8.6 g.; m. p. 127°. The analytical sample melted at 134–134.5°.

Anal. Calcd. for $C_{27}H_{29}ClO_3$: C, 74.20; H, 6.69. Found: C, 74.07; H, 6.73.

2-(*p*-Chlorophenyl)-2-mesitylvinyl Alcohol.—The decomposition of this peroxide, carried out in the usual way, yielded only a very small amount of the vinyl alcohol. It crystallized from its solution in low-boiling petroleum ether only after standing for several weeks. It was recrystallized from low-boiling petroleum ether. It formed colorless prisms melting at 92–93°. The analytical sample decomposed after standing five months.

Anal. Calcd. for $C_{17}H_{17}ClO$: C, 74.83; H, 6.28. Found: C, 74.65; H, 6.38.

1,3-Dimesityl-3-(*p*-bromophenyl)-1-propen-1-ol Peroxide.—The crude peroxide, prepared from *p*-bromobenzalacetomesitylene and mesitylmagnesium bromide, melted at 109–115°; yield 68% of the theory. It was recrystallized from ether and ligroin; m. p. 126.5–127°.

Anal. Calcd. for $C_{27}H_{29}BrO_3$: C, 67.36; H, 6.07. Found: C, 67.48; H, 6.73.

Attempts to obtain 2-(*p*-bromophenyl)-2-mesitylvinyl alcohol from this peroxide yielded oily materials which failed to crystallize.

Summary

A new method has been developed for the synthesis of 2,2-diarylvinyl alcohols. It consists in the condensation of a chalcone with a Grignard reagent, conversion of the resulting enol to a peroxide and, finally, thermal decomposition of the peroxide.

2-Mesityl-2-phenylvinyl alcohol, 2,2-dimesitylvinyl alcohol and 2-(*p*-chlorophenyl)-2-mesitylvinyl alcohol have been made by the new procedure.

It is concluded that the aldehydes, formed initially, rearrange spontaneously to the vinyl alcohols. Evidence is presented which indicates that this isomerization may be reversible.

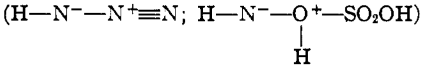
URBANA, ILLINOIS RECEIVED SEPTEMBER 19, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT SMITH COLLEGE]

The Reaction of Hydroxylamine-O-sulfonic Acid with Ketones[1]

BY JANET K. SANFORD,[2] FRANCES TATE BLAIR, JUSTA ARROYA AND K. W. SHERK

Keller and Smith[3] have shown recently that the aminating action of both hydroxylamine-O-sulfonic acid[4] and hydrogen azide upon aromatic hydrocarbons proceeds through a common intermediate, NH or NH_2^+. The relationship of these two compounds was also indicated by the preparation of the hydroxylamine derivative from hydrogen azide and fuming sulfuric acid.[5] Since both aminating agents may be considered as the requisite atoms of a neutral molecule coördinated to an HN group



$$(H{-}N^-{-}N^+{\equiv}N;\ H{-}N^-{-}\underset{\displaystyle H}{\overset{}{O^+}}{-}SO_2OH)$$

it is reasonable to expect both acids to yield the same products under reaction conditions that favor the separation of the neutral molecule (nitrogen or sulfuric acid) and the liberation of the HN fragment.

Keller and Smith offered evidence to show that the direct amination of aromatic hydrocarbons took place by a different mechanism than that of the Schmidt[6] reaction (hydrogen azide with the carbonyl group in the presence of an acidic catalyst, usually concentrated sulfuric acid) which has been the subject of much discussion.[7–13] It seemed to the authors that a series of reactions of hydroxylamine-O-sulfonic acid and hydrogen azide upon ketones might furnish information of interest concerning the mechanisms of these reactions, and carry the similarity of the two compounds a step further.

It has been the practice when utilizing the Schmidt reaction to use a chloroform, benzene or ether solution of hydrogen azide. In this work, the dry gaseous hydrogen azide was led into the ketone, sulfuric acid and solvent. This procedure eliminated the separate preparation of hydrogen azide solutions, was more direct, and was safer since no quantity of hydrogen azide capable of serious damage on explosion ever accumulated.

Experimental

Procedure with Hydroxylamine-O-sulfonic Acid.—This was prepared by the method of Specht, Browne and Sherk.[5] The material was assayed by treatment with acidified potassium iodide and titration of the liberated iodine with standard sodium thiosulfate solution. The product was shown to be 97% hydroxylamine-O-sulfonic acid (iodine equiv., 58.5; calcd., 56.5).

The ketone (0.025 mole) and the reagent were mixed in a large test-tube and, if necessary, slowly warmed in a water-bath until the reaction, noted by the evolution of

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(1) This paper is based in part upon the theses for the M. A. degree at Smith College by Janet K. Sanford, Frances Tate Blair and Justa Arroya.

(2) Present address, Arthur D. Little, Inc., Cambridge, Mass.

(3) R. N. Keller and Peter A. S. Smith, THIS JOURNAL, **66**, 1122 (1944).

(4) The confusion regarding the naming of the compound, H_2NOSO_3H, has been pointed out by Keller and Smith and, although one of us (K. W. S.) is partially responsible for the name aminomonopersulfuric acid, we are happy to adopt the name suggested by them.

(5) H. E. M. Specht, A. W. Browne and K. W. Sherk, THIS JOURNAL, **61**, 1083 (1939).

(6) K. F. Schmidt, *Ber.*, **57**, 704 (1924); U. S. Patent, 1,564,631.

(7) E. Oliveri-Mandalà, *Gazz. chim. ital.*, **55**, 271 (1925).

(8) K. F. Schmidt, *Ber.*, **58**, 2413 (1925).

(9) A. Bertho, *ibid.*, **59**, 589 (1926).

(10) T. Curtius and A. Bertho, *ibid.*, **59**, 565 (1926).

(11) M. A. Spielman and F. L. Austin, THIS JOURNAL, **59**, 2658 (1937).

(12) C. D. Hurd and Gilman, "Organic Chemistry," 1st ed., Vol. I, John Wiley and Sons, New York, N. Y., 1938, p. 698.

(13) L. H. Briggs and J. W. Littleton, *J. Chem. Soc.*, 421 (1943).

TABLE I

HYDROXYLAMINE-O-SULFONIC ACID WITH KETONES

Ketone	Reaction starts, °C.	Product	Yield, %	B. p. or m. p. exp.	B. p. or m. p. lit.
Dimethyl	20	Oxime	90	59	59 (61)
Methyl, ethyl	20	Oxime	87	152	152
Diethyl	20	Oxime	87	165	165
Methyl *n*-propyl	35	Oxime	90	167	167
Methyl isobutyl	40	Oxime	85	176	175
Methyl *n*-amyl	50	Oxime	87	192	
Methyl *n*-hexyl	80	Oxime	60	204–260 d.	213–214
Cyclohexanone	40	Oxime	89	87	89–90
Me phenyl	20	Acetanilide	90	113	113–114
Et phenyl	40	Propionanilide	75	105	105–106
Me *p*-tolyl	100	Acet-*p*-toluidide	90	146	155 (146)
Me *p*-anisyl	95	Acet-*p*-anisidide	90	126	130–132
Me β-naphthyl[a]	100	2-Acetnaphthalide	50	133	134
Diphenyl[b,c]		No reaction			
Phenyl, *p*-tolyl[c]	160	*p*-Toluic acid		175	181

[a] Violent above 100°; forms a white solid, m. p. above 280°, contains sulfur but no nitrogen; a sulfonic acid. [b] Heated till charring began; benzophenone the only substance identified. [c] No indication of a nitrogen containing organic product.

nitrogen bubbles, started. In those cases where the reaction was vigorous, the tube was cooled to prevent overheating. The reactions, once started, were all exothermic and were accompanied by the liberation of nitrogen and small amounts of ammonia. After the reaction was completed, water and ether were added to the cooled mixture and the ether layer, after washing well with water, sodium bicarbonate solution, and again with water until neutral, was dried with anhydrous magnesium sulfate. The solvent was removed and the product was identified by standard methods.

In the cases of the oximes, the identification involved hydrolysis, identification of hydroxylamine by the ferric chloride-benzoyl chloride test, and the formation of the semicarbazone of the ketone produced by the hydrolysis. In the cases of the substituted amides, the identification involved hydrolysis, and identification of the amine formed, except for acetanilide and propionanilide where the *p*-bromo derivative was used. In all the experiments the agreement between the melting point of the derivative and that recorded in Heilbron[14] was good (always within two degrees). Table I embodies the results of several experiments.

Procedure with Hydrogen Azide.—Dry hydrogen azide vapor mixed with dry air was drawn by suction, from an apparatus similar to that used for the preparation of hydroxylamine-O-sulfonic acid,[5] into a well-stirred mixture of the ketone (0.025 mole), 50 ml. of C. P. dry benzene and 5 ml. of concentrated sulfuric acid. The generator was charged with sodium azide (0.03 mole) and an excess of sulfuric acid (diluted 2:3 with water) and the flow regulated so that the hydrogen azide was delivered over a period of approximately one hour. Bubbles of nitrogen began to be liberated from the acid layer (visible when stirring was momentarily stopped) within the first few minutes. After the addition of the hydrogen azide, stirring was continued until the evolution of gas had ceased, or practically ceased (five to six hours). The sulfuric acid and benzene layers were separated and the acid poured over crushed ice. The precipitated product was dissolved in ether and combined with an ether washing of the diluted acid. These ether solutions were worked up, as described above, for the neutral fraction. No acidic nor basic products were observed. The product was crystallized from hot water or water–ethanol mixtures before identification. The substituted amides were hydrolyzed and the acid and amine so formed were identified by standard methods. The agreement of the observed and recorded[14] melting points of the derivatives was good. The results of several experiments are shown in Table II.

TABLE II

HYDROGEN AZIDE (IN PRESENCE OF CONCD. H_2SO_4) WITH KETONES

Ketone	Product	Yield, %	B. p. or m. p., °C. exp.	B. p. or m. p., °C. lit.
Methyl, ethyl	N-ethylacetamide	70	204	205
Me isobutyl	N-isobutylacetamide	71	221	227
Me phenyl[a]	Acetanilide	90	113	113–114
Me *p*-tolyl	Acet-*p*-toluidide	90	153	155 (146)
Me *p*-anisyl	Acet-*p*-anisidide	50	126	130–132
Me β-naphthyl	2-Acetnaphthalide	73	132	134
Ethylphenyl	Propionanilide	90	105	105–106
Diphenyl	Benzanilide	80	159	163
Phenyl *p*-tol	Phenyl-*p*-toluidide	82	156	158

[a] Schmidt (ref. 6) reported that acetophenone, acetone and cyclohexanone gave acetanilide, N-methylacetamide and ε-leucine lactam, respectively.

Discussion

The evidence presented in this work seems to the authors to be insufficient to allow a complete clarification of the mechanisms of the reactions studied. The results of the trials with hydroxylamine-O-sulfonic acid might indicate that the amides were rearrangement products of oximes which were first formed. Reasoning from this point, one would suggest a similar statement regarding the Schmidt reaction, but, that oximes are intermediates in the hydrogen azide–carbonyl system has been adequately disproven.[11,13] A choice of two views appears possible. One, that the reaction of ketones with the two reagents, hydrogen azide and hydroxylamine-O-sulfonic acid, takes place by different mechanisms and the products of the hydroxylamine-O-sulfonic acid reaction are oximes or their rearrangement products, determined by the nature of the groups attached to the carbonyl carbon. The other, that the two reactions are similar and take place

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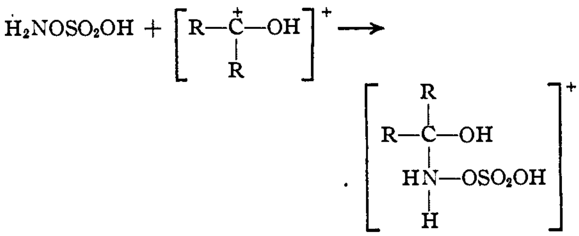
[14] I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1943.

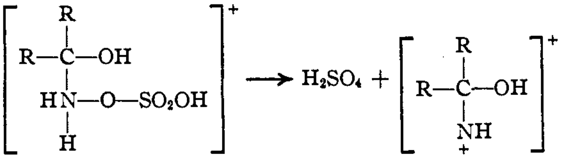
through the formation of a common unstable intermediate which rearranges in different ways, according to environment and substituent groups, to form oximes in some cases and amides in others. The actual formation of the oxime and its subsequent rearrangement would not be a requirement in those cases where an amide is the final product.

In spite of the lack of experimental evidence for the second choice, the similarity of the reagents lends it a certain amount of favor. The differences between the action of hydrogen azide and hydroxylamine-O-sulfonic acid with carbonyl compounds should be of degree rather than of kind. The first step of the reaction of hydroxylamine-O-sulfonic acid with ketones (if analogous to the mechanism[12,13,15] of the Schmidt reaction) would be the addition of the acid to the active form of the ketone:



$$H_2NOSO_2OH + \left[R-\overset{+}{\underset{R}{C}}-OH\right]^+ \longrightarrow \left[\begin{array}{l} \quad R \\ R-C-OH \\ \quad HN-OSO_2OH \\ \quad\ H \end{array}\right]^+$$

A shift[16] of a proton from the nitrogen to the adjacent oxygen and the splitting off of a sulfuric acid molecule lead to the residue postulated for the Schmidt reaction:



$$\left[\begin{array}{l} \quad R \\ R-C-OH \\ \quad HN-O-SO_2OH \\ \quad\ H \end{array}\right]^+ \longrightarrow H_2SO_4 + \left[\begin{array}{l} \quad R \\ R-C-OH \\ \quad \overset{}{NH} \\ \quad\ + \end{array}\right]^+$$

It seems possible that under the proper conditions the intermediate might change to the oxime and under other, probably more drastic, circumstances to the mixed amides found as products of the Schmidt reaction. The former case involves the shift of the OH group, while the latter requires the migration of the favored R group. The few experiments that involved different R groups show the following order in tendency to shift: *p*-anisyl, *p*-tolyl > phenyl > ethyl, isobutyl > methyl. It appears, that if an R group shifts, the group which is the most polarizable by the positive nitrogen of the intermediate is the favored one.

Another difference in the observed reactions of aromatic ketones with hydroxylamine-O-sulfonic acid and with hydrogen azide–sulfuric acid, the lack of carbon to nitrogen bond formation with the former, is easily explained. Fully aromatic ketones are known to be sluggish in addition reactions with such reagents as hydroxylamine and hydrazine where the addition depends upon the electrophilic nature of the carbonyl carbon. When one considers that there are six resonance forms for benzophenone other than that ordinarily written, $C_6H_5C{=}OC_6H_5$, which have the positive charge removed from the carbonyl carbon, the lessened tendency for the ketone to react with nucleophilic addenda is obvious. That hydroxylamine-O-sulfonic acid is less nucleophilic than hydrogen azide is indicated by its preparation from the latter and fuming sulfuric acid. A consideration of the structures and the electronegativities of the atoms attached to the potential nucleophilic nitrogen indicates that hydroxylamine-O-sulfonic acid should be less reactive toward ketones than hydroxylamine as well as hydrogen azide. It is believed that these two factors are sufficient to allow the Schmidt reaction to proceed and to prevent the reaction of hydroxylamine-O-sulfonic acid with fully aromatic ketones.

Further studies of the reactions of hydroxylamine-O-sulfonic acid with carbonyl compounds, which the authors hope will contribute to some of the unanswered questions, are in progress in this Laboratory.

Summary

1. The reaction of hydroxylamine-O-sulfonic acid with ketones has been studied. Aliphatic ketones yield oximes, mixed aliphatic-aromatic ketones yield N-aryl aliphatic amides, while fully aromatic ketones do not react.

2. A comparison of the action of hydroxylamine-O-sulfonic acid with that of hydrogen azide (in the presence of concentrated sulfuric acid) upon ketones has been made.

3. A tentative explanation of the course of the reactions and their significant differences has been offered.

NORTHAMPTON, MASSACHUSETTS

RECEIVED SEPTEMBER 8, 1945

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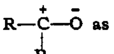
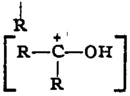
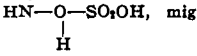
(15) Other authors[12,13] have used  $R-\overset{+}{\underset{R}{C}}-\overset{-}{O}$ as the active form of the ketone but we prefer the ion,  $\left[R-\overset{+}{\underset{R}{C}}-OH\right]^+$, since the reaction takes place in acid media. See also, G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, New York, N. Y., 1944, p. 244.

(16) The tautomeric form,  $\underset{H}{\overset{-}{HN}}-O-SO_2OH$, might be the addend, in which case the sulfuric acid could split off without any shift of a proton. Although this is more analogous to the splitting off of a molecule of nitrogen from hydrogen azide, the form in question has an unfavorable charge distribution and is believed to be less significant than the one used.