.44; H, 8.59. Found: C, 60.96; H, 8.82.

2,3-Dihydroxypivalophenone [(II), R = $(CH_3)_3C$, R′ = H]. A mixture of 10.33 g. of 2-pivaloylacetyl-2,5-dimethoxytetrahydrofuran (I. R = $(CH_3)_3C$) and 100 ml. of 0.1*N* hydrochloric acid was refluxed for 2 hr. The oily suspension was distilled on the steam bath under water pump vacuum. The residue was taken up in ether, washed with sodium bicarbonate solution, with saturated salt solution, and dried over anhydrous magnesium sulfate. Distillation of the dried extract yielded 6.3 g. (81%) of a viscous, yellow liquid, b.p. 114–119°/3 mm., n_D^{25} 1.5392. A center fraction was taken for analysis.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.95; H, 7.33.

The diacetate (II. R = $(CH_3)_3C$, R′ = CH_3CO), prepared in acetic anhydride with a trace of pyridine at room temperature, was obtained as coarse, colorless crystals, m.p. 70–71° (from methanol).

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 65.00; H, 6.71.

2,3-Dihydroxybenzophenone [(II), R = C_6H_5, R′ = H]. Acetophenone (24.0 g., 0.20 mole) was condensed with 38.0 g. (0.20 mole) of methyl 2,5-dimethoxytetrahydro-2-furoate and 4.8 g. (0.20 mole) of sodium hydride as in the procedure described above for compound I (R = CH_3). The crude 2-benzoylacetyl-2,5-dimethoxytetrahydrofuran (I. R = C_6H_5), which could not be distilled *in vacuo* without decomposition, was steam distilled to remove a little unchanged acetophenone and hydrolyzed by refluxing for 2 hr. in 400 ml. of 0.1*N* hydrochloric acid in 25% dioxane. The yellow oily layer was separated from the cooled suspension and the aqueous dioxane phase was concentrated to 100 ml. on the steam bath under reduced pressure to precipitate an additional quantity of the yellow oil. An aqueous methanol solution of the oil slowly deposited large, pale yellow blades of 2,3-dihydroxybenzophenone, m.p. 64–65° (reported[13] m.p. 65°).

The following procedure was found to be convenient for the isolation of larger quantities of 2,3-dihydroxybenzophenone. Crude 2,3-dihydroxybenzophenone (32.0 g. as precipitated from the aqueous dioxane hydrolysis) was dissolved in 150 ml. of acetic anhydride containing a few drops of pyridine. The solution was refluxed for 2 hr., cooled, and poured into 1 l. of ice water. The suspension was stirred for several hours when crystallization took place. The crude 2,3-diacetoxybenzophenone (II. R = C_6H_5, R′ = CH_3CO, 36.0 g., m.p. 85–87°) was recrystallized from cyclohexane yielding 29.0 g., m.p. 89–91°. For analysis a sample was recrystallized from aqueous methanol, m.p. 91–92°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.42; H, 4.78.

Twenty grams of once crystallized 2,3-diacetoxybenzophenone was dissolved in a hot solution of 1000 ml. of methanol, 400 ml. of water, and 200 ml. of concd. hydrochloric acid. The faintly cloudy solution was cooled to room temperature, seeded, and allowed to stand for 3 days in an open beaker. The yield of crystalline 2,3-dihydroxybenzophenone which separated was 13.6 g. (95%), m.p. 63–65°.

3-(2,3-Dihydroxybenzoyl)pyridine [(II), R = 3-C_5H_4N, R′ = H). A solution of 12.1 g. (0.1 mole) of 3-acetylpyridine in 50 ml. of anhydrous ether was added dropwise to a gently stirred mixture of 38.0 g. (0.20 mole) of methyl 2,5-dimethoxytetrahydro-2-furoate, 4.8 g. (0.20 mole) of sodium hydride and six glass marbles during 1 hr. with occasional ice bath cooling. Stirring was continued for 0.5 hr. longer when the evolution of hydrogen subsided and a viscous, amber suspension resulted. The mixture was allowed to stand overnight at room temperature and the product was separated by the procedure described for 2,3-dihydroxyacetophenone. 2-Nicotinoylacetyl-2,5-dimethoxytetrahydrofuran [(I). R = 3-C_5H_4N, 9.8 g., 35%] was obtained as a viscous, yellow liquid boiling at 150–158°/0.06 mm. with decomposition. A solution of 8.5 g. of the diketone [(I), R = 3-C_5H_4N] in 200 ml. of 0.5*N* hydrochloric acid was heated on the steam bath for 1 hr. and the cooled solution was neutralized with solid sodium bicarbonate. Recrystallization of the solid precipitate from heptane gave 3.8 g. (58%) of brilliant lemon yellow crystals, m.p. 149.5–150.5°. For analysis a sample was recrystallized several times from the same solvent, m.p. 154–156°.

Anal. Calcd. for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 67.03; H, 4.50; N, 6.37.

2-Acetoacetyl-2,5-dimethoxy-2,5-dihydrofuran (III). A solution of 58.0 g. (1.0 mole) of acetone in 100 ml. of anhydrous ether was added dropwise at 30–40° in 0.75 hr. to a slowly stirred suspension of 94.0 g. (0.5 mole) of methyl 2,5-dimethoxy-2,5-dihydro-2-furoate,[5] 24.0 g. (1.0 mole) of sodium hydride, and six glass marbles. The reaction began immediately with the evolution of hydrogen and the formation of a viscous, amber paste. Anhydrous ether (300 ml.) was added and the mixture was allowed to stand for 3 days at room temperature. Isolation of the product by the procedure described for compound I (R = CH_3) gave 84.5–96.3 g. (79–90%) of a light yellow liquid, b.p. 91–97°/0.07 mm., n_D^{25} 1.4884.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 56.27; H, 6.66.

3,3′-Diacetylbiphenyl-2,2′,4,4′,5,5′-hexol [(IVA), R′ = H] *and 2,3,6-trihydroxyacetophenone* [(IVB), R′ = H]. A suspension of 5.35 g. of 2-acetoacetyl-2,5-dimethoxy-2,5-dihydrofuran (III) in 50 ml. of 0.1*N* hydrochloric acid was stirred in a closed flask at room temperature. After 16 hr. there had separated 3.0 g. (71%) of an olive-green solid (m.p. 285° dec.). Recrystallization from ethanol gave deep yellow crystals of 3,3′-diacetylbiphenyl-2,2′,4,4′,5,5′-hexol, m.p. 280–284° dec.

Anal. Calcd. for $C_{16}H_{14}O_8$: C, 57.49; H, 4.22. Found: C, 57.30; H, 4.41.

Alcoholic ferric chloride gave a brownish yellow solution accompanied by the formation of a dark precipitate. Aqueous sodium hydroxide dissolved it with the formation of a deep green solution.

The acetate (IVA. R′ = CH_3CO) was prepared by allowing a solution of 1.75 g. of the hexol (IVA. R′ = H) in 5 ml. of pyridine and 10 ml. of acetic anhydride to stand overnight at room temperature. When diluted with 100 ml. of ice-water a rapidly solidifying oil precipitated. The crude product (2.80 g., 80%, m.p. 152°) melted at 156.5–158° when recrystallized from ethanol (reported m.p. 155°[7]).

Anal. Calcd. for $C_{28}H_{26}O_{14}$: C, 57.34; H, 4.47. Found: C, 57.23; H, 4.70. Mol. wt. calcd.: 586. Found (cryoscopic in benzene): 596.

When the aqueous hydrochloric acid filtrate from the diketone hydrolysis was cooled in ice 0.68 g. (16%) of brilliant yellow crystals of 2,3,6-trihydroxyacetophenone (m.p. 153–156°) separated. Sublimation *in vacuo* raised the m.p. to 157.5–159° reported m.p. 157°[6]).

Anal. Calcd. for $C_8H_8O_4$: C, 57.14; H, 4.80. Found: C, 57.39; H, 4.90.

Alcoholic ferric chloride gave a green solution which turned to brownish yellow with the formation of a dark precipitate. Aqueous sodium hydroxide gave an orange-yellow colored solution turning to green.

The acetate [(IVB), R′ = CH_3CO] was prepared by refluxing 0.50 g. of 2,3,6-trihydroxyacetophenone with 5 ml. of acetic anhydride for 1.5 hr. and diluting the cooled solution with water. The precipitate which separated upon cooling in ice melted at 94–96°. Recrystallization from methanol gave colorless blades melting at 97–98° (reported[15] m.p. 96°,[6] 93–95°).

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(15) N. N. Vorozhtsov and V. P. Mamaev, *Sbornik Statei Obshchei Khim. Akad. Nauk S. S. S. R.*, 1, 533 (1953).

Anal. Calcd. for $C_{14}H_{14}O_7$: C, 57.14; H, 4.80. Found: C, 57.30; H, 5.07. Mol. wt. calcd.: 294. Found (cryoscopic in benzene): 307.

Approximately the same ratio of dimer to monomer was obtained when the hydrolytic rearrangement was carried out under nitrogen or carbon dioxide in 0.1*N* hydrochloric acid which had boiled to expel dissolved air.

SOMERVILLE, N. J.

[CONTRIBUTION FROM EXPERIMENTAL STATION, EXPLOSIVES DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Beckmann Rearrangement. III. Rearrangement of Oxime *p*-Toluenesulfonates in Chloroform, Acetic Acid, and Methanol

WALTER Z. HELDT

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The ΔE_a and $\Delta S^{\ddagger}$ in the rearrangement of several oxime *p*-toluenesulfonates in chloroform, acetic acid, and methanol were determined. The rearrangement is fastest in methanol > acetic acid ≫ chloroform. The rate constant of the reaction in acetic acid decreases in the following sequence: cyclohexanone > benzophenone ≅ cycloheptanone ≅ cyclooctanone > cyclopentanone ≅ acetophenone > acetone. The rearrangement is believed to proceed with the formation of an azacyclopropene ring system in the transition state. Acid catalysis increases the rate of rearrangement in chloroform but decreases the rate in acetic acid.

Much work has been done on the mechanism of the Beckmann rearrangement and several reviews[1] summarize the published literature on the reaction.

Essentially, the rearrangement proceeds by intramolecular migration of the group "anti" to the departing $OR^{\oplus}$ group. Furthermore, Chapman[2] found that the rate of rearrangement increases with an increasing dielectric constant of the solvent. A study of the salt effects and the acetolysis of cyclopenta- and cyclohexanone oxime *p*-toluenesulfonates described in the previous paper[3] suggested a stable transitory ion pair which apparently contains an azacyclopropene ring system.

This paper describes the influence of solvent, structure, and acid catalysis upon the Beckmann rearrangement of oxime *p*-toluenesulfonates.

EXPERIMENTAL

Acetolysis of cycloalkanone oxime *p*-toluenesulfonates was measured as described previously[3] by titration of the *p*-toluenesulfonic acid formed. Acetic acid solutions were prepared by dissolving 1 g. of water weighed to ±1 mg. in 10 g. of 100% acetic acid, weighed to ±10 mg. and diluting this solution to the concentration indicated in Table I by means of a calibrated buret. The standard sodium acetate solution was prepared in the same solvent as that prepared for the reaction medium of each run. If the water concentration in acetic acid exceeded 0.35*M*, the 0.1% Bromphenol Blue solution could not be used as an indicator because of the sluggish color change. A solution of perchloric acid in 100% acetic acid was prepared according to the method of Kolthoff.[4] To a known amount of dry silver perchlorate in 100% acetic acid was added standard hydrochloric acid solution, prepared by bubbling dry hydrogen chloride into 100% acetic acid. The silver chloride was filtered off, and the resulting perchloric acid solution was standardized against sodium acetate. Each run was measured by titrating eight to ten fresh batches of the tosylate at increasing time intervals with standard sodium acetate. The rates were evaluated from the first order rate equation to about 80% reaction.

TABLE I

EFFECT OF (A) WATER AND (B) PERCHLORIC ACID ON THE RATE CONSTANT OF ACETOLYSIS OF CYCLOPENTANONE OXIME *p*-TOLUENESULFONATE

(Temp. = 35.55 ± 0.05°)

Oxime Tosylate mequiv.	Added	Mg.	Mequiv.	$k \times 10^{+4}$ sec.$^{-1}$
0.79	—	—	—	6.06
0.79	H_2O	20.4	1.11	5.80
0.79	"	40.0	2.22	5.89
0.79	"	80.4	4.44	6.29
0.79	"	160.0	8.88	6.06
0.79	"	400.0	22.22	6.13
0.79	$HClO_4$	8.5	0.085	4.49
0.79	"	42.4	0.424	4.03
0.79	"	84.4	0.847	3.64
0.79	"	169.4	1.694	3.74
0.79	"	248.1	2.481	2.69

Rate of solvolysis of oxime *p*-toluenesulfonates in methanol, ethanol, and alcohol-water mixtures were followed by titration of the *p*-toluenesulfonic acid formed with standard sodium methoxide or sodium ethoxide to *p*H = 8.0, using a *p*H-meter and a Bartlett-Swain titration cell equipped with a calomel- and a glass-electrode.[5] The standard solution consisted of the same solvent mixture as a solution in the titration cell. The rates followed the first order equation up to about 80% of complete reaction. The results are summarized in Tables II and III.

(1)(a) A. H. Blatt, *Chem. Rev.*, 12, 215 (1933); (b) B. Jones, *Chem. Rev.*, 35, 335 (1944); (c) I. L. Knunyants and B. P. Fabrichnyi, *Usepckhi Khimi*, 18, 633 (1949); (d) L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, XI, 1 (1960).

(2) D. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936).

(3) W. Z. Heldt, *J. Am. Chem. Soc.*, 80, 5972 (1958).

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