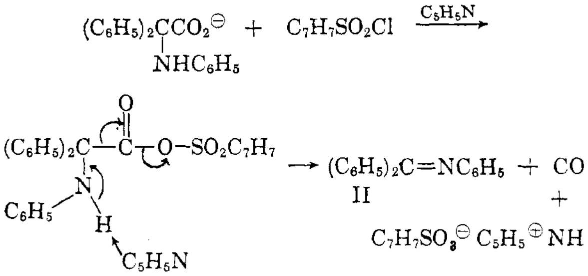
acids studied by Wiley. A reasonable alternative mechanism to explain our results would be attack of the acid anion on the *p*-toluenesulfonyl chloride to give the mixed anhydride, which then decomposes to the observed products. Mixed anhydrides



$$\underset{\displaystyle NHC_6H_5}{(C_6H_5)_2CCO_2^{\ominus}} + C_7H_7SO_2Cl \xrightarrow{C_5H_5N}$$

$$\longrightarrow \underset{\text{II}}{(C_6H_5)_2C{=}NC_6H_5} + CO + C_7H_7SO_3^{\ominus}\ C_5H_5^{\oplus}NH$$

of *p*-toluenesulfonic acid are known[5] and have been proposed[6] as highly reactive intermediates in acylation reactions. Apparently the reduced basicity of the amino group and steric factors favor reaction at the carboxyl group in this case.

EXPERIMENTAL[7]

α-Anilino-α,α-diphenylacetic acid (I).[8a,b] To a cooled (10°) solution of 1.2 ml. (1.22 g., 0.013 mole) of freshly distilled aniline in dry benzene was added, dropwise, a benzene solution of 1.4 g. (0.0057 mole) of α-chloro-α,α-diphenylacetic acid.[9] After the addition was complete (one-half hour) the reaction mixture was stirred at room temperature for an additional one-half hour. Aniline hydrochloride was removed by filtration and the combined benzene fractions were washed with water, dried (magnesium sulfate), and concentrated to one-quarter volume. Upon cooling, 1.36 g. of solid, m.p. 165–170°, was obtained. Addition of petroleum ether to the mother liquor and cooling afforded a second crop. The total yield of crude acid was 1.6 g. (93%). After a single recrystallization from benzene–petroleum ether the m.p. was 178–180° (lit.[8b] m.p. 174–175°). The acid obtained in this way was identical to a sample prepared by the somewhat more laborious procedure of Klinger and Standke.[8a]

Reaction of α-anilino-α,α-diphenylacetic acid (I) *with p-toluenesulfonyl chloride and pyridine.* To a suspension of 1 g. (0.0032 mole) of α-anilino-α,α-diphenylacetic acid (I) and 0.8 g. (0.0047 mole) of *p*-toluenesulfonyl chloride in 30 ml. of sodium-dried benzene was added 2.5 ml. of dry pyridine. The resulting light yellow solution was refluxed for seven hours. As the reaction progressed, the gas produced was swept from the reaction vessel in a slow stream of nitrogen, passed through a drying tube containing Drierite and Anhydrone, and collected in a gas cell. The infrared spectrum of the collected gases demonstrated that carbon monoxide (characteristic doublet at 2120 cm.$^{-1}$ and 2160 cm.$^{-1}$, identical to that of an authentic sample[10]) was the only gas present (other than the nitrogen diluent).

After the removal of the gases, the reaction mixture was cooled to room temperature. The pyridinium salts were removed by filtration and washed with benzene. The combined benzene extracts were washed with dilute acid, dilute base, and water and dried. After evaporation of the solvent and crystallization from methanol 0.53 g. (62.4%) of benzophenone anil (II), m.p. 109–112° (lit.[11] m.p. 112°), was obtained. The melting point was not depressed upon admixture with authentic benzophenone anil.[11] The infrared spectrum was identical with that of the authentic sample.

Addition of phenylhydrazine to an alcoholic solution of the crude residue after the methanol crystallization afforded the phenylhydrazone of benzophenone, m.p. 138–139° (lit.[12] m.p. 137°), not depressed by admixture with an authentic sample.

S-Benzylthiuronium salt. To a chilled aqueous solution of the crude salt mixture from the reaction described above was added an aqueous solution of *S*-benzylthiuronium chloride. The resulting heavy precipitate was collected by filtration and recrystallized from ethanol. The m.p. was 183–184° (lit.[13] m.p. for the corresponding derivative of *p*-toluenesulfonic acid, 181–182°) and the sample did not depress the m.p. of an authentic sample prepared from sodium *p*-toluenesulfonate.

The crude salt mixture failed to form a sulfone with 1-chloro-2,4-dinitrophenol, in the characteristic test for sulfinic acids.[14]

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(5) See, for example, H. P. Kaufmann and L. S. Huang, *Ber.*, **75B**, 1214 (1942).

(6) J. H. Brewster and C. J. Ciotti, *J. Am. Chem. Soc.*, **77**, 6214 (1955).

(7) Melting points are corrected. The authors are indebted to Mrs. N. Alvord for the infrared spectra.

(8) (a) H. Klinger and O. Standke, *Ber.*, **22**, 1212 (1889). (b) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 484 (1914).

(9) J. Klosa, *Arch. Pharm.*, **288**, 42 (1955).

(10) G. Jacini, *Chimica e Industria*, **29**, 204 (1947); *Chem. Abstr.*, **44**, 9844 (1950).

(11) E. Knoevenagel, *J. prakt. Chem.*, (2) **89**, 37 (1914).

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Wiley, New York, 1956, p. 318.

(13) E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941).

(14) J. P. London, *J. Chem. Soc.*, 537 (1935).

The Reaction of Aldoximes with Alkali[1]

Henry Rapoport and William Nilsson

Received August 21, 1961

During the course of another investigation[2] it was found that phenylacetaldoxime, when subjected to the action of alkali at 170°, was converted in 78% yield to phenylacetic acid. This reaction seemed to have sufficient potential as a synthetic tool to merit further investigation, and its application to a variety of aldoximes is the subject of the present report.

The only similar case of such a conversion of an aldoxime to an acid by means of hot alkali[3] involved the conversion of benzaldoxime and several substituted benzaldoximes, as well as fur-

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(1) Sponsored in part by the United States Atomic Energy Commission.

(2) H. Rapoport and W. Nilsson, *J. Am. Chem. Soc.*, **83**, 4262 (1961).

(3) E. Jordan and C. R. Hauser, *J. Am. Chem. Soc.*, **58**, 1304 (1936).

TABLE I

Products Resulting from the Action of Potassium Hydroxide on Aldoximes

Aldoxime	M.P.	Solvent[a]	Time, Hr.	Temp.	Yield, % Acid	Yield, % Other
Phenylacetaldoxime	101–102[b]	A	3	190	80	—
Enanthaldoxime	57[c]	A	3	190	63[d]	—
		C	16	80	21[d]	50, oxime 20, amide[d]
Isobutyraldoxime	141–142[e] (b.p.)	A	3	170	88[f]	—
		B	8	120	89[f]	—
Pivaldoxime	38–39[g]	A	3	170	38[h]	15, amide
		A	6	120	4	42[i]
anti-Cinnamaldoxime	131–132[j]	A	3	190	68	—
syn-Benzaldoxime	30–32[k]	A	3	170	95	—
		B	6	120	15	40, oxime 30, amide 4, nitrile

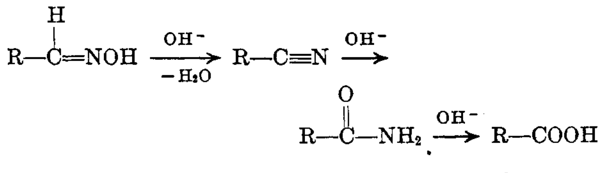
[a] Solvents: A, diethylene glycol; B, 2-methoxyethanol; C, 80% aqueous ethanol. [b] Reported[5] m.p. 99–100°. [c] Reported m.p. 57° [E. Bamberger and F. Elger, *Ann.*, **475,** 288 (1929)]. [d] Enanthic acid was identified as its amide, m.p. 93°; reported m.p. 93–94° [O. Aschan, *Ber.*, **31,** 2344 (1898)]. [e] Reported b.p. 141–142° [J. Petraczek, *Ber.*, **15,** 2783 (1882)]. [f] Identified as the amide, m.p. 128°; reported m.p. 128° [A. W. Hofmann, *Ber.*, **15,** 977 (1882)]. [g] Reported m.p. 41° [A. Richard, *Ann. chim.* (*Paris*), [8], **21,** 371 (1910)]. [h] Identified as the anilide, m.p. 135°; reported m.p. 131–132° [G. Schroeter, *Ber.*, **44,** 1201 (1911)]. [i] This was separated into oxime (mostly) plus amide and nitrile. [j] Reported m.p. 135° [O. L. Brady and R. F. Goldstein, *J. Chem. Soc.*, 1918 (1926)]. [k] Reported m.p. 35° [O. L. Brady and R. F. Goldstein, *J. Chem. Soc.*, 1918 (1926)].

furaldoxime, to the corresponding acids by heating in 2*N* aqueous sodium hydroxide at 100°. The *syn*-oximes were transformed to acids in considerably lower yields than were the *anti*-isomers, and the unchanged oximes were recovered in considerable quantity. The *anti*-oximes were converted to acids in 38–62% yield, the remainder being converted to the more stable *syn*-isomer.

In the present work the reaction conditions most frequently employed have been diethylene glycol as solvent at a temperature of 170–190°. Under these conditions, all the aldoximes tested were converted by potassium hydroxide to carboxylic acids in good yields except for pivalic acid which was obtained in 38% yield. Here, however, high volatility may account for loss of material during the reaction and isolation.

The reaction has been found to be quite general for aliphatic aldoximes as well as aromatic aldoximes. It may offer a useful alternative to the commonly employed conversion of aldehydes to acids through dehydration of aldoximes under acidic conditions followed by hydrolysis of the resulting nitrile. The results of the various reactions are presented in Table I.

The reaction appears to be a base-catalyzed dehydration of the aldoxime to the nitrile followed by hydrolysis of the nitrile through the amide to the acid. This sequence is borne out by the detection of both the nitrile and the amide as intermediates in those cases where the reaction was incomplete. Alkali is needed, since heating *syn*-benzaldoxime at 120° for twelve hours in the absence of alkali in 2-methoxyethanol yielded no nitrile, amide, or acid. The oxime was quantitatively recovered. The reaction is sensitive to steric factors. As seen from the table, lowering the reaction temperature from 190° to 120° does not affect the high yield of isobutyric acid from isobutyraldoxime, but it drastically reduces the yields of pivalic acid from the more highly hindered pivaldoxime, which remains largely unchanged at this lower temperature.



$$R-\overset{H}{\overset{|}{C}}=NOH \xrightarrow[-H_2O]{OH^-} R-C\equiv N \xrightarrow{OH^-} R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{OH^-} R-COOH$$

At 120°, *syn*-benzaldoxime reacts slowly, only a 15% yield of benzoic acid being isolated after six hours. About 40% of the oxime is recovered, while the yields of nitrile and amide are about 4% and 30%, respectively. Hauser and Jordan[3] similarly report only a 10% yield of acid at 100° from *syn*-benzaldoxime. The reaction gives a virtually quantitative yield of benzoic acid at 170°. Thus, it appears that a relatively high activation energy is associated with the dehydration of aldoxime to nitrile; a somewhat lower energy is required for conversion of amide to acid; and a much lower activation energy is associated with hydrolysis of the nitriles to the amides. The reaction is not merely a thermal dehydration followed by alkaline hydrolysis of the resulting nitrile, since thermal dehydration requires significantly higher temperatures and longer reaction times.

It should be mentioned that the recently reported[4] conversion of aldoximes to amides by means of nickel tetraacetate in xylene involves an entirely different mechanism, since the nitrile has been shown not to be intermediate in that case.

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(4) L. Field, P. B. Hughmark, S. H. Shumaker, and W. S. Marshall, *J. Am. Chem. Soc.*, **83,** 1983 (1961).

EXPERIMENTAL

Oximes were prepared by heating the aldehyde with hydroxylamine hydrochloride and sodium acetate in aqueous ethanol, except for phenylacetaldoxime which was made by the method of Weerman.[5] The aldehydes were all commercially available except for pivalaldehyde, prepared according to the method of Roberts and Teague.[6]

The reaction of aldoximes with alkali. The general procedure used was as follows: The aldoxime (10 mmoles) was heated in 100 ml. of the solvent indicated at the temperature indicated in Table I with about 50 mmoles of potassium hydroxide, and the heating was carried out under a nitrogen atmosphere.

At the end of the reaction time, the cooled mixture was diluted with water and extracted four times with half volumes of methylene chloride; these combined extracts being washed with 100 ml. of aqueous sodium chloride solution. Drying the organic extracts over sodium sulfate, filtering, and evaporating the solvent left as a residue the neutral fraction of the reaction mixture. The original aqueous alkaline solution then was acidified with hydrochloric acid to *p*H 7, and again extracted with methylene chloride. A similar treatment of the organic phase yielded the weakly acidic products. Finally, acidification of the aqueous solution to *p*H 2 and similar extraction with methylene chloride yielded the strongly acidic products. The products were then identified by mixed m.p. and infrared comparison with authentic samples.

The thermal dehydration of syn-benzaldoxime. A solution of 1.09 g. of *syn*-benzaldoxime in 80 ml. of 2-methoxyethanol was heated at 120° for 12 hr. under a nitrogen atmosphere with no alkali present. The product was isolated as described above and found to consist entirely of unreacted oxime.

A solution of 1.04 g. benzaldoxime in 50 ml. of diethylene glycol was heated 10 hr. at 200° under a nitrogen atmosphere. The product was entirely neutral and consisted of nitrile and amide. No unchanged oxime or acid was present.

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[5] R. A. Weerman, *Ann.*, 401, 1 (1913).

[6] T. G. Roberts and P. C. Teague, *J. Am. Chem. Soc.*, **77**, 6258 (1955).

Condensed Cyclobutane Aromatic Compounds. XVI. Methylenebenzocyclobutene

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This note describes a synthesis of methylenebenzocyclobutene (I), the simplest styrene analog in the benzocyclobutene series.

Benzocyclobutene-1-carboxylic acid (II), prepared by an improved one-step hydrolysis of the corresponding nitrile,[1] was reduced with lithium aluminum hydride to 1-hydroxymethylbenzocyclobutene (III). Reaction of alcohol III with *p*-toluenesulfonyl chloride in pyridine gave the corresponding crystalline tosyl ester (IV). Reduction of tosylate IV with lithium aluminum hydride afforded 1-methylbenzocyclobutene (V), the ultraviolet spectrum of which was virtually superimposable upon that of benzocyclobutene itself.[2] Reaction of IV with potassium *t*-butoxide in *t*-butyl alcohol gave methylenebenzocyclobutene (I), purified at 135° by gas chromatography. The new olefin, which absorbed bromine rapidly, was found to have an ultraviolet spectrum (Fig. 1) somewhat similar to that of *o*-methylstyrene.[3] The spectrum of I, however, showed more detail and higher resolution.

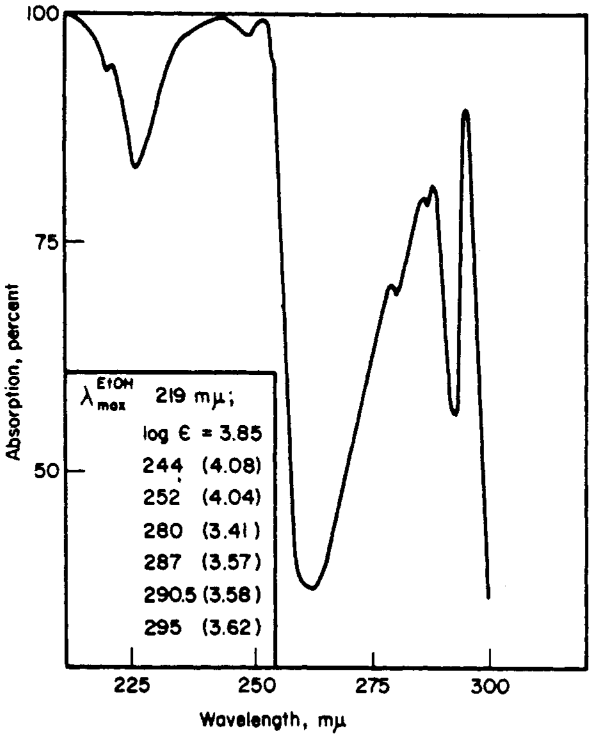
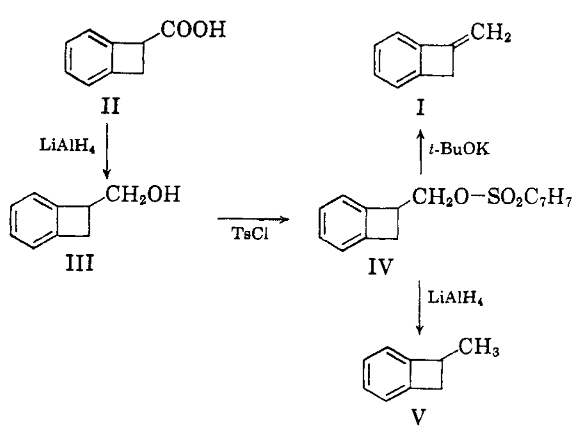


Fig. 1. Ultraviolet spectrum of methylenebenzocyclobutene

As expected, mild catalytic reduction of I occurred readily with saturation of the olefinic double bond to give hydrocarbon V, as evidenced



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[2] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

[3] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York (1951).