TABLE III

Compounds	Molecular formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
t-Butyl acid phthalate	$C_{12}H_{14}O_4$	64.83	6.35	64.60	6.30
t-Butyl acid 3-nitrophthalate	$C_{12}H_{13}O_6N$	53.91	4.90	53.88	4.88
t-Amyl acid 3-nitrophthalate	$C_{13}H_{15}O_6N$	55.49	5.38	55.22	5.06
t-Butyl acid tetrachlorophthalate	$C_{12}H_{10}O_4Cl_4$	39.98	2.80	39.65	3.05
t-Amyl acid tetrachlorophthalate	$C_{13}H_{12}O_4Cl_4$	41.69	3.23	41.58	3.12
Triethylcarbinyl acid tetrachlorophthalate	$C_{15}H_{16}O_4Cl_4$	44.75	4.01	44.47	3.95
Tri-*n*-propylcarbinyl acid tetrachlorophthalate	$C_{18}H_{22}O_4Cl_4$	48.62	4.99	48.49	5.03
Tri-*n*-butylcarbinyl acid tetrachlorophthalate	$C_{21}H_{28}O_4Cl_4$	51.82	5.67	51.64	5.60
Tri-*n*-amylcarbinyl acid tetrachlorophthalate	$C_{24}H_{34}O_4Cl_4$	54.54	6.49	54.41	6.85

ester in 74% yield. The reaction mixture was kept at 0° for twenty hours, and the acid ester separated by procedure A. The product melted at 164–165° and possessed a neutral equivalent of 333. Calcd. for $C_{21}H_{16}O_4$, 332.

By heating equimolar amounts of diphenylcarbinol with phthalic anhydride at 110° for fifteen hours, a yield of 18% of the diphenylcarbinyl acid phthalate resulted.

Summary

The reaction between *t*-alkoxymagnesium bromides and tetrachlorophthalic anhydride produces the *t*-alkyl acid tetrachlorophthalates in 36–66% yields. These solid esters may be characterized by their neutral equivalents and decomposition points.

The acid phthalate of diphenylcarbinol may be prepared in 74% yield by the reaction between phthalic anhydride and the alkoxymagnesium bromide.

URBANA, ILLINOIS

RECEIVED MAY 14, 1936

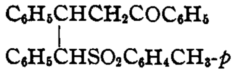
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE JOHN HARRISON LABORATORY OF CHEMISTRY AT THE UNIVERSITY OF PENNSYLVANIA]

The Michael Condensation. IV. The Active Methylene Group in Sulfones

BY RALPH CONNOR, C. L. FLEMING, JR., AND TEMPLE CLAYTON

Sulfones having the structure RCH_2SO_2R' (in which R is either aryl or another sulfone grouping) are of interest because the methylene group is attached to two activating groups, yet enolization is not possible unless sulfur expands its valence shell. Previous investigators[1] have shown that methylene disulfones form sodio derivatives and may be alkylated by methods similar to those used for the alkylation of 1,3-diketones and that benzyl phenyl sulfone forms a sodio derivative (but may not be alkylated). These are apparently the only characteristic reactions of the active methylene group which have previously been shown to apply to sulfones of this type.[2] This paper demonstrates the ability of benzyl *p*-tolyl sulfone to undergo the Michael condensation.

The product (I) obtained from the condensation of benzyl *p*-tolyl sulfone with benzalacetophenone



$$\begin{array}{l} C_6H_5CHCH_2COC_6H_5 \\ \quad\; | \\ C_6H_5CHSO_2C_6H_4CH_3\text{-}p \end{array} \qquad \text{(I)}$$

was present in two stereoisomeric forms, m. p. 139–141° and 197–197.5°. The total yield of the pure products was 26%; this does not represent the actual extent of the reaction, however, because of the losses encountered in the difficult separation of the isomers from each other and from unreacted benzyl *p*-tolyl sulfone.

The addition of benzyl *p*-tolyl sulfone to benzalacetophenone is similar to the behavior of the ketonic analog of the former[4] (desoxybenzoin). The analogy between the reactions of ketones and sulfones in the Michael condensation may be carried still further. Both dibenzoylmethane[5] and bis-(phenylsulfonyl)-methane do not condense with benzalacetophenone and both benzyl *p*-tolyl sulfone and desoxybenzoin fail to react with methyl cinnamate. However, the failure of

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(1) Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930).

(2) Aside from active methylene compounds, three other points of similarity may be noted[3] in the behavior of sulfones and their ketonic analogs: (1) the addition reactions of α,β-unsaturated sulfones, (2) the condensation of benzaldehyde with methyl *p*-tolyl sulfone and (3) the reaction of the Grignard reagent with sulfones to give magnesium derivatives similar to those obtained with certain ketones.

(3) Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935).

(4) Knoevenagel and Schmidt, *Ann.*, **281**, 53 (1894).

(5) Connor and Andrews, THIS JOURNAL, **56**, 2713 (1934).

methyl *p*-tolyl sulfone to react with benzalacetophenone is in contrast to the behavior of acetophenone.[6]

Other typical reactions of the active methylene group were tested with these sulfones. The mercuric chloride test[7] for enolic substances was positive with bis-(phenylsulfonyl)-methane and negative with benzyl *p*-tolyl sulfone. All of the other reactions attempted (bis-(phenylsulfonyl)-methane and benzyl *p*-tolyl sulfone with benzaldehyde, *p*-chlorobenzaldehyde, selenium dioxide, nitrous acid and isoamyl nitrite in the presence of sodium ethoxide) were unsuccessful. In all cases the sulfones were recovered unchanged. While the usual caution in interpreting negative results must be observed, these data definitely form grounds for assuming a profound difference in the reactivity (if not in the nature of the reactions) of the methylene group in sulfones and in their ketonic analogs.

As regards the reactivity of benzyl *p*-tolyl sulfone in the Michael condensation and the reactivity of the disulfone with mercuric chloride, the choice between explanations assuming that the enol forms of the sulfones need not be involved or that sulfur may expand its valence shell,[8] is not clear. The former explanation agrees with the fact that it has been shown[5] that the reactivity of an addendum in the Michael condensation is not related to its tendency to enolize. However, the recognized ability of elements other than those of the first period to give transitory reaction intermediates and in some cases stable compounds with expanded valence shells, makes the latter explanation plausible.

Experimental Part

Condensation of Benzyl *p*-Tolyl Sulfone with Benzalacetophenone.—To a solution of 49.2 g. (0.2 mole) of benzyl *p*-tolyl sulfone[1] and 41.6 g. (0.2 mole) of benzalacetophenone in 1700 ml. of dry thiophene-free benzene was added a sodium methoxide solution prepared by dissolving 4.6 g. (0.2 gram atom) of sodium in 60 ml. of absolute methanol. Because of the formation of two liquid phases, the mixture was stirred with a mechanical stirrer. After a reaction period[9] of one week at room temperature 15 ml. of glacial acetic acid was added and the mixture washed with water to remove sodium acetate. The aqueous layer contained an emulsion; this layer, upon separation from the benzene gave, upon standing, 4.8 g. of product which upon recrystallization from benzene gave 2.2 g., m. p. 194–195° (corr.).

The benzene extracts were distilled until 1300 ml. of benzene had been removed. Upon cooling, 16.4 g. (m. p. 164–170°) of solid was obtained, which after recrystallization from benzene gave 9.8 g. melting at 197–197.5° (corr.).

Further concentration of the benzene extracts gave 14.1 g. (m. p. 134–136°) which, upon recrystallization from alcohol gave 11.3 g. of benzyl *p*-tolyl sulfone, m. p. 141–142° (corr.), which suffered no depression of the melting point when mixed with an authentic sample of benzyl *p*-tolyl sulfone.

All of the solvent was removed from the benzene extracts and ether added. The sulfones, which are quite insoluble in ether, are readily separated from benzalacetophenone in this manner. The ether-insoluble residue was washed with ether, giving 29.0 g., m. p. 104–111°, which, after seven recrystallizations from alcohol, gave 7.0 g., m. p. 139–141° (corr.). This product, when mixed with benzyl *p*-tolyl sulfone, gave a mixture melting at 111–113°.

The mother liquors from all the above recrystallizations were combined, concentrated and recrystallized many times from alcohol. The total yields of pure substances, including those mentioned above, finally isolated from the reaction were as follows. There was obtained 13.4 g. (14.7%) of the higher melting condensation product, m. p. 197–197.5° (corr.).

Anal. Calcd. for $C_{29}H_{26}O_3S$: S, 7.0. Found: S, 7.2, 7.2.

In addition to 11.3 g. (23%) of unreacted benzyl *p*-tolyl sulfone (m. p. 141–142°, corr.) there was obtained 10.3 g. (11.4%) of the lower melting isomer of the condensation product, m. p. 139–141° (corr.).

Anal. Calcd. for $C_{29}H_{26}O_3S$: S, 7.0. Found: S, 6.6.

The mother liquors from the crystallizations contained 10.4 g. of a mixture, m. p. 96–118°.

Other Reactions.—Under conditions similar to those described above, the reactions of benzyl *p*-tolyl sulfone and desoxybenzoin with methyl cinnamate, and of bis-(phenylsulfonyl)-methane[10] and methyl *p*-tolyl sulfone with benzalacetophenone were unsuccessful. Using conventional methods, the reactions of bis-(phenylsulfonyl)-methane and benzyl *p*-tolyl sulfone with benzaldehyde,[11] *p*-chlorobenzaldehyde,[11] selenium dioxide,[12] nitrous acid,[13] and isoamyl nitrite[14] (in the presence of sodium ethoxide) were tested. The recovery of unchanged sulfone was above 90% in the majority of the cases and was never below 75%.

Application of the mercuric chloride test[7] gave a positive result with bis-(phenylsulfonyl)-methane but was negative with benzyl *p*-tolyl sulfone.

Summary

The addition of benzyl *p*-tolyl sulfone to benzalacetophenone has been described and certain

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[6] Andrews and Connor, THIS JOURNAL, **57**, 895 (1935).

[7] Connor and Van Campen, *ibid.*, **58**, 1131 (1936).

[8] The consideration of the electronic structure of sulfones has been adequately discussed by others[1,3] in relationship to similar questions.

[9] Another run in which the reaction period was twenty-four hours gave similar results, but slightly lower yields of condensation products.

[10] Kohler and Tishler, THIS JOURNAL, **57**, 223 (1935).

[11] Tröger and Nolte, *J. prakt. Chem.*, **101**, 136 (1920).

[12] "Organic Syntheses," John Wiley and Sons, New York, 1935, Vol. XV, p. 67.

[13] *Ibid.*, p. 17.

[14] Tröger and Lux, *Arch. Pharm.*, **247**, 618 (1909).

similarities in the behavior of sulfones and ketones in the Michael condensation pointed out. The mercuric chloride test was positive with bis-(phenylsulfonyl)-methane but negative with benzyl *p*-tolyl sulfone. The other reactions of active methylene compounds tested were not successful with these sulfones.

PHILADELPHIA, PENNA. RECEIVED JUNE 3, 1936

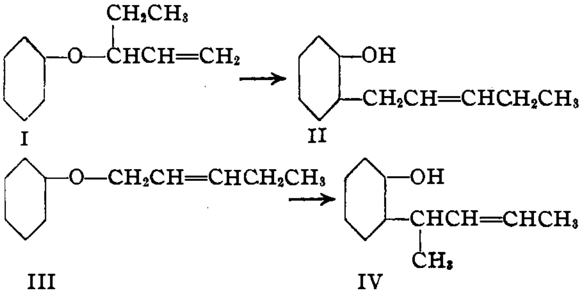
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Phenyl Allyl Ethers[1]

BY WALTER M. LAUER AND WILLIAM F. FILBERT

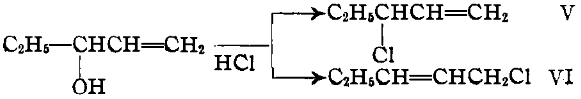
The results of Claisen's investigations dealing with the rearrangement of phenyl allyl ethers are well known. It is sufficient for our present purpose to recall that the migrating allyl group shows a preference for the ortho position and that the point of attachment of the allyl group in the cases hitherto investigated is shifted from the alpha to the gamma carbon atom. The rearrangement of a number of substituted phenyl allyl ethers has been examined,[2] but no study has been made of an isomeric pair of the type, $C_6H_5OCH(R)CH{=}CH_2$ and $C_6H_5OCH_2CH{=}CHR$. This omission presumably is due to the difficulty of obtaining the isomeric halides necessary for the usual synthesis of these ethers. Fortunately, however, Meisenheimer and Link[3] have shown that the action of hydrogen chloride on ethylvinylcarbinol leads to a mixture of $CH_3CH_2CHClCH{=}CH_2$ and $CH_3CH_2CH{=}CHCH_2Cl$, which may be separated by means of a careful fractional distillation. It was therefore considered not without interest to prepare such a pair of isomeric ethers and to study their rearrangement.

The ether I yielded the expected rearrangement product, II, but its isomer, III, quite unexpectedly, yielded IV.



The Isomeric Ethers

The two isomeric chlorides, 3-chloro-1-pentene and 1-chloro-2-pentene, were prepared by the action of gaseous hydrogen chloride upon ethylvinylcarbinol.



The two isomeric ethers, I and II, were obtained from these chloropentenes by treatment with phenol and potassium carbonate in the presence of acetone. On account of the possibility of an alpha-gamma transposition, it was especially important to establish the structures of these ethers. This was accomplished by oxidation: I yielded α-phenoxybutyric acid, $C_6H_5OCH(C_2H_5)COOH$, whereas III under similar conditions gave phenoxyacetic acid, $C_6H_5OCH_2COOH$.

The preparation of *1-chloro-2-pentene* (VI) and *3-chloro-1-pentene* (V) was carried out as follows. Ninety-nine grams (1.15 moles) of freshly distilled ethylvinylcarbinol was saturated with dry hydrogen chloride at 0°. After standing for three hours in an ice box, the reaction mixture was again saturated at 0°. This process was then repeated after standing overnight. The total gain in weight was 62 g. Finally after standing for twenty-four hours in an ice box, the lower aqueous layer was separated and the mixed chlorides were placed over anhydrous potassium carbonate for two weeks. The mixture was filtered and then fractionally distilled using a 60-cm. Widmer column. Refractionation gave the following results: (1) $C_2H_5CHClCH{=}CH_2$, b. p. 50–50.2° (150 mm.), 42.1 g.; (2) intermediate, b. p. 50.2–62° (149 mm.), 2.1 g.; (3) $C_2H_5CH{=}CHCH_2Cl$, b. p. 62° (149 mm.) to 63.2° (146 mm.), 43.5 g.; (4) residue 3.7 g.

γ-Ethylallyl Phenyl Ether (III).—A mixture of 18.8 g. of phenol (0.2 mole), 20.9 g. of 1-chloro-2-pentene (0.2 mole), 29.0 g. (0.21 mole) of anhydrous potassium carbonate and 20 cc. of acetone, combined in the order named, was placed in a 200-cc. round-bottomed flask. The reaction mixture was refluxed on the steam-bath for eighteen hours, cooled, taken up in water and 25 cc. of ether added. After separating the aqueous layer, it was again extracted with ether. The combined ether extract was then shaken twice with 15–20 cc. of 20% sodium hydroxide. After drying

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[1] Abstract of a thesis submitted to the Graduate Faculty of the University of Minnesota by William F. Filbert for the degree of Doctor of Philosophy, August, 1934.

[2] For an excellent discussion see Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., N. Y., 1929, p. 214 *et seq.*; also Hurd *et al.*, THIS JOURNAL, **52,** 1700, 3356 (1930); **53,** 1068, 1917 (1931); **54,** 1648 (1932).

[3] Meisenheimer and Link, *Ann.*, **479,** 211 (1930).