

proton transfer. Loss of the carbanion is undoubtedly favored by the presence of the stabilizing sulfone group.

Experimental Section

Benzyl 2-Ketocyclopentyl Sulfone (3a).—The sulfone was prepared analogously to the cyclohexyl⁴ sulfone and, after recrystallization from ethanol, melted at 94–95° (74%). The nmr spectrum has peaks at $\tau = 2.5$ –2.7 (m, phenyl), 5.16, 5.40, 5.62, 5.86 (AB, $J = 14.0$ cps, benzylic), 6.3–6.6 (m, CHSO_2), and 7.4–8.3 ppm (m, remaining protons) in an area ratio of 5:2:1:6.

Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$: C, 60.5; H, 5.9; S, 13.4. Found: C, 60.4; H, 6.1; S, 13.2.

Cleavage of Acyclic β -Keto Sulfones with Pyrrolidine.—The β -keto sulfone was heated under reflux for 1 hr with a solution of 10 g of pyrrolidine in 200 ml of benzene. The sulfone was obtained by concentration of the solution and was recrystallized from ethanol. The ethanol filtrate, upon concentration, was found to contain 1-(phenylacetyl)pyrrolidine and identified by comparison of its infrared spectrum and gas chromatographic retention time with those of an authentic sample.⁵ It was isolated by distillation in 62% yield from cleavage of 1a. Each sulfone was identified by comparison of its infrared spectrum with that of authentic material; mixture melting points were not depressed. See Table I for weights and yields.

TABLE I

β -Keto sulfone ^a	g (mole)	Sulfone	Yield, %
1a	5.0 (0.012)	2a	98
1b	3.4 (0.0093)	2b	100
1c	2.2 (0.0076)	2c	70
1d	0.40 (0.0014)	2d	58

Cleavage of Cyclic β -Keto Sulfones.—By using the procedure described for cleavage of acyclic β -keto sulfones, 1.0 g (0.0040

(5) J. W. Cusic, U. S. Patent 2,776,282; *Chem. Abstr.*, **51**, 8813 (1957).

mole) of benzyl 2-ketocyclohexyl sulfone⁴ was converted into 0.55 g (43%) of amide **4b**, mp 112–113°. It was isolated by recrystallization of the reaction mixture from ligroin–benzene.

Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{S}$: C, 63.1; H, 7.8; N, 4.3; S, 9.9. Found: C, 63.0; H, 7.5; N, 4.2; S, 9.8.

The nmr spectrum had peaks at $\tau = 2.65$ (s, phenyl), 5.82 (s, benzylic), 6.5–6.7 (m, pyrrolidino), 7.20–7.3 (t, $J = 7$ cps, CH_2 adjacent to SO_2), and 7.8–8.5 ppm (overlapping multiplets, remaining protons) in an area ratio of 5:2:4:2:12.

A solution of 8.5 g (0.034 mole) of benzyl 2-ketocyclohexyl sulfone in 300 ml of benzene containing 30 ml of pyrrolidine was heated at reflux for 16 hr and the water was separated. Concentration and addition of absolute ethanol caused a solid to separate which was recrystallized from ethanol to give 4.8 g (46%) of enamine **5b**, mp 95–96°. From the filtrate was obtained 0.6 g (6%) of amide **4b**. On standing a few minutes open to the air, the enamine was hydrolyzed to the starting ketone.

Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{S}$: C, 67.0; H, 7.6; N, 4.6; S, 10.5. Found: C, 66.8; H, 7.3; N, 4.3; S, 10.8.

The nmr spectrum had peaks at $\tau = 2.65$ (s, phenyl), 5.05 (t, $J = 3.0$ cps, olefinic), 5.62 and 5.64 (benzylic, AB), 6.08 (m, allylic adjacent to SO_2), and 6.5–8.3 ppm (m, remaining overlapping peaks) in an area ratio of 5:1:2:1:14.

A 4.8-g (0.020 mole) portion of benzyl 2-ketocyclopentyl sulfone (**3a**) was cleaved by each of the procedures described for β -keto sulfone **3b**. When the reaction time was 1 hr, amide **4a** was obtained in 67% yield upon recrystallization of the product from benzene, mp 125–126°. With a 16-hr reaction time and water separation, 4.8 g (80%) of the amide was isolated. Enamine **5a** was not isolated from the filtrates.

Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_3\text{S}$: C, 62.1; H, 7.5; N, 4.5; S, 10.4. Found: C, 61.9; H, 7.8; N, 4.3; S, 10.6.

The nmr spectrum of amide **4a** had peaks at $\tau = 2.57$ (s, phenyl), 5.75 (s, benzylic), 6.4–6.7 (m, pyrrolidino), 7.10 (t, $J = 8.0$ cps, CH_2SO_2), 7.73 (t, $J = 6.0$ cps, CH_2CO), and 8.0–8.3 ppm (m, remaining protons) in an area ratio of 5:2:4:2:8.

Hydrolysis of Enamine 5b.—A solution of 0.50 g (0.0016 mole) of the enamine in 10 ml of 1,2-dimethoxyethane and 10 ml of 3 *N* hydrochloric acid was heated on a steam bath for 30 min and concentrated. The residue was extracted into ether, washed with water, dried, and concentrated to give 0.39 g (100%) of benzyl 2-ketocyclohexyl sulfone, mp 100–101°. A mixture melting point with an authentic sample⁴ was not depressed.

Preparation of Sulfones.—*p*-Chlorobenzyl benzyl sulfide was prepared from 8.0 g (0.050 mole) of α ,*p*-dichlorotoluene, 6.2 g (0.050 mole) of α -toluenethiol, 50 ml of ethanol, and 2.0 g (0.050 mole) of sodium hydroxide, bp 154° (0.1 mm), 8.7 g (62%).

Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClS}$: C, 67.5; H, 5.3; Cl, 14.3; S, 12.9. Found: C, 67.6; H, 5.2; Cl, 14.6; S, 13.2.

Oxidation of 2.5 g of this sulfide with potassium permanganate gave 2.2 g (98%) of sulfone **2a**, mp 168–169° (lit.⁶ mp 167–168°).

Benzyl methyl sulfone was prepared (65%) by potassium permanganate oxidation of the corresponding sulfide,⁷ mp 125–126° (lit.⁸ mp 127°).

Dibenzyl sulfone was prepared (78%) by potassium permanganate oxidation of the corresponding sulfide, mp 150–151° (lit.⁸ mp 150°).

Acknowledgment.—The author is grateful to Dr. T. H. Regan for the nmr spectra.

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C^{14} Tracer Studies in the Wallach Transformation

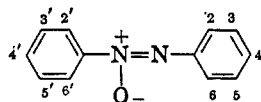
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In the Wallach transformation azoxybenzene is converted into 4-hydroxyazobenzene (among other prod-

ucts) by sulfuric acid.¹ Shemyakin, Maimind, and Vaichunaite² rearranged azoxybenzene with N¹⁵ as a label and reported that the oxygen had appeared at the erstwhile 4 and 4' positions on the hydroxyazobenzenes and observed that the 4 position was slightly favored. It was felt by us that employment of ring labeling



would provide a firmer basis for considering a possible mechanism for the rearrangement, since the use of N¹⁵ assumes that each nitrogen remains attached to its ring throughout the rearrangement, certainly a reasonable hypothesis but one violated to some extent with diazonium ions.³ Therefore, azoxybenzene-1-C¹⁴ of known structure was prepared⁴ by vigorous oxidation of 2-(phenyl-1-C¹⁴)-3-cyanoindazole 1-oxide, followed by decarboxylation of the resultant azoxybenzene-2'-carboxylic acid-1-C¹⁴. The indazole was synthesized by condensing *o*-nitrobenzaldehyde and aniline-1-C¹⁴, followed by converting the anil thus formed to the cyano compound, and closing the ring with elimination of water.

The azoxybenzene-1-C¹⁴ was rearranged to hydroxyazobenzene by heating with concentrated sulfuric acid. The location of the tracer carbon atom was determined by reductive cleavage to aniline and *p*-aminophenol. Radioactive assays of the azoxybenzene, *p*-aminophenol, and acetanilide, to which the aniline had been converted, showed that the oxygen had appeared at the erstwhile 4 and 4' positions on the hydroxyazobenzenes, with the 4' position slightly favored.

Our results are therefore in essential agreement with those previously reported² though the slight excess of the 4' vs. 4 substitution, the opposite of that previously reported, remains unexplained. At any rate, a symmetrical intermediate appears to play an important part.^{5,6}

Experimental Section

2-(Phenyl-1-C¹⁴)-3-cyanoindazole Oxide.—A 30.2-g portion of *o*-nitrobenzaldehyde was condensed with 18.6 g of aniline-1-C¹⁴ and the resulting anil was converted to 2-(phenyl-1-C¹⁴)-3-cyanoindazole 1-oxide, mp 194–195°, by the method of Behr.⁴ The yield was 15.0 g (70% over-all).

Azoxybenzene-1-C¹⁴-2'-carboxylic Acid.⁴—2-(Phenyl-1-C¹⁴)-3-cyanoindazole 1-oxide (12.0 g) was heated under reflux for 2 hr with chromic anhydride and acetic acid, allowed to cool, and poured into water. Successive extractions with ether and 10% aqueous sodium hydroxide, followed by acidification with 10% phosphoric acid, precipitated a sticky substance which later solidified. The solid was air dried and recrystallized from benzene-hexane as small, orange crystals, mp 102–103°, yield 8.0 g (64%).

Azoxybenzene-1-C¹⁴.—Azoxybenzene-1-C¹⁴-2'-carboxylic acid (8.0 g) was heated under reflux with copper powder and a trace of cupric acetate in pyridine for 18 hr. After the flask had cooled, the contents were filtered and the insoluble material was washed with ether. The combined filtrate was poured into 500 ml of ether and the ether solution was washed successively

with 10% hydrochloric acid, water, 5% aqueous sodium hydroxide, and again with water. The solution was dried and the ether was evaporated. The crude azoxybenzene (6.0 g), mp 32–34°, was separated from impurities by chromatography on an alumina column with hexane the mobile solvent. The yield was 4.5 g (68%) of azoxybenzene-1-C¹⁴, mp 35–36°.

The Wallach Transformation.—A solution of 4.0 g of azoxybenzene-1-C¹⁴ in 40 ml of 83% sulfuric acid was heated at 90° for 30 min and the products were separated and purified according to the procedure of Gore and Hughes.⁷ Crude *p*-hydroxyazobenzene in an amount of 2.2 g was obtained. Recrystallization from benzene gave 2.0 g (50%) of the phenol, mp 152–153°.

Reductive Cleavage of *p*-Hydroxyazobenzene-C¹⁴.—*p*-Hydroxyazobenzene⁸ (1.72 g) was reductively cleaved in the manner described in the literature to give *p*-aminophenol and aniline.

The *p*-aminophenol was recrystallized from 95% ethanol and weighed 0.474 g (50%), mp 193–194°. The aniline was converted to acetanilide which, after two crystallizations from water, weighed 0.603 g (51% over-all), mp 114°.

Radioactivity Assays.—The samples were assayed in duplicate with an error of about ±2%, or less, which is approximately that to be expected for samples of this level of radioactivity. The results are given in the Table I.

TABLE I

RADIOACTIVITY OF C ¹⁴	
Compd	μcurie/mmole
Azoxybenzene	0.3550
Acetanilide	0.1730
<i>p</i> -Aminophenol	0.1627

Acknowledgment.—The authors are indebted to Dr. C. J. Collins for the radioactivity assays.

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1,1,4,6,7-Pentamethylindan

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Isoprene combines with 1,2,4-trimethylbenzene (pseudocumene) in the presence of concentrated sulfuric acid to give a crystalline hydrocarbon, mp 74–76°, in 70% yield. 1,1,4,6,7-Pentamethylindan (1) was suggested² as the most likely structure for this new hydrocarbon. The most convincing argument for this assignment is the known course of electrophilic substitution of 1,2,4-trimethylbenzene in comparable reactions and comparison with products obtained from other cyclalkylation reactions. The nmr, mass, and infrared spectra of the new hydrocarbon clearly showed it to be a pentamethylindan. However, these data failed to eliminate conclusively structure 2 as a possibility. It is recognized that an appropriate catalog of nmr spectra

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