

Attempted Condensation of 1-Propanol with Benzyl Alcohol to 1-Phenyl-1-propanol at 400° and 40 Atmospheres.—A mixture of benzyl alcohol (64% by weight) and 1-propanol (36%), charged at a rate of 5.5 mole/kg. soda lime/hr., produced gas amounting to 0.41 mole/mole and 83% of a complex liquid product containing

Water	8.7% by weight
Benzene ^a	4.3
1-Propanol	19.3
3-Pentanol	2.5
2-Methyl-1-pentanol	1.1
Toluene ^b	4.8
Benzyl alcohol	21.6
Benzaldehyde ^c	4.9
2-Benzyl-1-propanol ^a	8.9
Other	23.9

^a Azeotrope with water; b.p. 67°, n_D^{20} 1.4712 after separa-

ration from water. ^b Azeotrope with 1-propanol; b.p. 97°, n_D^{20} 1.4942 after washing with water and drying. ^c B.p. 177–179°, n_D^{20} 1.5454; by Cannizzaro reaction with concentrated aqueous KOH gave benzoic acid, m.p. 120.5–122°. ^d B.p. 91° (2 mm.), n_D^{20} 1.5296; oxidation with acidic potassium permanganate, followed by treatment with thionyl chloride, then ammonia, gave 2-benzylpropanamide, m.p. 105–106.5°.

Acknowledgments.—Chemical analyses were performed by Miss Dottie Carter, Mr. B. B. Buchanan and Mr. J. F. Eberle. Spectrometric analyses were performed by Mr. J. A. Favre, Mr. H. A. Price and Mr. H. W. Rollmann. Phillips Petroleum Company granted permission to publish the data.

(6) L. Edeleanu, *Ber.*, **20**, 618 (1887).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

α,β -Unsaturated Sulfonyl Compounds in the Diels-Alder Reaction. II

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β -Benzoylvinyl phenyl sulfone is found to be an active dienophile, giving adducts with cyclopentadiene, 2,3-dimethylbutadiene, isoprene and butadiene in excellent yields. These adducts have been obtained only as high-boiling viscous oils, but crystalline dibromides or dinitrophenylhydrazones are readily formed from them. Anthracene gives a crystalline adduct; furan does not react under any conditions tried. 1,2-Di-*p*-toluenesulfonylethylene also is an active dienophile; crystalline adducts are formed in almost quantitative yield from the simple diolefins, but none has been obtained from furan. Anthracene gives two crystalline adducts, presumably the *meso* and racemic forms.

Previous work in this Laboratory¹ has indicated that a single sulfonyl group imparts a significant dienophilic activity to a double bond on which it resides. The purpose of the present work was to extend this study to compounds in which the double bond is activated by both a sulfonyl and a carbonyl group, and by two sulfonyl groups. The addition of butadiene to a compound in which the double bond was activated by both a sulfonyl and a carbonyl group, 1,4-thiapyrone-1-dioxide was reported by Fehnel and Carmack,² but no further investigations of the dienophilic properties of this compound were made.

trans- β -Benzoylvinyl phenyl sulfone was prepared by the method of Kohler and Larsen.³ β -Chloropropiophenone was condensed with sodium benzenesulfinate to give β -benzoylethyl phenyl sulfone. Treatment with bromine in chloroform converted this material to β -bromo- β -benzoylethyl phenyl sulfone, and dehydrobromination was effected by methanolic potassium acetate. The product was the pure *trans* isomer; it was treated with the same dienes that Adams and Gold⁴ used with *trans*-dibenzoylethylene.

trans- β -Benzoylvinyl phenyl sulfone was found to be a very reactive dienophile. The reactions with cyclopentadiene and 2,3-dimethylbutadiene were essentially complete in about five minutes at room temperature in benzene solution. Isoprene

and butadiene reacted somewhat more slowly, but gave comparable yields of the adducts (*ca.* 95%). Furan did not form an adduct in refluxing benzene solution, but the possibility of reaction under more vigorous conditions is not excluded. Anthracene did not form an adduct in refluxing benzene solution, but fusion of the reactants resulted in the formation of the adduct. The anthracene adduct was a solid, but all the others were viscous, high-boiling oils; they were analyzed as the crystalline dibromides or dinitrophenylhydrazones.

The Diels-Alder reaction always involves *cis*-addition of the diene to the multiple bond of the dienophile. Since the diene reactions were carried out only with the pure *trans*- β -benzoylvinyl phenyl sulfone, the *trans* relationship of the benzoyl and benzenesulfonyl groups must be retained in the adducts. Each adduct derived from a symmetrical diene therefore should consist of a single racemate. In the case of the unsymmetrical diene, isoprene, addition could occur in either one of two directions or in both directions simultaneously. Either of, or a mixture of, two racemates could be produced. It seems unlikely that a single, apparently pure (sharp-melting) dibromide could have been isolated if the adduct were a mixture of racemates, and hence it is believed that the diene addition proceeded in one direction almost exclusively. The direction of addition has not been determined.

1,2-Di-*p*-toluenesulfonylethylene (probably *trans*) was prepared by a modification of the method of Fromm and Seibert.⁵ The first step in the synthesis involves the condensation of *p*-thiocresol

(1) H. R. Snyder, H. V. Anderson and D. P. Hallada, *THIS JOURNAL*, **73**, 3258 (1951); see also C. S. Rondstvedt and J. C. Wygant, *ibid.*, **73**, 5785 (1951).

(2) E. Fehnel and M. Carmack, *ibid.*, **70**, 1813 (1948).

(3) E. P. Kohler and R. G. Larsen, *ibid.*, **57**, 1448 (1935).

(4) R. Adams and M. Gold, *ibid.*, **62**, 56 (1940).

(5) E. Fromm and E. Seibert, *Ber.*, **55**, 1014 (1922).

with 1,2-dichloroethylene (or the corresponding dibromo compound) in alcoholic potassium hydroxide. The reaction product, 1,2-di-*p*-toluenethioethylene, is oxidized to the desired 1,2-di-*p*-toluenesulfonylethylene by hydrogen peroxide in acetic acid solution.

1,2-Di-*p*-toluenesulfonylethylene also was found to be a very reactive dienophile. The reaction with cyclopentadiene was complete in five minutes at room temperature in benzene solution. The yields with the simple dienes, cyclopentadiene, 2,3-dimethylbutadiene, isoprene and butadiene were excellent (ca. 95%). Furan did not form an adduct with 1,2-di-*p*-toluenesulfonylethylene in refluxing benzene, but no tests have been made under more strenuous conditions. Anthracene did not form an adduct in refluxing benzene solution, but fusion of the two reactants resulted in the formation of two isomeric products in approximately equal amounts. Mixed melting points of the two materials showed a large depression. The infrared spectra were very similar with slight displacement of the bands due to the sulfonyl groups. These two products are therefore believed to be the *meso* and racemic forms of the adduct.

Experimental^{6,7}

trans- β -Benzoylvinyl Phenyl Sulfone.—This material was prepared by the method of Kohler and Larsen.³ By reworking the mother liquors from the last step it was possible to raise the yield in the dehydrohalogenation reaction to 99% of material melting at 110.5–113.5° (lit.³ 114°).

3,6-Methylene-4-benzenesulfonyl-5-benzoylcyclohexene.—A solution of 6.1 g. of cyclopentadiene dissolved in 20 ml. of benzene was added to a solution of 1.0 g. of *trans*- β -benzoylvinyl phenyl sulfone in 10 ml. of benzene. The yellow color of the sulfone disappeared in five minutes. After the reaction mixture stood at room temperature for two days the excess diene and solvent were removed under reduced pressure. The product was a clear brown oil, weight 1.2 g. (96%). To prepare the dinitrophenylhydrazone a solution containing 0.5 g. of 3,6-methylene-4-benzenesulfonyl-5-benzoylcyclohexene, 0.5 g. of 2,4-dinitrophenylhydrazine and 1.0 ml. of concentrated hydrochloric acid in 30 ml. of ethanol was boiled and reduced in volume to ca. 15 ml. The orange product which slowly separated from the cooled solution was removed by filtration and recrystallized from ethanol. The fine orange needles melted at 194.5–196°.

Anal. Calcd. for $C_{23}H_{24}O_3SN_4$: C, 59.99; H, 4.65. Found: C, 60.21; H, 4.52.

1,2-Dimethyl-4-benzoyl-5-benzenesulfonylcyclohexene.—A mixture of 4.0 g. of β -benzoylvinyl phenyl sulfone and 25 ml. of freshly distilled dimethylbutadiene was refluxed on a steam-bath. The solid went into solution and the yellow color due to the sulfone disappeared in about five minutes. The reaction mixture was allowed to stand at room temperature for 18 hours. The solution was filtered, and the solvent was removed under reduced pressure. The viscous residue weighed 5.0 g. (96%). To prepare the crystalline dibromide, a solution of bromine in chloroform was added dropwise to a solution of 1.0 g. of the adduct in 50 ml. of chloroform until no more was decolorized. The solvent was removed under reduced pressure at room temperature. The resulting oil crystallized slowly. This material was washed with cold ethanol. After recrystallization from ethanol the product melted at 157.5–159.5°.

Anal. Calcd. for $C_{21}H_{22}O_3SBr_2$: C, 49.04; H, 4.31. Found: C, 49.21; H, 4.59.

1(or 2)-Methyl-4-benzoyl-5-benzenesulfonylcyclohexene.—Four grams of β -benzoylvinyl phenyl sulfone and 10 mg.

of hydroquinone were placed in a 100-ml. flask fitted with a reflux condenser. About 25 ml. of freshly distilled isoprene was added and the mixture was refluxed for two days. The reaction mixture became colorless. The cooled reaction mixture was filtered, and the excess diene was removed under reduced pressure. The residue consisted of 4.9 g. (97%) of colorless, glassy oil. The dibromide prepared in the previously described manner melted at 167–168°.

Anal. Calcd. for $C_{20}H_{20}O_3SBr_2$: C, 48.01; H, 4.03. Found: C, 48.09; H, 4.21.

4-Benzoyl-5-benzenesulfonylcyclohexene.—A mixture of 0.5 g. of β -benzoylvinyl phenyl sulfone, 20 ml. of butadiene and 50 ml. of benzene was sealed in a steel bomb and heated on a steam-bath for 24 hours. The excess butadiene was allowed to evaporate, and the solvent was removed under reduced pressure. The resulting viscous oil weighed 0.58 g. (96%). The 2,4-dinitrophenylhydrazone prepared in the previously described manner melted at 193–195°.

Anal. Calcd. for $C_{25}H_{22}O_3SN_4$: C, 59.28; H, 4.38. Found: C, 59.00; H, 4.64.

The Adduct Derived from Anthracene and β -Benzoylvinyl Phenyl Sulfone.—A mixture of 0.5 g. of β -benzoylvinyl phenyl sulfone and 0.293 g. of anthracene was fused and heated in an oil-bath at 155–160° for 20 hours. The reaction mixture was dissolved in ethanol, boiled with charcoal, and filtered hot. The solution was concentrated to ca. 25 ml. An almost white solid separated from the cooled solution. The solid weighed 0.35 g. (44%). After recrystallization from ethanol the solid melted at 198.5–199.5°.

Anal. Calcd. for $C_{29}H_{22}O_3S$: C, 77.31; H, 4.92. Found: C, 77.04; H, 5.06.

1,2-Di-*p*-toluenethioethylene.—The method of Fromm and Seibert⁵ was modified in this preparation. A solution containing 52.0 g. of potassium hydroxide and 65.5 g. of *p*-thiocresol in 740 ml. of ethanol was placed in a 2-l. flask fitted with a stirrer and reflux condenser. To the stirred solution was slowly added a solution of 50.0 g. of 1,2-dibromoethylene in 290 ml. of ethanol. After the addition was completed the reaction mixture was refluxed for three hours. The solution was filtered hot. When the filtrate cooled, the product crystallized in long thin needles and was removed by filtration. The yield of crude product was 43.0 g. (59%). The melting point of this material was 91–92° (lit.⁵ 93°).

1,2-Di-*p*-toluenesulfonylethylene.—This preparation follows the method of Fromm and Seibert.⁵ To a suspension of 40.0 g. of 1,2-di-*p*-toluenethioethylene in a mixture of 200 ml. of water and 900 ml. of acetic acid was added 200 ml. of 30% hydrogen peroxide solution. The reaction mixture was heated on a steam-bath for eight hours. To the hot solution was added 400 ml. of water. The product which crystallized in long white needles was removed from the cooled solution by filtration; it weighed 35.0 g. (moist). The crude product was recrystallized from ethanol. The resulting white solid weighed 21.0 g. (47%), m.p. 146–148° (lit.⁵ 149–150°).

3,6-Methylene-4,5-di-*p*-toluenesulfonylcyclohexene.—To a mixture of 1.0 g. of di-*p*-toluenesulfonylethylene and 40 ml. of benzene contained in a flask fitted with a reflux condenser was added a solution of 6.1 g. of cyclopentadiene in 20 ml. of benzene. The small amount of solid originally suspended in the liquid rapidly went into solution. After standing about one minute the clear solution deposited a white crystalline solid. The reaction appeared to be complete after five minutes. After standing at room temperature for four hours, the solid was removed by filtration, and weighed 1.1 g. (93%). After recrystallization from ethanol the solid melted at 272–274° dec. (tube inserted in bath at 268°).

Anal. Calcd. for $C_{21}H_{22}O_4S_2$: C, 62.66; H, 5.51. Found: C, 62.46; H, 5.76.

1,2-Dimethyl-4,5-di-*p*-toluenesulfonylcyclohexene.—In a flask fitted with a reflux condenser were placed 1.0 g. of 1,2-di-*p*-toluenesulfonylethylene, 10 ml. of freshly distilled dimethylbutadiene, 20 ml. of benzene and ca. 5 mg. of picric acid. The reaction mixture was refluxed for 20 hours. The solvent and excess diene were removed under reduced pressure. The viscous, oily residue was triturated with 10 ml. of ethanol, and it soon crystallized. The product weighed 1.15 g. (93%). Recrystallization of the crude material from ethanol produced a white crystalline solid, m.p. 158.5–160.5°.

(6) Microanalyses were performed by Miss Emily Davis, Miss K. Pih and Mrs. Jean Fortney. Infrared spectra were determined and interpreted by Miss Elizabeth Petersen.

(7) All melting points are corrected.

Anal. Calcd. for $C_{22}H_{26}O_4S_2$: C, 63.13; H, 6.26. Found: C, 63.10; H, 6.25.

1-Methyl-4,5-di-*p*-toluenesulfonylcyclohexene.—To a solution of 2.0 g. of 1,2-di-*p*-toluenesulfonylethylene in 50 ml. of benzene was added 15 ml. of freshly distilled isoprene. The resulting solution was refluxed for two days. The excess diene and the solvent were removed under reduced pressure. The residue was a viscous oil, weight 2.3 g. (96%). After standing in a refrigerator for two weeks, the adduct crystallized. After recrystallization from ethanol the product melted at 130–132°.

Anal. Calcd. for $C_{21}H_{24}O_4S_2$: C, 62.35; H, 5.98. Found: C, 62.48; H, 6.24.

4,5-Di-*p*-toluenesulfonylcyclohexene.—A mixture of 1.0 g. of 1,2-di-*p*-toluenesulfonylethylene, 20 ml. of butadiene and 50 ml. of benzene was sealed in a steel bomb and heated on a steam-bath for 24 hours. The excess diene was allowed to escape and the solvent was removed under reduced pressure. The resulting oil was dissolved in hot ethanol. The product which crystallized from the cooled solution weighed 1.0 g. (95%). After recrystallization from ethanol the adduct was a white solid, m.p. 164–165° dec.

Anal. Calcd. for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68. Found: C, 61.80; H, 5.92.

The Adducts Derived from Anthracene and 1,2-Di-*p*-toluenesulfonylethylene.—A mixture of 0.5 g. of 1,2-di-*p*-toluenesulfonylethylene and 0.265 g. of anthracene was fused and heated at 155–160° for 20 hours. The reaction mixture was boiled with 50 ml. of ethanol. The cooled mixture was filtered and concentrated to half its original volume. The white solid which crystallized when the solution cooled was removed by filtration; it weighed 0.18 g. (24%). After recrystallization from acetone–water this material melted at 254–255°.

Anal. Calcd. for $C_{30}H_{26}O_4S_2$: C, 70.01; H, 5.09. Found: C, 70.30; H, 5.28.

The ethanol-insoluble material (0.22 g., 28%) was triturated with hot ethanol. Recrystallization from acetone–water produced a white solid, m.p. 239.5–241°.

Anal. Calcd. for $C_{30}H_{26}O_4S_2$: C, 70.01; H, 5.09. Found: C, 69.74; H, 5.17.

The mixed melting point of the two substances was 212–240°. The infrared spectra of the two compounds were very similar, with slight displacements of the bands due to the sulfonyl groups. These compounds are believed to be the *meso* and racemic forms of the adduct.

URBANA, ILLINOIS

[CONTRIBUTION NO. 870 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Preparation of δ -Ketoacids and δ -Ketonitriles from Monocyanoethylated β -Ketoesters¹

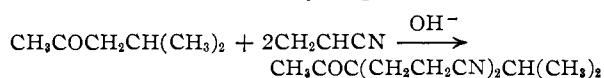
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A method has been developed for the indirect monocyanoethylation of methyl ketones at the methyl group. The procedure involves treating the appropriate β -ketoesters with acrylonitrile and hydrolyzing the compounds so formed to give either δ -ketonitriles or δ -ketoacids.

Numerous investigators² have found that the base-catalyzed Michael condensation of acrylonitrile with active hydrogen compounds leads to the formation of polycyanoethylated derivatives as the main reaction products. To our knowledge,² very few ketones have been monocyanoethylated with acrylonitrile and in each case low yields of product were obtained.

Furthermore, while from structural considerations, symmetrical dialkyl ketones such as acetone, diisopropyl ketone and diisobutyl ketone; and alkyl aryl and alkyl heterocyclic ketones such as acetophenone, methyl 2-thienyl ketone and methyl 2-furyl ketone could give rise to only one monocyanoethylated derivative; unsymmetrical dialkyl ketones such as methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone might give rise to isomeric monocyanoethylated products. Actually,² as shown in the following equation, the condensation of acrylonitrile with methyl alkyl ketones occurs at that α -carbon atom which is more highly substituted to give dicyanoethylated products if the α -carbon carries two hydrogen atoms.



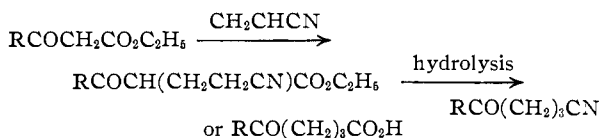
For some time now we have been interested in

(1) This report is based on a thesis presented by Clayton W. Yoho to the graduate faculty of the University of Pittsburgh in partial fulfillment of the requirements for the M.S. degree.

(2) See H. A. Bruson, in "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 2.

developing methods for monocyanoethylating or monocarboxyethylating methyl alkyl ketones and in determining whether the reactions could be effected at the α -methyl group carbon atom of these compounds. Recently,³ we studied the reaction of several methyl alkyl ketone anions (prepared from the ketones and sodium amide) with β -chloropropionitrile and found that the chloronitrile underwent β -elimination to form acrylonitrile, which then condensed at the α -methylene or α -methinyl carbon atom of the ketone to give either a monocyanoethylated compound or a mixture of mono- and dicyanoethylated products.

It occurred to us that, as shown in the following scheme, it might be possible to monocyanoethylate or monocarboxyethylate ketones indirectly by treating β -ketoesters with acrylonitrile under appropriate reaction conditions and hydrolyzing the resulting condensation products to the corresponding δ -ketonitriles or δ -ketoacids. Thus, if R is the isopropyl group, ethyl isobutyrylacetate,



prepared by the general method of Levine and Hauser,⁴ may be cyanoethylated to give ethyl α -(β -cyanoethyl)-isobutyrylacetate which may then

(3) L. B. Barkley and R. Levine, *THIS JOURNAL*, **72**, 3699 (1950).

(4) R. Levine and C. R. Hauser, *ibid.*, **66**, 1768 (1944).