continued careful neutralization a small amount of material precipitated and was collected on a filter. Several recrystallizations from ethanol gave 62 mg of pale yellow crystals, mp 139–140°. The infrared spectrum showed the presence of an OH group in the molecule.

Anal. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38. Found: C, 61.91; H, 4.60.

Sodium Salt of 2-(2-Nitro-4-carboxybenzyl)pyridine.—To 2-(2-nitro-4-carboxybenzyl)pyridine[2] (0.1987 g) in 5 ml of water a stoichiometric amount of standardized sodium hydroxide solution was added. The solution was then clarified by filtration, and the filtrate was evaporated to dryness with a current of nitrogen. The white residue was recrystallized three times from a mixture of ethanol and acetone. An infrared spectrum showed strong absorptions at 1410 and 1615 cm^{-1} characteristic for the carboxylate anion group. (The precursor acid showed the carboxylic acid group at 1712 cm^{-1}.) The preparation of all the other compounds was described previously.[1,2,11]

Anal. Calcd for $C_{13}H_9N_2NaO_4$: C, 55.71; H, 3.24; N, 10.00. Found: C, 55.63; H, 3.13; N, 9.74.

Kinetic Measurements.—Samples for rate measurements were recrystallized or redistilled at reduced pressure before use. 2-(2-Nitro-4-aminobenzyl)pyridine was purified by chromatographic adsorption on a silica gel (Davison Chemical Co., grade 950) column and elution with 95% benzene–5% ethyl acetate, followed by recrystallization from ethanol to give bright yellow crystals, mp 127–128°. Spectro Grade absolute alcohol was used to prepare 10^{-4} *M* solutions.

The flash photolysis equipment and techniques used for the kinetic studies were described previously.[1,12] Measurements were made at 25°. The decrease in absorbance of the visible absorption band produced by ultraviolet irradiation was followed at 580 mμ with respect to time for all compounds except 2-(2-nitrobenzyl)pyridine and 2-(2-nitro-4-aminobenzyl)pyridine. For these compounds the dark reaction was followed at 400 and 500 mμ, respectively.

Values of the first-order rate constant, *k*, were calculated from the slope of the straight line in plots of log optical density *vs.* time. The reactions were followed for at least three half-lives.

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(11) A. J. Nunn and K. Schofield, *J. Chem. Soc.*, 583 (1952).
(12) L. Lindqvist, *Rev. Sci. Instr.*, **35**, 993 (1964).

Aralkyl Hydrodisulfides. VI. The Reaction of Benzhydryl Hydrosulfide with Several Nucleophiles

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In a previous paper,[1] reactions of benzyl hydrodisulfide with several inorganic anions and benzenethiolate ion were studied. It was reported that hydroxide and sulfite ions, which have weak nucleophilicity toward sulfur, attack initially the sulfenyl sulfur atom of the hydrodisulfide, yielding about 0.5 mole each of hydrogen sulfide and diaralkyl disulfide and various amounts of the other products but no thiol, and also that cyanide and thiolate ions having strong nucleophicity attack both sulfenyl and sulfhydryl sulfur. Attack on sulfhydryl sulfur was postulated to give the thiol besides other sulfur-containing compounds. In the reaction mechanism, any steric factor of the substrate of the reactants was not taken into consideration. In the present paper several inorganic anions and benzenethiolate ion were allowed to react with benzhydryl (diphenylmethyl) hydrodisulfide which may suffer steric hindrance as compared with the benzyl compound. The reactions were carried out under conditions similar to previous ones[1] and indicated similar features. The products are summarized in Table I. The variety and amounts of the products from the reaction of benzhydryl hydrodisulfide with hydroxide ion are quite similar to those from the benzyl compound. Therefore, the reaction seems to proceed through the same mechanism as reported in previous paper, *i.e.*, through sulfenyl sulfur attack. In the reactions of benzhydryl hydrodisulfide with cyanide and benzenethiolate ions, the distribution of the products was not greatly different from that from the benzyl hydrodisulfide reaction in the previous paper. However, a slight dissimilarity was observed about a little increased amount of the thiol in Table I compared with the corresponding one in the previous paper. This suggests that the attack on sulfenyl sulfur atom was sterically hindered, and that the attack on the alternative sulfhydryl sulfur contributed to the reaction more predominantly than in the case of the benzyl compound.

The most prominent distinction between the results in Table I and those in the previous paper is that in the reaction of benzhydryl hyrodisulfide with sulfite ion about 0.1 mole of diphenylmethanethiol was obtained from 1 mole of the hydrodisulfide, while the thiol was reported not to be detected from benzyl hydrodisulfide.[1] The formation of a detectable amount of the thiol may be interpreted by assuming that sulfhydryl sulfur attack contributes to the reaction at the expense of the sulfenyl sulfur attack by analogy with the above discussion. However, this presumption is denied for the following reason. The distribution of the products with cyanide will be discussed as representative of the mechanism for both sulfenyl and sulfhydryl sulfur attacks. In the case of benzenethiolate the distribution is made complexing because of the participation of benzenethiolate in the products and therefore kept away. The reaction mechanism with cyanide is again cited (Scheme I) from the previous paper.[1]

SCHEME I

Attack on sulfenyl sulfur

$$RSSH + CN^- \longrightarrow \underset{\uparrow CN^-}{RS{-}SH} \longrightarrow RSCN + SH^-$$

$$RSSH + RSCN \longrightarrow RSSR + HSCN$$

Attack on sulfhydryl sulfur

$$RSSH + CN^- \longrightarrow \underset{\uparrow CN^-}{RS{-}SH} \longrightarrow RS^- + HSCN$$

$$RS^- + RSSH \longrightarrow RSSR + SH^-$$

A detailed examination of Scheme I leads to the relationships that the amount of the diaralkyl disulfide is equal to that of hydrogen sulfide, and that the amount of thiocyanate is equal to the sum of the amounts of thiol and hydrogen sulfide (or the disulfide), whatever

(1) Part IV: S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *J. Org. Chem.*, **30**, 2711 (1965).

TABLE I

THE PRODUCTS FROM THE REACTION OF $(C_6H_5)_2CHSSH$ WITH NUCLEOPHILES (1:1 IN MOLES)[a]

Nucleophile	Thiol, mole	H_2S, mole	Free sulfur, g-atom	Combined sulfur, g-atom	Disulfide,[b] mole	SCN^-, mole	$S_2O_3^{2-}$, mole	Material balance H	Material balance S	Material balance $(C_6H_5)_2CH$
$C_6H_5S^-$	0.460[c] (0.310)[d]	0.688		0.202						
CN^-	0.366	0.270		0.185	0.272	0.639		91	100	91
SO_3^{2-}	0.110	0.390		0.327	0.256		0.140	89	74	62
OH^-	0	0.430	0.407		0.477			86	91	95

[a] Experiments were carried out in a small scale but the amounts of products were recalculated to a 1-mole scale for convenience of discussion. [b] The value containing the disulfide derived from polysulfide. [c] The sum of benzenethiol and diphenylmethanethiol. [d] The amount of benzenethiol only.

proportion of sulfenyl or sulfhydryl attack contributes to the reaction. The result with cyanide in Table I satisfied the above relationships almost completely. A similar result was obtained also in previous paper[1] on the product distribution from benzyl hydrodisulfide with cyanide. As to the products with sulfite in the present paper, the amount of thiosulfate is far less than the amount of thiocyanate, and the distribution of the products is different from that with cyanide. The result excludes the mechanism by both sulfenyl and sulfhydryl sulfur attacks. Moreover, the sulfenyl sulfur attack is eliminated also for the reason that Bunte salt $RSSO_3^-Na^+$ of diphenylmethanethiol could not be prepared in spite of all our efforts, while that of α-toluenethiol was prepared easily by the method in the literature.[2] Probably the sulfenyl sulfur attack is prohibited by steric hindrance of both substrate and sulfite ion, the nucleophilic center of which is considered to be located at the sulfur atom and hence surrounded by oxygen atoms. However, some extent of contribution of sulfhydryl sulfur attack to the reaction cannot be excluded. From the point of view of steric hindrance, triphenylmethyl hydrodisulfide, the sulfenyl sulfur of which is sterically most hindered in the present aralkyl series, was allowed to react with potassium hydroxide. Although all the products, unfortunately, could not be isolated, triphenylmethanethiol alone was detected qualitatively. Therefore, it seems clear that even the least bulky nucleophile such as hydroxide can hardly attack the sulfenyl sulfur in triphenylmethyl hydrodisulfide. A previous paper[3] reported that triphenylphosphine attacks triphenylmethyl hydrodisulfide exclusively on sulfhydryl sulfur atom. The remaining step of predominant reaction with sulfite may be hydrogen abstraction from the sulfhydryl group; this and the probable succeeding steps are indicated in Scheme II.

SCHEME II

$$RSSH + SO_3^{2-} \longrightarrow RSS^- + HSO_3^-$$

$$RSS^- + RSSH \xrightarrow{H^+} 2RSH + 2S \text{ or}$$

$$\longrightarrow RSSSR + SH^-$$

Since sulfite ion converts the atomic sulfur formed in the reaction to thiosulfate, the relationship that the amount of the thiol is equal to that of thiosulfate will hold. Furthermore, since trisulfide produced in the reaction is not desulfurated by sulfite at room temperature, the relationship that the amount of trisulfide is equal to that of hydrogen sulfide also will hold. The values indicated in Table I almost satisfy the above two requirements. Therefore, sulfite ion is considered to be forced to abstract the proton attached to the sulfhydryl group and/or attack the sulfhydryl sulfur atom. This leads to the formation of a certain amount of various anions such as RS^-, RSS^-, and SH^-, which in turn attack hydrodisulfide by various possible ways and make the distribution of products complex. In view of the several reaction mechanisms with the nucleophiles, a brief summary will be made. As reported in the previous paper, in the absence of steric hindrance the weaker nucleophiles, such as hydroxide and sulfite ions, attack exclusively the sulfenyl sulfur of benzyl hydrodisulfide. In the presence of steric hindrance, as in benzhydryl hydrodisulfide, only less bulky ions like hydroxide can react on the sulfenyl sulfur. More bulky ions, such as sulfite, cannot, however, react with the sulfenyl sulfur of benzhydryl hydrodisulfide but may induce the decomposition to yield a complicated distribution of products. Stronger nucleophiles, such as cyanide and thiolate ions, attack both sulfenyl and sulfhydryl sulfur atoms, but sulfhydryl sulfur attack in benzhydryl hydrodisulfide is more predominant than in the benzyl compound.

Experimental Section

Materials.—Benzhydryl[4] and triphenylmethyl[5] hydrodisulfides were prepared by the methods reported elsewhere.

The Reaction of Benzhydryl Hydrodisulfide with Potassium Hydroxide, Cyanide, and Benzenethiolate.—Benzhydryl hydrodisulfide, 3–4.5 g, in dioxane was allowed to react with each of the above nucleophiles in a nitrogen stream at room temperature. Crystals appeared in the solution after 2 or 3 hr. The reaction mixture was extracted with benzene. The benzene extract was examined and reaction products were identified by the previous method.[1] Other experimental conditions and procedures were similar to those of previous paper.

Reaction of Benzhydryl Hydrodisulfide with Potassium Sulfite.—Benzhydryl hydrodisulfide, 3 g (0.0129 mole) in 20 ml of dioxane was allowed to react with an equimolar amount of potassium sulfite dihydrate in 10 ml of water. The reaction mixture became brown, turned to yellow, and faded after a few minutes. After being kept overnight, it was neutralized (pH 6). Most of hydrogen sulfide evolved before the neutralization. Organic products were extracted with benzene after a large amount of water was added. The amount of thiosulfate ion in the water layer was determined by a previously described method.[1] For the determination of the amount of diphenylmethanethiol formed, see the following paragraph. An aliquot was used to determine the amount of polysulfidic sulfur by triphenylphosphine.[1] The remaining benzene extract was evaporated under reduced pressure and a white solid was obtained. This

(2) R. A. Purgotti, *Gazz. Chim. Ital.*, **20**, 25 (1890).

(3) Part III: J. Tsurugi, T. Nakabayshi, and T. Ishihara, *J. Org. Chem.*, **30**, 2707 (1965).

(4) J. Tsurugi and T. Nakabayashi, *ibid.*, **24**, 807 (1959).

(5) T. Nakabayashi, J. Tsurugi, and T. Yabuta, *ibid.*, **29**, 1236 (1964).

solid showed mp 60–120° after desulfurization with sodium sulfite and was fractionated by treatment with *n*-hexane into two parts: a very viscous oil and white crystals. The latter was dibenzhydryl disulfide, mp 150–151°; the mixture melting point with an authentic sample was undepressed. The former, which could not be identified, was excluded from the material balance in Table I. Other procedures were the same as those given in a previous paper.[1]

Identification and Estimation of the Reaction Products.—In the case of the reaction of benzhydryl hydrodisulfide with potassium hydroxide, sulfur was separated as follows. An appropriate amount of dimethylformamide was added to the solid which was obtained from the benzene extract by removal of solvent. The solution immediately became red, and then turned to yellow. The yellow crystals precipitated, were filtered, collected, and recrystallized from benzene: mp 118–119°, mmp 118–119° with authentic sulfur. Diphenylmethanethiol was titrated with 0.1 *N* sodium thiosulfate solution after the addition of an excess of 0.1 *N* alcoholic iodine solution. Quantitative analyses of other products—hydrogen sulfide, polysulfidic sulfur, inorganic ions, etc.—were carried out as described in a previous paper[1] and are listed in Table I.

Reaction of Triphenylmethyl Hydrodisulfide with Potassium Hydroxide.—Triphenylmethyl hydrodisulfide, 1.99 g (0.0065 mole), in 25 ml of dioxane was allowed to react with an equimolar amount of potassium hydroxide in 10 ml of water under a nitrogen stream at room temperature. The solution became immediately red and then orange. Hydrogen sulfide, 0.0016 mole (0.249 mole/mole), was evolved when it was neutralized with 4 *N* hydrochloric acid after being kept overnight. In the reaction mixture a yellow precipitate was formed, which sintered at 155° and melted at 160° (unidentified with any known substances). Then organic material was extracted with benzene. The existence of triphenylmethanethiol in the benzene layer was recognized qualitatively by its characteristic odor and by using rubeanic acid as a detecting reagent for thiol. Other reagents, such as lead acetate, nitrosyl chloride, and sodium nitroprusside, for detection of thiols did not react with authentic triphenylmethanethiol.

Carbon-14 Isotope Effects in the Beckmann Rearrangement[1a]

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The transformation of ketoximes to amides ($R_2C{=}NOH \rightarrow RCONHR$) is catalyzed by such acidic reagents as phosphorus pentachloride, phosphorus pentoxide, and sulfuric acid. It is well established that the migrating group in the Beckmann rearrangement approaches the nitrogen from the side opposite that of the departing oxygen atom. It is not possible to say whether the cleavage of the N–O bond and the shift of the alkyl (or aryl) group are concerted. Yukawa and Kawakami[2] have reported relatively large reverse carbon-14 isotope effects in the rearrangement of methylene-labeled phenyl-2-propanone oxime and phenyl-1-labeled acetophenone oxime ($k_{14}/k_{12} = 1.052$ and 1.121, respectively). These results were thought to favor a mechanism in which the migrating group participates in the fission of the N–O bond.

Small secondary reverse isotope effects of carbon-14 have been reported,[3,4] but heretofore no primary reverse isotope effect of carbon-14 has been substantiated.

We have repeated the work of Yukawa and Kawakami; the pertinent data are given in Table I. Our observations do not substantiate their findings. It is significant that considerable hydrolysis of the oximes to the parent ketones occurs during the reaction. Acetophenone oxime was treated with concentrated sulfuric acid at 62 ± 1° for 40 min. The nmr spectrum of the chloroform extract of the acetophenone oxime reaction mixture shows methyl resonances characteristic of acetophenone a well as of the oxime and acetanilide (see Table II). For this reason the determination of acetanilide was considered to be of little value. Hydrolysis of the phenyl-2-propanone oxime is likewise evident from the nmr spectrum of the chloroform extract of the reaction mixture. Furthermore, no resonances characteristic of N-benzyl acetamide appear, and all attempts to isolate the amide failed.

Since the oxime is partly destroyed by hydrolysis, little significance can be attached to the small normal isotope effect observed for both labeled species of acetophenone oxime. Within the limits of experimental error (<1%), no isotope effect was observed in the reaction of methylene-labeled and carbonyl-labeled phenyl-2-propanone oxime.[5]

It is questionable whether the sulfuric acid catalyzed reaction of phenyl-2-propanone oxime is truly a Beckmann rearrangement. This reaction has been treated as a special case by Horning and co-workers.[6] The rearrangement can be effected by catalsis with baron trifluoride in acetic acid[7] or with polyphosphoric acid.[6] We have been unable to detect any amide produced on treatment of the oxime with concentrated sulfuric acid. Phenyl-2-propanone oxime was difficult to purify, giving first an oil composed of both *syn* and *anti* forms (nmr spectrum) and, after considerable manipulation, a solid consisting of the pure *anti* isomer (mp 69–70°). The isomerization of this oxime has been discussed in the literature.[8] If carbon-14-labeled ketoxime were diluted with nonlabeled material containing a different ratio of the *syn* and *anti* forms, then it is possible that an apparent (but unreal) isotope effect would seem to accompany the reaction. Such a difficulty, together with the inaccuracies of solid counting, might account for the unusual observations reported by Yukawa and Kawakami.

Experimental Section

Rearrangement of Acetophenone Oximes.—Cold concentrated sulfuric acid (50 ml, Du Pont reagent grade, 95–98%, sp gr 1.84) was added with stirring to the oxime (*ca.* 2.00 g) in an ice-cooled 125-ml erlenmeyer flask. The reaction vessel was immersed in hot water, swirled until the temperature reached

(1) (a) Research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.; (b) U. S. Atomic Energy Commission Postdoctoral Fellow under appointment from the Oak Ridge Institute of Nuclear Studies.

(2) Y. Yukawa and M. Kawakami, *Chem. Ind.* (London), 1401 (1961).

(3) V. F. Raaen, A. K. Tsiomis, and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 5502 (1960).

(4) V. F. Raaen and C. J. Collins, *Pure Appl. Chem.*, **8**, 347 (1964).

(5) Because at least one competitive reaction (hydrolysis) occurs in this low-yield rearrangement, the determination of residual oxime plus ketone is of limited use although this method was used in the earlier study.[2] We have used the same general procedure in order to validate the comparison of isotope effect data and not because we believe that oxime concentration is always relevant to the Beckmann rearrangement.

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

(7) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1482 (1955).

(8) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).