

butene was approximately 20:4:1 in each case. The concentration of 2-phenylbutene in the reaction mixture had decreased appreciably in the course of 7.1 hours.

A solution of 2.7 g. of *cis*-II²⁵ in 150 ml. of formic acid, f.p. 8.0°, was heated at 79.7 ± 0.1° for 17 hours. The reaction mixture was worked up as before and distilled to give a trace of forerun, which was discarded, and 1.7 g. of product, b.p. 140–142° (0.8 mm.), *n*_D²⁰ 1.5638.

Anal. Calcd. for C₂₀H₂₄: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 90.88; H, 9.14; mol. wt., 235.

The dimeric hydrocarbon gave negative tests for unsaturation with potassium permanganate in acetone and bromine in carbon tetrachloride. The infrared spectrum of this product showed no indication of an olefinic double bond. Redistillation caused no significant changes in either the infrared spectrum or the elementary analysis.

The Racemization of (–)-*threo*-3-Phenyl-2-butanol ((–)-*threo*-IV).—Racemic *threo*-3-phenyl-2-butyl acid phthalate, m.p. 131–132° (lit.⁵ m.p. 130–131°), was resolved by the procedure of Cram.⁵ Saponification of (–)-*threo*-3-phenyl-2-butyl acid phthalate, m.p. 102–103° (lit.⁵ m.p. 101–102°), gave (–)-*threo*-IV, b.p. 107° (12 mm.) (lit.⁵ b.p. 108° (10 mm.)) which had a single elution peak in gas chromatography.

Three samples of (–)-*threo*-IV were heated at 80.2 ± 0.1° in formic acid, f.p. 7.8°. The reaction mixtures were removed from the constant temperature bath at various times, and the ester products were converted into carbinol with lithium aluminum hydride in ether for measurement of

optical rotation. The results are summarized in Table IV. Flash distillation of the product gave, in each case, 80 to 90% recovery of *threo*-IV, which had a single elution peak in gas chromatography, and which had an infrared spectrum like that of the starting material.

The Reaction of 1-Octene with Formic Acid.—A solution of 1-octene (9.00 g., 0.0802 mole) in 200 ml. of formic acid, f.p. 7.5°, was heated at 80.2 ± 0.1° for 45 minutes. The reaction mixture was neutralized with cold 10% sodium hydroxide solution and extracted with ether. The ether solution was washed with water, dried, and evaporated. The residue was examined by means of gas chromatography (Table V) then distilled to give 3.68 g. of recovered olefin, b.p. 121–122°; 0.56 g. of an intermediate fraction, b.p. 122–191°; 6.45 g. of 2-octyl formate, b.p. 181–183° (lit.²⁶ b.p. 81–82° (20 mm.)); and 0.2 g. of pot residue. The infrared spectrum of the olefin fraction was identical in every major respect with that of authentic 1-octene. The ester fraction was treated with excess lithium aluminum hydride in ether, and the recovered alcohol was distilled. This product gave a single elution peak in gas chromatography and its infrared spectrum was like that of authentic 2-octanol except for an unidentified peak at 7.53μ which was not present in the spectrum of authentic 3- or 4-octanol, nor in that of the formate before treatment with lithium aluminum hydride, and thus seems to be due to accidental contamination of the sample or sample cell.

(26) R. H. Pickard, J. Kenyon and H. Hunter, *J. Chem. Soc.*, **123**, 1 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Some Condensations at the Methylene and Terminal Methyl Groups of Benzenesulfonylacetone Through its Mono- and Dipotassio Salts^{1,2}

BY WM. IVO O'SULLIVAN,³ DONALD F. TAVARES AND CHARLES R. HAUSER

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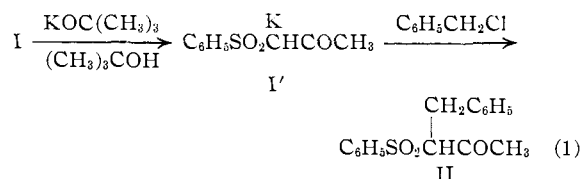
Benzenesulfonylacetone was benzylated and benzoylated at its methylene group through its monopotassio salt to form the C-benzyl and O-benzoyl derivatives, respectively. The benzyl derivative was coupled with benzenediazonium chloride to give an azo compound, whereas benzenesulfonylacetone was converted by this reagent to a phenylhydrazone. Benzenesulfonylacetone was benzoylated and benzoylated at its terminal methyl group through its dipotassio salt to form the corresponding C-derivatives. The dipotassio salt was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. The benzoyl derivative was cyclized with hydrazine to give a pyrazole, nitrosated with nitrous acid to produce an oxime, and independently synthesized from 1-bromobenzoylacetone and sodium benzenesulfinate.

Benzylation and benzoylation at the methylene and terminal methyl groups of benzoylacetone have been effected previously through its mono- and dialkali salts, respectively.⁴

In the present investigation such condensations at the methylene and terminal methyl groups of benzenesulfonylacetone (I) were effected.

Results with Monopotassio Salt of I.—Because I is similar to β-diketones having a reactive methylenic⁵ or methinyl hydrogen,⁶ it was converted by potassium *t*-butoxide in *t*-butyl alcohol to its monopotassio salt I', which was alkylated with benzyl chloride in this medium to give the methylene derivative II in 75% yield (eq. 1).

That the product was the expected C-benzyl derivative II and not the possible O-benzyl derivative was shown by its infrared spectrum, which



gave a strong band at 5.8 μ for the carbonyl group.⁷ Moreover the product gave a positive carbonyl group test with 2,4-dinitrophenylhydrazine.

Structure II was further established by coupling it with benzenediazonium chloride in the presence of sodium acetate to form azo derivative III. Also the original sulfone-ketone I reacted with this reagent but the resulting azo derivative underwent isomerization to give phenylhydrazone IV.⁸ Methylene substituted and unsubstituted β-diketones are known to undergo analogous reactions to produce the corresponding azo compound and phenylhydrazone, respectively.⁹ For example, acet-

(7) See L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 132.

(8) Only one of the two possible geometric isomers appeared to be obtained; its structure was not determined.

(9) See S. M. Farmerter, "Organic Reactions," Vol. X, John Wiley and Sons, Inc., New York, N. Y., 1959, Chap. 1.

(1) Supported by the U. S. Army Research Office (Durham).

(2) Reported at the Cleveland, Ohio, Meeting of the American Chemical Society, April, 1960.

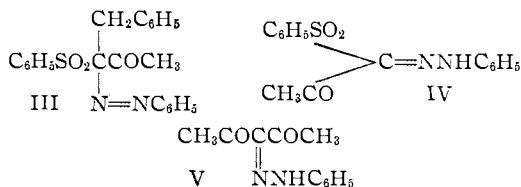
(3) On leave from the University College, Dublin, Ireland.

(4) See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

(5) See D. F. Martin, W. C. Fernelius and M. Shamma, *ibid.*, **81**, 130 (1959).

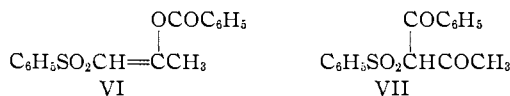
(6) See P. J. Hamrick, C. F. Hauser and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959).

ylacetone forms phenylhydrazone V,¹⁰ which was prepared for the purpose of comparison.



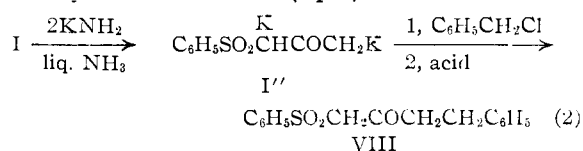
Hydrazone IV and V showed ultraviolet absorption maxima in the 350–400 $m\mu$ region as reported for ordinary phenylhydrazones¹¹ and both were soluble in dilute alkali. The azo compound III had no such absorption and it was insoluble in dilute alkali.

Next sulfone-ketone I was converted by a molecular equivalent of potassium amide to its monopotassium salt I', which was benzoylated with benzoyl chloride¹² in ether to form a product (42–52%) that appeared to be the O-benzoyl derivative VI, not the C-benzoyl derivative VII.



That the product was VI, not VII, was supported by its failure to form a copper chelate or a 2,4-dinitrophenylhydrazone under the usual conditions and by its infrared spectrum, which showed a strong band in the carbonyl region at 5.71 μ . This value is slightly higher than that (5.65 μ) reported for a vinylic or phenolic ester group,¹³ but this might be due to an inductive effect of the benzenesulfonyl group. The value expected for a β -diketone such as VII would be considerably higher (6.1–6.5 μ).¹⁴

Results with Dipotassio Salt I.—Similar to benzoylacetone,⁴ sulfone-ketone I was converted by two molecular equivalents of potassium amide in liquid ammonia to dipotassio salt I'',¹⁵ which was alkylated with benzyl chloride to form the terminal methyl derivative VIII (eq. 2).



That the product was the expected C-benzyl derivative VIII, not a possible O-benzyl derivative, was established by the strong carbonyl band in its infrared spectrum and by the formation of a phenylhydrazone on treatment with phenylhydrazine. The product from I'' was shown not to be the only

(10) C. Bülow and F. Schlotterbeck, *Ber.*, **35**, 2187 (1902).

(11) R. H. Wiley and C. H. Jarboe, Jr., *J. Am. Chem. Soc.*, **77**, 403 (1955); F. Ramirez and A. F. Kirby, *ibid.*, **75**, 6026 (1953); **76**, 1037 (1954).

(12) Methyl benzoate was not tried since the equilibrium between esters and the monocarbanions of diacyl compounds is generally on the side of the ester; see C. R. Hauser and B. E. Hudson, Jr., "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 298.

(13) See ref. 7, page 182.

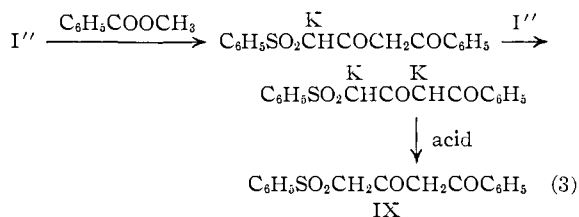
(14) See ref. 7, page 142.

(15) For the present purpose only the dicarbanion resonance form is shown, although other resonance forms may contribute more to the structure of the molecule.

other possible C-benzyl derivative II (see above) by comparison of infrared spectra and by the mixed melting point method.

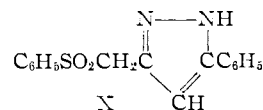
Whereas the benzylation of dipotassio benzoylacetone has been effected in 60% yield in liquid ammonia,⁴ that of I'' gave only a 15% yield under similar conditions. The latter reaction was accompanied by the formation of stilbene (10–40%) and some of I was recovered. This may indicate that an appreciable amount of potassium amide is present in equilibrium with I'' (first step in eq. 2), since benzyl chloride is known to be converted to stilbene by the amide ion.¹⁶ In line with this, I appears to be a slightly weaker acid than benzoylacetone.¹⁷ Better yields (35–39%) of VIII were obtained when the benzylation was completed in pyridine or benzene (see Experimental).

Also similar to dipotassio benzoylacetone,^{4,18} dipotassio salt I'' underwent benzylation with methyl benzoate in liquid ammonia to form the terminal methyl derivative IX in 60% yield (eq. 3).



Since half of the dipotassio salt I'' was neutralized (to I') in converting the benzylation product to its dipotassio salt (second step in eq. 3), only one-half of a molecular equivalent of methyl benzoate was employed, the yield of IX being based on the ester.

In agreement with structure IX, the product gave a positive enol test with ethanolic ferric chloride, formed a copper chelate with cupric acetate, and cyclized with hydrazine to produce a pyrazole, presumably X.



These β -diketone properties showed that the product was not an O-benzoyl derivative, for example VI, but they did not establish structure IX, since the possible methylene derivative VII is also a β -diketone. Incidentally, the starting sulfone-ketone I has been reported not to form a copper chelate,¹⁷ and we have observed that neither does it give a positive enol test.

That the product was the terminal methyl derivative IX was indicated by its nuclear magnetic resonance spectrum,¹⁹ which showed, besides the phenyl peak, two small peaks at 20 cycles and 151 cycles on the high field side of benzene. Although the product was too insoluble in the chloroform employed as solvent for a completely satisfactory

(16) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

(17) E. H. Holst and W. C. Fernelius, *J. Org. Chem.*, **23**, 1881 (1958).

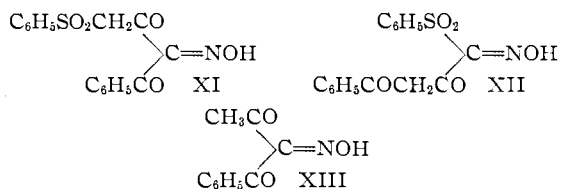
(18) R. J. Light and C. R. Hauser, *ibid.*, **25**, 538 (1960).

(19) We are indebted to Dr. G. S. Paulett of Rohm and Haas Co., Huntsville, Ala., for this determination and interpretation.

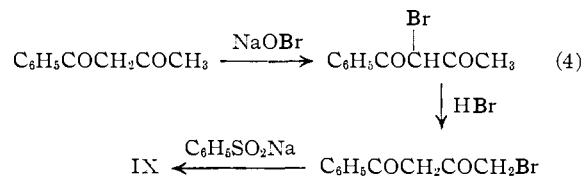
spectrum, the data favor IX over VII since a chemical shift of 151 cycles is rather small to be attributed to the methyl group adjacent to a carbonyl in the latter compound. Indeed, I, which gave a good spectrum, showed a methyl peak at 173 cycles above benzene.

Structure IX was supported by the infrared spectrum of its copper chelate, which showed bands in the regions of 6.10–6.45 and 6.5–6.6 μ as reported for the chelates of β -diketones unsubstituted at the methylene carbon.²⁰ Only the latter band was found in the spectrum of the chelates of alkyl substituted β -diketones.²⁰ However, structure VII is a benzenesulfonyl substituted β -diketone, and exceptions to these rules have been observed recently.²¹

Structure IX was established by treatment with nitrous acid in acetic acid to form an oxime,²² since such a structure as VII could afford only a nitroso derivative.²³ Of the two possible oximes, XI and XII, the former appears more likely since its infrared spectrum was similar to that of the known²⁴ oxime XIII, which was prepared for the purpose of comparison. Presumably in both reactions, nitroso derivatives were intermediates, which isomerized.²³



Structure IX was confirmed by an independent synthesis from sodium benzenesulfinate and 1-bromobenzoylacetone, which was prepared by a modification of the method given by Krohnke and Timmler²⁵ (eq. 4).



That the conversion of 3-bromobenzoylacetone to 1-bromobenzoylacetone had occurred was demonstrated not only by the preparation of the known pyridinium derivative of the latter compound,²⁵ but also by showing that the product no longer contained active halogen (see Experimental). Moreover, the 3-bromo- β -diketone and sodium benzenesulfinate failed to give the product formed in the benzoylation of dipotassio salt I'. Instead there were obtained benzoylacetone (22–25%), sodium benzenesulfonate and benzenesulfonylacetone-

(20) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

(21) J. P. Collman, R. A. Moss, S. D. Goldby and W. S. Trahanovsky, *Chemistry and Industry*, 1213 (1960); and private communication.

(22) An attempt to convert IX to a phenylhydrazone with benzenediazonium chloride under the conditions used with I was unsatisfactory.

(23) See O. Touster, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. 6, pp. 330–336.

(24) V. L. Wolff, P. Bock, B. Lorentz and P. Trappe, *Ann.*, **325**, 134 (1902).

(25) See F. Krohnke and H. Timmler, *Ber.*, **69B**, 614 (1936).

phenone (18%). The first product evidently was formed by reduction of 3-bromo-benzoylacetone, and the second by oxidation of sodium benzenesulfinate. The third product appears to have arisen through cleavage of the acetyl group from VII, although none of this sulfone- β -diketone was isolated. A similar cleavage has been reported in the treatment of 3-bromobenzoylacetone with pyridine.²⁵

Experimental²⁶

Benzenesulfonylacetone (I) (m.p. 57°) was prepared from chloroacetone and sodium benzenesulfinate in ethanol.²⁷

Its n.m.r. spectrum in chloroform showed a phenyl peak at 49 cycles on the low field side of benzene and a CH₂ peak at 93 cycles and a CH₃ peak at 173 cycles on the high field side of benzene.

Benzoylation of the Monopotassio Salt of I.—The method employed was essentially that described⁵ for the alkylation of β -diketones. To a hot, stirred solution of 0.05 mole of potassium *t*-butoxide (prepared from 2 g. of potassium) in 60 ml. of *t*-butyl alcohol was added, during 10 min., 14.85 g. (0.075 mole) of benzenesulfonylacetone (I) to form salt I'. After refluxing for 30 min., 6.33 g. (0.05 mole) of benzyl chloride was added during 30 min. After 1 hr., 1 g. of potassium iodide was added, and the reaction mixture was stirred at reflux for 6 hr. Most of the *t*-butyl alcohol was removed by distillation, and the residue stirred with 50 ml. of water. The resulting mixture was extracted with ether, and the ethereal extract washed with water. The ethereal solution soon deposited white crystals, which were collected on a funnel and dried to give 7.8 g. of 3-benzenesulfonyl-4-phenylbutane-2-one (II), m.p. 97–99°. Removal of the ether from the filtrate gave 2.9 g. more of II, m.p. 98–99°, total yield 75%. Recrystallization from methanol raised the m.p. to 99–100°.

Anal. Calcd. for C₁₆H₁₆O₂S: C, 66.63; H, 5.59; S, 11.12. Found: C, 66.71; H, 5.51; S, 10.86.

Its infrared spectrum showed bands at 3.28, 3.35, 3.45, 5.8, 6.23, 7.4, 7.6, 7.68, 8.7 and 8.77 μ . Its 2,4-dinitrophenylhydrazone melted at 222–225°.

Coupling Reactions of Benzenediazonium Chloride. (A) With Benzenesulfonylacetone (I).—The experimental conditions employed were adapted from those described for the reactions of diazonium salts with aliphatic compounds.²⁸ The diazonium solution, prepared at 0–5° from 1.825 g. (0.026 mole) of sodium nitrite, 6 ml. of water, 2.325 g. (0.025 mole) of aniline and 12.5 ml. of 5 *N* hydrochloric acid (made alkaline to congo red), was added slowly, with stirring, to a cold (10°) slurry of 4.95 g. (0.025 mole) of benzenesulfonylacetone (I), 3.0 g. (0.0365 mole) of sodium acetate, 5 ml. of water and 20 ml. of ethanol. The mixture was stirred for 30 min. at 5–10° and for 90 min. at room temperature, and water (30 ml.) then was added. The precipitate was collected on a funnel, washed several times with water and recrystallized from ethanol to give 6.5 g. (81%) of yellow crystals of 1-benzenesulfonylpropane-1,2-dione-1-phenylhydrazone (IV), m.p. 151–156°. Further recrystallizations from ethanol raised the melting point to 153–158°. The compound was soluble in 5% sodium hydroxide solution. Its ultraviolet spectrum had λ_{max} 239, 356 m μ , log ϵ 4.02, 4.26. Its infrared spectrum showed peaks at 3.12, 3.3, 5.98, 6.25, 6.52, 6.93, 7.67, 8.5 and 8.85 μ .

Anal. Calcd. for C₁₅H₁₄O₂N₂S: C, 59.58; H, 4.67; N, 9.27; S, 10.60. Found: C, 59.73; H, 4.85; N, 9.24; S, 10.39.

(B) With 3-Benzenesulfonyl-4-phenylbutane-2-one (II).—This reaction was carried out as described for the similar coupling of I, except on four-tenths the scale. The product obtained on addition of the reaction mixture to water was

(26) Melting points were taken on a Fisher–Johns melting point apparatus. Infrared spectra were produced with a Perkin–Elmer model 21 infrared spectrophotometer by the potassium bromide method. Ultraviolet spectra were determined with a Warren Spectracord spectrophotometer using 2 \times 10⁻⁵ *M* solution in methanol with a 1-cm. sample cell. Elemental analyses were by Galbraith Microchemical Laboratories, Knoxville, Tenn.

(27) R. Otto and W. Otto, *J. prakt. Chem.*, [2] **36**, 403 (1887).

(28) See ref. 9, pp. 30–34.

collected on the funnel, washed with water, and recrystallized from ethanol to give 3.35 g. (85%) of yellow crystals of 3-benzenesulfonyl-3-phenylazo-4-phenylbutane-2-one (III), with m.p. 105–106°. Further recrystallizations from ethanol and finally from *n*-hexane raised the melting point to 107–108°. The compound did not dissolve in 5% sodium hydroxide solution, nor did it give an enol test with ethanolic ferric chloride. Its ultraviolet spectrum had λ_{\max} 291 m μ , $\log \epsilon$ 3.97; its infrared spectrum at 3.27, 3.43, 5.8, 6.23, 6.3, 6.67, 7.57, 7.68, 8.5 and 8.75 μ .

Anal. Calcd. for C₂₂H₂₀O₂N₂S: C, 67.33; H, 5.14; N, 7.14; S, 8.17. Found: C, 67.22; H, 5.33; N, 7.10; S, 7.99.

Benzoylation of the Monopotassio Salt of I.—To a stirred solution of 0.05 mole of potassium amide in anhydrous liquid ammonia was added 10 g. (0.05 mole) of benzenesulfonylacetone (I) to form I'. The ammonia was evaporated, and 200 ml. of dry benzene was added. The resulting suspension was refluxed for 0.5 hr. (to remove dissolved ammonia), and 2.03 g. (0.05 mole) of benzoyl chloride was added. After refluxing for 4 hr., the reaction mixture was cooled, neutralized with dilute hydrochloric acid, and the two layers were separated. The benzene layer was extracted with saturated sodium bicarbonate solution, then with 10% sodium hydroxide, and finally with water. The benzene solution was dried over anhydrous magnesium sulfate, and the solvent removed. The residual sirup (12 g.) was recrystallized from ethanol to give 6.35 g. (42%) of the O-benzoyl derivative VI (white crystals), m.p. 66–67°.

Anal. Calcd. for C₁₆H₁₄O₄S: C, 63.56; H, 4.66; S, 10.60. Found: C, 63.59; H, 4.59; S, 10.53.

It failed to produce a color with ethanolic ferric chloride, or to form derivatives with copper acetate or 2,4-dinitrophenylhydrazine. Its infrared spectrum showed peaks at 3.25, 3.43, 5.7, 6.03, 6.2, 6.3, 7.6, 7.67, 8.5, 8.7 and 8.8 μ .

Some (1.5 g.) of the starting sulfone-ketone I was recovered on acidification of the sodium hydroxide extract of the benzene solution of the product.

Similar results were obtained when the liquid ammonia containing the monopotassio salt I' was replaced with ether or pyridine and the benzoyl chloride then added. The yields of slightly impure VI were 52 and 44%, respectively.

Dipotassio Salt I''.—To a stirred solution of 0.2 mole of potassium amide in 300–400 ml. of liquid ammonia⁴ was added 19.82 g. (0.1 mole) of benzenesulfonylacetone (I) to give a brown-green solution. After about 29 min., a precipitate formed. Stirring was continued for 15–20 min. longer before using this dipotassio salt I'' as described below.

Benzoylation of Dipotassio Salt I''. (A) **In Benzene.**—To a stirred suspension of 0.1 mole of dipotassio salt I'' in 300 ml. of liquid ammonia was added 12.66 g. (0.1 mole) of benzyl chloride. The liquid ammonia was replaced by an equal volume of ether,⁴ and the latter was then replaced by an equal volume of benzene. The resulting suspension was stirred at reflux for 4 hr. and shaken with 200 ml. of water. The two layers were separated. The aqueous layer was acidified, and the product was extracted with ether. The ether solution was washed with sodium bicarbonate solution, dried over anhydrous magnesium sulfate and the solvent removed. The residue was distilled *in vacuo* to give 11.1 g. (39%) of 1-benzenesulfonyl-4-phenylbutane-2-one (VIII), b.p. 192–193° at 2 mm., m.p. 43–44° after recrystallization from methanol. Its infrared spectrum showed peaks at 3.26, 3.3, 3.42, 5.8, 7.57 and 8.7 μ .

Anal. Calcd. for C₁₆H₁₆O₂S: C, 66.63; H, 5.59; S, 11.12. Found: C, 66.53; H, 5.76; S, 11.34.

It gave a phenylhydrazone, m.p. 167–168°.

Anal. Calcd. for C₂₂H₂₂O₂N₂S: C, 69.80; H, 5.86; N, 7.4; S, 8.47. Found: C, 70.09; H, 5.87; N, 7.58; S, 8.60.

(B) **In Pyridine and Liquid Ammonia.**—A suspension of 0.05 mole of dipotassio salt I'' was prepared in 100 ml. of liquid ammonia. After evaporating most of the ammonia, 60 ml. of pyridine was added, part of the salt dissolving. Benzoyl chloride (6.33 g., 0.05 mole) was then added to give, within 2 min., a red solution. After stirring at room temperature for 2 hr., the reaction mixture was neutralized with hydrochloric acid in crushed ice. There was obtained 4.2 g. (35%) of VIII, b.p. 188–190° at 0.5 mm., m.p. 42–45° after recrystallization from methanol. The melting point was not depressed on admixture with a sample of VIII pre-

pared in (A). Some (2.7 g., 27%) of the starting sulfone-ketone I was recovered.

(C) **In Liquid Ammonia and Ether.**—To a stirred suspension of 0.1 mole of I'' in 300 ml. of liquid ammonia was added 12.66 g. (0.1 mole) of benzyl chloride in an equal volume of ether. The purple-red color associated with the formation of stilbene⁶ was observed. After stirring for 2 hr., excess ammonium chloride was added, and the liquid ammonia was replaced with ether. The resulting ether suspension was worked up to give 3.85 g. (39%) of recovered sulfone-ketone I, m.p. 53–56°, 1.4 g. (31%) of stilbene, m.p. 125°; and 2.2 g. (15%) of product VIII, b.p. 192–195° at 0.25 mm. (identified by infrared spectrum).

In another experiment, the liquid ammonia was replaced by ether after 2 hr., and the resulting ethereal suspension was stirred for 2 hr. Acidification with hydrochloric acid afforded 2.85 g. (20%) of VIII, b.p. 130–135° at 0.1 mm. and 1.8 g. (40%) of stilbene.

Benzoylation of I''.—To a stirred suspension of 0.1 mole of dipotassio salt I'' in 300 ml. of liquid ammonia was added 6.81 g. (0.05 mole) of methyl benzoate. After stirring for 3 hr., the liquid ammonia was replaced by ether and the resulting suspension was refluxed for 1 hr. Water (200 ml.) was added and the white suspension was filtered. The potassium salt of IX on the funnel was shaken with dilute acid and ether, and the layers were separated. The ether solution was evaporated, and the residue was recrystallized from ethanol to give 6.83 g. (45.2%) of 4-benzenesulfonyl-1-phenylbutane-1,3-dione (IX), m.p. 145–146.5°. It gave a cherry-red enol test with ethanolic ferric chloride. Its infrared spectrum showed peaks at 3.28, 3.35, 3.43, 6.2–6.4 (broad), 6.7, 6.8, 6.93, 7.15, 7.65 (broad) and 8.65 (broad) μ .

Anal. Calcd. for C₁₆H₁₄O₄S: C, 63.56; H, 4.67; S, 10.60. Found: C, 63.47; H, 4.58; S, 10.54.

The two phases of the ether-aqueous filtrate obtained above on removing the white solid were separated. The aqueous layer was acidified and extracted with ether. The ether extract was shaken with a saturated, aqueous copper acetate solution to precipitate 2.5 g. (15%) of the copper chelate of IX, m.p. 207–209°, and at 216–218° after recrystallization from hexane-acetone (Dry Ice cooling). The infrared spectrum of the chelate showed peaks at 3.28, 3.43, 6.27, 6.42, 6.6, 6.7, 7.7, 7.8, 8.48 and 8.6 μ .

Anal. Calcd. for C₃₂H₂₆O₈S₂Cu: C, 57.5; H, 3.94; S, 9.62; Cu, 9.54. Found: C, 57.58; H, 4.25; S, 9.54; Cu, 9.75.

The combined yield of IX and its chelate was 60%. A sample of IX was converted to the chelate, which was identical with the chelate described above.

3-Benzenesulfonylmethyl-5-phenylpyrazole (X).—A mixture of 4-benzenesulfonyl-1-phenylbutane-1,3-dione (1 g.) and hydrazine hydrate (1 g.) in ethanol was refluxed for 2 hr. The cooled reaction mixture was poured onto water, and the resulting precipitate was recrystallized from ethanol to give 1 g. of white crystals of 3-benzenesulfonylmethyl-5-phenylpyrazole (X), m.p. 173°.

Anal. Calcd. for C₁₆H₁₄O₂N₂S: C, 64.37; H, 4.73; N, 9.39; S, 10.72. Found: C, 64.28; H, 4.53; N, 9.42; S, 11.16.

Nitrosation Reactions of Nitrous Acid. (A) **With Benzoylacetone.**—This reaction was effected with sodium nitrite and acetic acid as described previously²⁴ to form 2-oximino-1-phenyl-1,3-butanedione (XIII), m.p. 127–128.5° (reported²⁴ m.p. 124–126°), in 80% yield. Its infrared spectrum showed peaks at 2.86, 5.92, 6.22, 6.85, 7.27, 7.55, 7.66, 7.96 and 8.47 μ .

(B) **With 4-Benzenesulfonyl-1-phenylbutane-1,3-dione (IX).**—This reaction was effected by an adaptation of that employed with benzoylacetone.²⁴ To a stirred solution of 0.5 g. (1.6 moles) of IX in 15 ml. of glacial acetic acid and 10 ml. of ether kept at 10–15° was added slowly a cooled solution of 0.2 g. of sodium nitrite in a minimum of water. The cooling bath was removed and the stirring continued for 3 hr. The reaction mixture was poured into cold, saturated sodium bicarbonate solution, and the resulting mixture was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed to give 229.0 mg. (42%) of an oxime (XI or XII), m.p. 188–188.5° after recrystallization from hexane-ethyl acetate. Its infrared spectrum showed peaks at 2.92, 5.91, 6.25, 7.22, 7.55 and 8.64 μ .

Anal. Calcd. for $C_{16}H_{15}O_4NS$: C, 58.01; H, 3.96; N, 4.23; S, 9.66. Found: C, 57.90; H, 4.03; N, 4.25; S, 9.74.

Independent Synthesis of IX.—To a stirred, cooled solution of 4 g. (0.0247 mole) of benzoylacetone in 120 ml. of 0.25 *N* sodium hydroxide was added slowly a cold solution of 3.7 g. (0.0231 mole) of bromine and 10 g. of sodium bromide in 40 ml. of water, followed by 5 ml. of 1 *N* hydrobromic acid. The resulting oil was taken up in ether. The ether solution was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature to leave 5.93 g. (99%) of crude 3-bromobenzoylacetone as a pale yellow oil.²⁹ Addition of a drop of this product to a solution of potassium iodide in 2 ml. of water and 5 ml. of acetic acid under nitrogen produced immediately the dark brown color of iodine.

To a solution of 1.5 g. of crude 3-bromobenzoylacetone in 5 ml. of glacial acetic acid was added 5 ml. of 30–32% acetic acid–hydrogen bromide solution (Eastman Kodak Co). After stirring for 5 hr. at room temperature, the reaction mixture was poured into water, and the resulting mixture was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature to leave 9–10 g. of an acetic acid solution of 1-bromobenzoylacetone, the maximum yield of which would be 1.5 g.³⁰ A negative test³¹ for active halogen was obtained with a few drops of this solution (see above). The remainder of the solution was placed under reduced pressure until most of the acetic acid was removed. The residue was taken up in 5 ml. of dry acetonitrile, and 1 ml. of dry pyridine was added. After adding dry ether to produce cloudiness, the mixture was cooled in a refrigerator for 3 days to give 0.65 g. (35%) of 1-benzoylacetone pyridinium bromide, m.p. 177–182° dec. and at 181.5–183° dec. after recrystallization from a minimum of hot anhydrous ethanol, reported²⁵ m.p. 181° dec. The infrared spectrum of the pyridinium bromide showed peaks at 3.32, 5.77, 5.94, 6.12, 6.26, 6.35, 6.70, 7.52 and 8.26 μ .

The isomerization of 1.5 g. of crude 3-bromobenzoyl-

(29) Krohnke and Timmler²⁵ reported that this product could not be distilled.

(30) An attempt to distil this solution at 0.2 mm. led to decomposition with foaming near 100°, leaving in the flask an acetone-insoluble black gum.

(31) In this test only a yellow color was produced like that observed with chloroacetone under similar conditions.

tone was repeated to give the acetic acid solution of 1-bromobenzoylacetone (maximum yield 1.5 g., 0.0062 mole). This solution and 1.35 g. (0.0065 mole) of sodium benzenesulfinate dihydrate were dissolved in 50 ml. of 95% ethanol and the solution was refluxed for 24 hr. Most of the alcohol was removed under reduced pressure and cold water was added to the residue. The resulting precipitate was collected on a funnel and washed with water to give 1.05 g. (56%, based on crude 3-bromobenzoylacetone) of sulfone- β -diketone IX, m.p. 143–145° after recrystallization from hexane–ethyl acetate. This m.p. was not depressed on admixture with a sample of IX obtained as described above; the infrared spectra of the two samples were identical.

Treatment of 3-Bromobenzoylacetone with Sodium Benzenesulfinate.—A solution of 1.0 g. (0.0041 mole) of crude 3-bromobenzoylacetone and 0.90 g. (0.0043 mole) of sodium benzenesulfinate dihydrate in 100 ml. of 95% ethanol was refluxed for 24 hr. The ethanol was evaporated, and the residue was triturated with dry ether, only part of the residue dissolving. The ether-insoluble material (0.679 g.) evidently contained sodium benzenesulfonate, not sodium benzenesulfinate, since its infrared spectrum (in KBr) was identical with that of the former salt and quite different from that of the latter salt. The ether-insoluble solid also appeared to contain some sodium bromide, since treatment of it with aqueous silver nitrate gave a precipitate that was insoluble in concentrated nitric acid. Silver benzenesulfonate (or benzenesulfinate) is soluble in this acid.

The ether solution obtained as described above was washed with sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue (which did not give a test for active halogen) was recrystallized from benzene–hexane to give 0.191 g. (18%) of benzenesulfonylacetophenone, m.p. 70–80° and at 94–95° after recrystallization from methanol. This product was identified by the mixed melting method and by comparison of infrared spectra employing an authentic sample (m.p. 93–94°) prepared from sodium benzenesulfinate and α -chloroacetophenone.³²

The benzene–hexane filtrate (see above), on standing and evaporation of some of the solvent, gave a precipitate of 0.148 g. (22%) of benzoylacetone, m.p. 50–53° (identified by infrared spectrum).

The experiment was repeated with 0.001 mole each of crude 3-bromobenzoylacetone and sodium benzenesulfinate, and the reaction mixture (after 24 hr.) was poured into ice-water to precipitate benzoylacetone, m.p. 53–55°, in 25% yield.

(32) See J. Troger and O. Beck, *J. prakt. Chem.*, [2] **97**, 295 (1913).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO., SOUTH CHARLESTON 3, W. VA.]

A New Reaction of Allylic Sulfones¹

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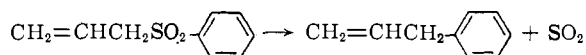
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Allylic sulfones have been found to undergo a thermal rearrangement accompanied by loss of sulfur dioxide to give olefinic products. Thus, when allyl benzyl sulfone is heated at a temperature of 215°, 4-phenyl-1-butene and sulfur dioxide are obtained as products. This reaction provides a novel method for lengthening carbon chains. The mechanism of the reaction is discussed.

Although there is considerable information on thermal reactions and rearrangements of allylic compounds in general, relatively little can be found regarding allylic sulfones. Allylic sulfones were the subject of one earlier study² to determine whether thermal rearrangement to the corresponding sulfinic esters occurred. No rearrangement was detected and in fact it was noted that one of

the sulfones studied, allyl phenyl sulfone, was stable up to about 250°.

We have found that allylic sulfones, including allyl phenyl sulfone at higher temperatures, undergo a thermal rearrangement to give olefinic compounds and sulfur dioxide. For example, allyl phenyl sulfone, when heated to 300–400°, yields allylbenzene and sulfur dioxide as



The reaction has been found to be general, but the temperature required to cause the pyrolysis is

(1) Presented in part before the Division of Organic Chemistry, 135th Meeting of the American Chemical Society, Boston, Mass., April 5–10, 1959.

(2) A. C. Cope, D. E. Morrison and L. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950).