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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Received November 19, 1965

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

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(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.

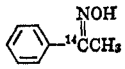
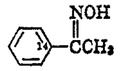
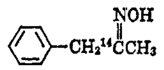
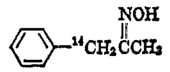
(6) E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.*, **74**, 5153 (1952).

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

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

TABLE I

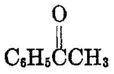
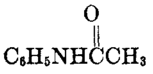
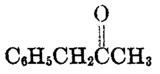
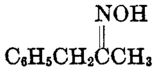
PERCENT REACTION AND RATIO OF MOLAR RADIOACTIVITIES OF RESIDUAL OXIME

Ketoxime	Temp, °C	Time, min	% reaction[a]	Ratio of molar radioactivities[b]
	26 ± 1	40	28	1.000
		100	48	1.030
		325	84	1.050
		420	91	1.067
	62 ± 1	60	36	1.034
		170	64	1.032
		255	76	1.050
		385	88	1.067
	50 ± 1	2	7	0.9959
		31	32	0.9937
		61	47	0.9967
		91	56	0.9995
	50 ± 1	2	7	1.000
		26	29	1.006
		56	44	1.001
		86	54	1.002
		163	72	1.004

[a] Determined by isotope dilution of combined ketone and unreacted oxime. [b] Obtained by dividing the molar radioactivity of the residual ketoxime–ketone mixture by the molar radioactivity of the ketoxime before reaction.

TABLE II

CHEMICAL SHIFTS OF REACTANTS AND PRODUCTS[a]

Compd	Protons	Chemical shift[b,c] ppm
 $C_6H_5C(=O)CH_3$	C_6H_5 CH_3	7.60 2.60
 $C_6H_5C(=NOH)CH_3$	C_6H_5 CH_3	7.51 2.28
 $C_6H_5NHC(=O)CH_3$	C_6H_5 CH_3	7.30 2.10
 $C_6H_5CH_2C(=O)CH_3$	C_6H_5 CH_3 CH_2	7.25 3.58 2.01
 $C_6H_5CH_2C(=NOH)CH_3$	C_6H_5 CH_2 CH_3	7.20 3.50 1.80
 $C_6H_5CH_2C(=NOH)CH_3$	C_6H_5 CH_2 CH_3	7.20 3.75 1.76
 $C_6H_5CH_2NHC(=O)CH_3$	C_6H_5 CH_2 CH_3	7.13 4.15 (doublet) 1.76

[a] All spectra were taken in chloroform with the Varian A-60 nmr spectrophotometer. [b] Chemical shift measured from TMS internal standard. [c] All methylene and methyl resonances were singlets except for the methylene doublet indicated.

61–62°, and immediately transferred to a constant-temperature bath at 62 ± 1°.

At various time intervals a 10-ml aliquot of the reaction mixture was pipetted into 10 ml of cold ethanol (95%) in a 125-ml erlenmeyer flask, and 50 ml of 0.1 *N* 2,4-dinitrophenylhydrazine reagent solution (prepared by adding 15 ml of concentrated sulfuric acid, 15 ml of water, and 250 ml of ethanol to 5.0 g of 2,4-dinitrophenylhydrazine) was added. The mixture was heated on a steam bath for 30 min and was cooled to 0°; the precipitate was collected on a sintered-glass funnel. The 2,4-dinitrophenylhydrazone was washed with cold ethanol (95%) and was recrystallized to a constant melting point from chloroform–ethanol mixtures. Acetophenone oxime gives the derivative in quantitative yield; phenyl-2-propanone ketoxime gives the 2,4-dinitrophenylhydrazone in 96% yield. The use of 2,4-dinitrophenylhydrazones as derivatives was validated in other isotope effect studies.[1]

The 2,4-dinitrophenylhydrazones were burned in a Preg microcombustion apparatus similar to that described by Tolbert and Siri.[9] The labeled carbon dioxide was swept into an ionization chamber for measurement on an electrometer.

Reaction of Phenyl-2-propanone Oximes.—The procedure described for acetophenone oximes was followed except that the reaction was carried out at 50 ± 1° and the aliquots were pipetted into 10 ml of cold water instead of ethanol.

Determination of Percent Reaction.—Nonradioactive oximes were subjected to the reaction conditions described above, and the aliquots were pipetted into cold ethanol or water that contained a weighed amount of labeled oxime. After the determination of the radioactivity, the percent reaction was calculated by the isotope-dilution method.

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[9] B. M. Tolbert and W. E. Siri, "Technique of Organic Chemistry," Vol. I, Part IV, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 3431, 3432.

Cycloaddition of 6,6-Dimethylfulvene with Benzynes[1]

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Received November 24, 1965

Because of interest in the homobenzylic behavior observed at the 7-position of benzonorbornene derivatives,[2] a good synthetic method for these derivatives has been required by us. This report describes the cycloaddition of benzynes to 6,6-dimethylfulvenes (**1**) (Scheme I) by a modified Wittig's procedure[3,4] and some interesting properties of the derived cycloadducts, which have a new conjugated system.

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[1] Part XIII of a series on Bicyclic Systems. Part XII: H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864 (1966).

[2] (a) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (b) H. Tanida, H. Miyazaki, and H. Ishitobi, *Can. J. Chem.*, **44**, 98 (1966).

[3] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[4] H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Japan*, **37**, 40 (1964).