Methylation of 2,6-diethoxyphenol with methyl sulfate gave **1,3-diethoxy-2-methoxybenzene** (77%), b.p. 168–174° (84 mm.). On redistillation the middle colorless fraction boiled at 145–146° (34 mm.).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.75; H, 8.28.

2,3-Dihydroxy-4,6-dimethoxyacetophenone.—The following is typical of the method used to prepare the 2,3-dihydroxyacetophenones in Table II. A solution of 2.66 g. of 2-hydroxy-3,4,6-trimethoxyacetophenone, m.p. 108–112°, in 37.5 ml. of acetic acid was combined with 7.5 ml. of 30% hydrogen bromide–acetic acid and allowed to stand at room temperature for 24 hr. The solution was treated at 0° with 160 ml. of 10% sodium hydroxide and extracted four or five times (or continuously in an extractor) with ether. Evaporation of the ether gave crystals which were then recrystallized from benzene, 0.9 g. (42%), m.p. 146–154°. Further purification brought the melting point to 165.2–166.5°. The compound gave a black color with ferric chloride and depressed the melting point of 2,3,6-trihydroxy-4-methoxyacetophenone which was prepared by reduction of the quinone above.

Anal. Calcd. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.96; H 5.71.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Anomalous Reaction of Methylmagnesium Iodide with the Tosylate of *p*-Hydroxybenzaldehyde[1]

BY WESLEY J. DALE AND HENRY E. HENNIS

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The addition of methylmagnesium iodide to the tosylate of *p*-hydroxybenzaldehyde did not give the expected product, *p*-vinylphenyl tosylate; rather, *p*-isopropenylphenyl tosylate was obtained in 52% yield. The structure of the anomalous product was determined by an independent synthesis. It is postulated that a small amount of the normal Grignard complex, in the presence of an excess of the aldehyde, serves as a Tischenko catalyst to form the ditosylate of *p*-hydroxybenzyl *p*-hydroxybenzoate. Reaction of this ester with methylmagnesium iodide, followed by dehydration of the resulting tertiary carbinol, gives *p*-isopropenylphenyl tosylate.

In a study concerning the preparation of various esters of *p*-vinylphenol, addition of methylmagnesium iodide to the tosylate of *p*-hydroxybenzaldehyde (I) *via* the inverse technique did not yield the expected product, *p*-vinylphenyl tosylate. Instead, a brown oil was obtained which could not be induced to crystallize from a variety of solvents tried, but which gave, upon distillation *in vacuo*, a single white solid III having the composition of a homolog of *p*-vinylphenyl tosylate.

The structure of this unexpected product was determined by the reactions shown below (I–VII). Compound III added bromine readily but failed to give a crystalline bromine derivative. When III was saponified and the basic hydrolysis mixture was carbonated, a white crystalline solid IV separated whose physical properties did not resemble those of either *p*-propenylphenol[2] or *p*-allylphenol.[3] Since IV was not very stable and became yellow on contact with air, it was converted to its benzoate derivative V whose composition again indicated that the parent phenol was a homolog of *p*-vinylphenol. It was apparent that III was the tosylate of *p*-isopropenylphenol. An authentic sample of III was prepared by the reaction of methylmagnesium iodide with *p*-carboethoxyphenyl tosylate (VI). The product of this reaction possessed physical properties identical to those of III obtained from I and the mixed melting point of III with authentic *p*-isopropenylphenyl tosylate was not depressed. When a sample of authentic *p*-isopropenylphenyl tosylate was converted to its benzoate without isolation of the intermediate phenol, the melting point of the product was identical to that of V obtained from the anomalous reaction and the mixed melting point with V was not depressed. Further, authentic III, like the product obtained from I, absorbed bromine but also failed to give a solid bromine derivative.

It seemed most likely that the anomalous compound III was obtained from the dehydration of a tertiary alcohol which could result from the reaction of the Grignard reagent with a ketone, such as the tosylate of *p*-hydroxyacetophenone, or with some ester of the tosylate of *p*-hydroxybenzoic acid. The possibility was first examined that a substituted acetophenone was the precursor of *p*-isopropenylphenyl tosylate, although no evidence of the presence of even a trace of ketone was detected in the product of the anomalous reaction. When methylmagnesium iodide was added to *p*-acetylphenyl tosylate under the conditions of the original Grignard reaction, no distillable products were obtained and, in another experiment, the only volatile product obtained was unreacted *p*-acetylphenyl tosylate (15% recovery). It was concluded that even if *p*-acetylphenyl tosylate had been generated in the original reaction mixture, its reaction with methylmagnesium iodide would not lead to the formation of *p*-isopropenylphenyl tosylate under the conditions of our experiments.

An ester therefore appeared to be the more probable precursor, especially since Franke and Kohn[4] obtained an ester, hydroxypivalyl hydroxypivalate, from the reaction of hydroxypivalaldehyde with ethylmagnesium bromide. The most plausible explanation for the origin of III therefore seems to be that a Tischenko type of reaction is involved once a Grignard complex is formed; the over-all reaction can thus be imagined to proceed through the series of transformations shown below (VIII–

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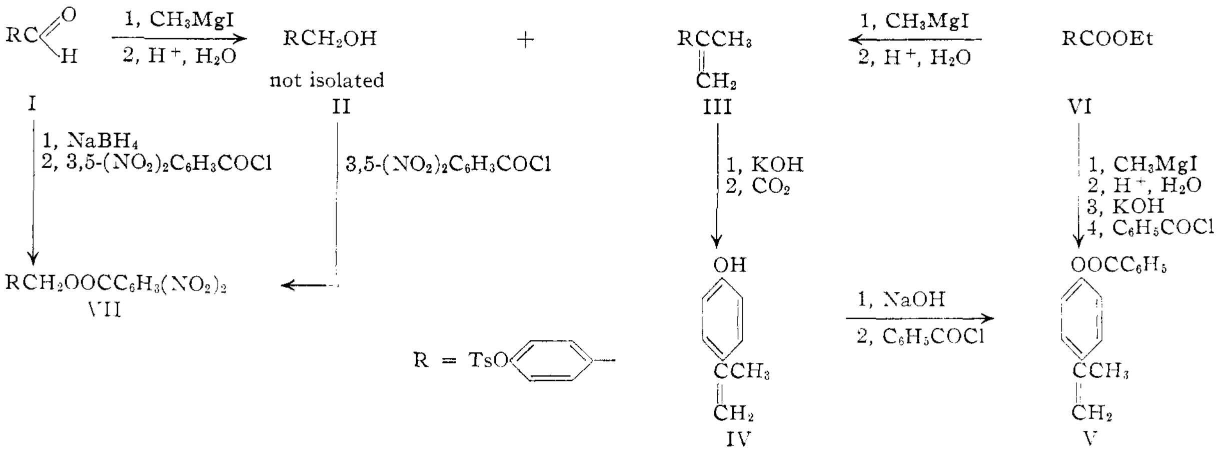
[1] Abstracted from a portion of a thesis to be submitted by H. E. H. to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the Ph.D. degree.

[2] R. Stoermer and B. Kahlert, *Ber.*, **34**, 1812 (1901).

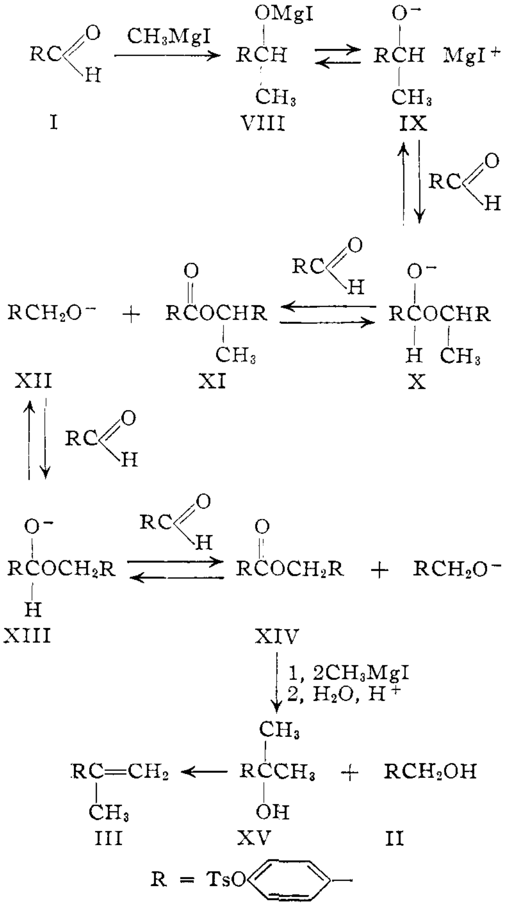
[3] J. F. Eykman, *ibid.*, **22**, 2736 (1889).

[4] A. Franke and M. Kohn, *Monatsh.*, **25**, 865 (1904).



XV). To demonstrate the role of the proposed intermediate ester XIV in providing the anomalous product, methylmagnesium iodide was caused to react with the ditosylate of *p*-hydroxybenzyl *p*-hydroxybenzoate under the conditions of the original Grignard reaction; a 41% yield of *p*-isopropenylphenyl tosylate was obtained.

The first portion of methylmagnesium iodide introduced into the presence of the aldehyde I probably reacts normally to form the addition complex VIII which dissociates, to some extent, into its ions IX. The excess aldehyde may then undergo nucleophilic addition by the anion IX of the normal addition complex VIII to give the anion X. Another molecule of aldehyde may then react with X to give the free ester XI and the anion of *p*-tosyloxybenzyl alcohol XII. In the presence of the more conventional type of Tischenko catalyst XII, the Tischenko reaction can now be perpetuated by further reaction of XII with excess aldehyde to give ester XIV. The ester XI is probably present only in small amounts since no products were isolated which would suggest that this ester was present in detectable amounts. Finally, two moles of methylmagnesium iodide can react with ester XIV in the normal fashion and decomposition of the Grignard complex would give the carbinol XV in addition to *p*-methylolphenyl tosylate (II). XV then suffers dehydration, either during the decomposition of the Grignard intermediate or during the distillation of the product, to give *p*-isopropenylphenyl tosylate (III). An excess of the aldehyde is apparently important in this reaction sequence, since the Grignard reaction carried out in the normal way, by addition of the aldehyde to the solution of methylmagnesium iodide, failed to give any of the anomalous product.



Since a by-product of the above series of reactions is *p*-methylolphenyl tosylate (II), proof of the presence of this alcohol in the original reaction mixture is of importance to the proposed mechanism. Attempts to obtain *p*-hydroxybenzyl alcohol by saponification of the crude reaction mixture were unsuccessful. This was not too surprising, since *p*-hydroxybenzyl alcohol is quite water soluble[5] and decomposes to a colorless resin when heated above 100°.[6] Another portion of the crude reaction mixture was dissolved in pyridine and caused to react with 3,5-dinitrobenzoyl chloride in the attempt to obtain the slightly soluble and high melting derivative VII. A crystalline compound was obtained which was very difficult to obtain pure, but whose carbon and hydrogen content agree closely with the theoretical values calculated for VII. Authentic VII was obtained by the reduction of the tosylate of *p*-hydroxybenzaldehyde with sodium borohydride to *p*-methylolphenyl tosylate, which was converted to its 3,5-dinitrobenzoate derivative. The mixed melting point of authentic VII with the 3,5-dinitrobenzoate prepared from the original reaction mix-

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(5) J. Biedermann, *Ber.*, **19**, 2373 (1886).

(6) Fabriques de produits de chimie organique de Laire, German Patent 189,262; *Chem. Zentr.*, **98**, II, 2002 (1907).

ture was not depressed and, further, the infrared absorption spectra of the two compounds were virtually identical in the region 1110 to 1850 cm.$^{-1}$.

It is true that the carbinol XV could possibly be obtained from ester XI by reaction of XI with excess methylmagnesium iodide. However, if this were the route by which XV was formed, we should have detected evidence of the presence of methyl *p*-tosyloxyphenyl carbinol, or of its corresponding dehydration product—the tosylate of *p*-vinylphenol—among the products of the anomalous reaction. It is highly improbable that the tosylate of *p*-vinylphenol, if formed in the reaction mixture, would have escaped detection because of its complete polymerization, since we have observed that this substance is sufficiently stable to permit its distillation under reduced pressure. Also, if the direct reaction of XI with methylmagnesium iodide were the major route to XV, the formation of II in a relatively large amount would not be accounted for satisfactorily.

Since *p*-vinylphenyltosylate was not obtained by the reaction of methylmagnesium iodide with the tosylate of *p*-hydroxybenzaldehyde, it was synthesized by another route. The tosylate of *p*-hydroxybenzaldehyde was condensed with malonic acid in the presence of a trace of pyridine to give the tosylate of *p*-hydroxycinnamic acid. The cinnamic acid was then decarboxylated with copper and quinoline to give *p*-vinylphenyl tosylate. *p*-Vinylphenyl tosylate has a lower melting point and a lower boiling point than the product obtained from the above anomalous Grignard reaction. It adds bromine to give a crystalline derivative, in contrast to *p*-isopropenylphenyl tosylate, which gives only a noncrystallizable oil.

Experimental

All melting points and boiling points are uncorrected.

Tosylate of *p*-Hydroxybenzaldehyde.—This compound was first prepared by the oxidation of the tosylate of *p*-cresol.[7] However, the sample used in this study was prepared by the tosylation of *p*-hydroxybenzaldehyde. A mixture consisting of 20.0 g. (0.492 mole) of sodium hydroxide dissolved in 180 ml. of water, 50.0 g. (0.410 mole) of *p*-hydroxybenzaldehyde and 85.5 g. (0.450 mole) of *p*-toluenesulfonyl chloride was stirred at room temperature for 1 hr. and then cooled in an ice-bath. The solid which separated was collected, dissolved in hot aqueous ethanol, clarified with charcoal and recrystallized from the same solvent to give 104 g. (92%) of white crystalline material, m.p. 72–73° (lit.,[7] m.p. 73–74°).

The Reaction of Methylmagnesium Iodide with the Tosylate of *p*-Hydroxybenzaldehyde; *p*-Isopropenylphenyl Tosylate and its Conversion to *p*-Isopropenylphenyl Benzoate.—The Grignard reagent was prepared in the usual manner from 5.45 g. (0.224 atom gram) of magnesium turnings and 35.5. g. (0.250 mole) of methyl iodide in 150 ml. of absolute ether. To a slurry of 61.9 g. (0.224 mole) of *p*-tosyloxybenzaldehyde and 150 ml. of absolute ether, the Grignard reagent was added, dropwise and with stirring; the addition was complete in 1 hr. A heavy yellow sludge formed during the addition which made stirring difficult. When the addition of the Grignard reagent was complete, the reaction mixture was stirred and heated at the reflux temperature for 4 hr. Since the sludge could not be poured from the reaction flask, the reaction flask was placed in an ice-bath and a solution containing 200 ml. of water and 30 ml. of concentrated hydrochloric acid was added dropwise, with stirring. It was necessary for the mixture to remain at room temperature for 24 hr. before decomposition of the complex was complete. The ethereal layer was separated and the aqueous layer was extracted twice with ether. The combined ether extracts were washed with water, twice with 5% sodium hydroxide solution, twice with 10% sodium bisulfite solution, once again with water and then dried over anhydrous sodium sulfate. The ether was removed by distillation; the residue, a viscous brown oil, could not be induced to crystallize from a variety of solvents tried. The oil was distilled under reduced pressure, b.p. 203–210° (1 mm.); the major fraction boiled at 207–209°. The pale yellow distillate solidified on cooling. There remained in the distilling flask 41 g. of a dark red non-distillable tar. The distillate was recrystallized from aqueous ethanol to give 16.7 g. (52%, calculated on the basis of the stoichiometry indicated in series VIII–XV) of white crystalline solid, m.p. 84–86°. Further recrystallization from aqueous ethanol gave stout white needles, m.p. 88.5–90°.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.67; H, 5.51.

A chloroform solution of the product absorbed bromine. Evaporation of the solvent left a yellow viscous residue which could not be induced to crystallize.

A mixture consisting of 5 g. of sodium hydroxide dissolved in 50 ml. of water, 50 ml. of ethanol and 2.18 g. (0.00757 mole) of *p*-isopropenylphenyl tosylate obtained from the above Grignard reaction was allowed to remain at room temperature for one day, during which time the undissolved ester was saponified and went into solution. The solution was extracted twice with petroleum ether (b.p. 60–68°) to remove unreacted starting material and the aqueous solution was carbonated with Dry Ice to the saturation point. The weakly alkaline solution was extracted twice with ether, and the combined ethereal extracts were dried over anhydrous sodium sulfate. The ether was removed by evaporation under slightly reduced pressure, leaving a pale yellow solid residue which was recrystallized from petroleum ether (b.p. 60–68°) to give 0.56 g. (55%) of white plates, m.p. 74–75°. The compound had a phenolic odor and rapidly turned yellow in air. A portion of the phenol was dissolved in 5% sodium hydroxide solution and treated with benzoyl chloride. The white solid which formed was collected on a Buchner funnel and recrystallized from aqueous ethanol and then from ethanol itself to give fine white needles, m.p. 112–113.5°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.48; H, 5.73.

***p*-Carboethoxyphenyl Tosylate.**—A mixture containing 17.0 g. (0.425 mole) of sodium hydroxide dissolved in 200 ml. of water, 55.7 g. (0.336 mole) of ethyl *p*-hydroxybenzoate and 76.0 g. (0.400 mole) of *p*-toluenesulfonyl chloride was stirred vigorously for 1 hr. and then cooled in an ice-bath. The product was collected, washed with water and recrystallized from aqueous ethanol to give 48.8 g. (45%) of a white crystalline solid, m.p. 56–58°. After further recrystallization from petroleum ether (b.p. 60–68°) the white solid melted at 58–59°.

Anal. Calcd. for $C_{16}H_{16}O_5S$: C, 59.98; H, 5.04. Found: C, 60.09; H, 5.23.

***p*-Isopropenylphenyl Tosylate from the Reaction of *p*-Carboethoxyphenyl Tosylate with Methylmagnesium Iodide; Conversion to *p*-Isopropenylphenyl Benzoate.**—Methylmagnesium iodide was prepared in the usual manner from 7.15 g. (0.294 gram atom) of magnesium turnings, 42.0 g. (0.296 mole) of methyl iodide and 100 ml. of absolute ether. The Grignard reagent was added dropwise, with stirring, to a slurry of 45.0 g. (0.140 mole) of *p*-carboethoxyphenyl tosylate and 150 ml. of absolute ether. Two liquid phases separated during the addition. The reaction mixture was stirred and heated at the reflux temperature for 4 hr., during which time one of the liquid phases solidified. The mixture was poured onto a mixture of ice and hydrochloric acid, the layers were separated and the aqueous layer was extracted twice with ether. The combined ethereal solutions were washed successively with small portions of 5% sodium carbonate solution, 5% sodium hydroxide solution and water and then dried over anhydrous sodium sulfate. The ether was removed by distillation, leaving a pale yellow solid residue which was distilled to give a pale yellow oil, b.p. 212–219° (1.5 mm.), the major fraction distilling at 213–215°; the distillate solidified upon cooling. A dark red, tarry residue (23 g.) remained in the distilling flask. The distillate was recrystallized from aqueous ethanol to afford

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[7] Badische Anilin- u. Soda-Fabrik, German Patent 162,322; *Chem. Zentr.*, **96**, II, 726 (1905).

14.9 g. (37%) of a colorless solid, m.p. 86–87°. Further recrystallization from ethanol yielded stout white needles, m.p. 90–90.5°. An intimate mixture (1:1) of *p*-isopropenylphenyl tosylate obtained from this experiment and the product obtained from the reaction of methylmagnesium iodide with *p*-tosyloxybenzaldehyde melted at 89–90°. A chloroform solution of the product absorbed bromine, but the bromide could not be induced to crystallize.

A mixture containing 5.00 g. (0.0173 mole) of *p*-isopropenylphenyl tosylate, prepared as described above, 10 g. of sodium hydroxide dissolved in 75 ml. of water and 25 ml. of ethanol was stirred at room temperature for one day, during which time complete solution was effected. With stirring, 2.8 g. (0.020 mole) of benzoyl chloride was added. The product was collected on a Buchner funnel, washed with water and recrystallized from aqueous ethanol to give 1.57 g. (38%) of white crystalline solid, m.p. 112–113°. A sample was recrystallized from ethanol; fine white needles, m.p. 113–114°, were obtained. An intimate mixture (1:1) of this compound with the benzoate ester derived from the anomalous reaction melted at 112–113°.

***p*-Acetylphenyl Tosylate.**—The white solid obtained from the reaction of a mixture of 8.8 g. (0.22 mole) of sodium hydroxide dissolved in 200 ml. of water, 9.8 g. (0.065 mole) of *p*-hydroxyacetophenone and 29 g. (0.18 mole) of *p*-toluenesulfonyl chloride was recrystallized from petroleum ether (b.p. 60–68°) to give 14.0 g. (74%) of white crystalline product, m.p. 71–72°. Further recrystallization from the same solvent afforded fine white needles, m.p. 72–73°.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86. Found: C, 62.33; H, 5.19.

The *p*-nitrophenylhydrazone was recrystallized from ethyl acetate to give golden needles, m.p. 219–219.5°.

Anal. Calcd. for $C_{21}H_{18}O_5N_3S$: C, 59.42; H, 4.27. Found: C, 59.55; H, 4.59.

Reaction of *p*-Acetylphenyl Tosylate with Methylmagnesium Iodide.—Methylmagnesium iodide was added to *p*-acetylphenyl tosylate under the conditions of the original Grignard reaction, and the product was treated in the same manner as in the Grignard reactions previously described. From the first experiment, no distillable product was obtained and a residue of black, tarry material remained in the distilling flask. In the second experiment, 15% of unreacted *p*-acetylphenyl tosylate was recovered in the distillate, and the residue was again a tar.

***p*-Methylolphenyl Tosylate.**—The general method of Chaikin and Brown[8] for the reduction of aldehydes to alcohols with sodium borohydride was employed, using 143 g. (0.518 mole) of *p*-tosyloxybenzaldehyde mixed with 200 ml. of methanol and 5.8 g. (0.15 mole) of sodium borohydride dissolved in 100 ml. of methanol. There was obtained 136 g. (94%) of crude pale yellow solid, m.p. 41–44°, which decomposed when subjected to attempted distillation even under very low pressures. A pure sample was obtained by recrystallization from ether–petroleum ether (b.p. 60–68°) mixtures at Dry Ice temperature to give very fine white needles, m.p. 44–45°.

Anal. Calcd. for $C_{14}H_{14}O_4S$: C, 60.41; H, 5.07. Found: C, 60.15; H, 5.16.

Tosylate of *p*-Hydroxybenzoic Acid.—This compound had been prepared previously by the oxidation of the tosylate of *p*-cresol.[7] It was prepared for this study by the reaction of a mixture containing 100 g. (0.725 mole) of *p*-hydroxybenzoic acid, 170 g. (0.900 mole) of *p*-toluenesulfonyl chloride and 80.0 g. (1.97 moles) of sodium hydroxide dissolved in 400 ml. of water. The sodium salt of the product separated during the reaction. The addition of more water (100 ml.) and heat were necessary to dissolve the salt. The solution was acidified with hydrochloric acid to precipitate the acid, which was recrystallized from aqueous ethanol to give 173 g. (82%) of white crystalline product, m.p. 167–169° (lit.[7] m.p. 168–170°).

Tosylate of *p*-Hydroxybenzoyl Chloride.—A mixture containing 100 g. (0.342 mole) of the tosylate of *p*-hydroxybenzoic acid, 61 g. (0.56 mole) of thionyl chloride and 300 ml. of dry benzene was stirred at the reflux temperature for 4 hr., during which time solution became complete. The excess thionyl chloride and the benzene were removed by distillation under slightly reduced pressure. The residue was recrystallized from a benzene–petroleum ether (b.p. 60–68°) mixture to give 107 g. (100%) of white crystalline product, m.p. 73–74°. Further recrystallization from the same solvent afforded flat white needles, m.p. 75–77°.

Anal. Calcd. for $C_{14}H_{11}O_4SCl$: C, 54.11; H, 3.57. Found: C, 54.13; H, 3.93.

The amide, prepared from aqueous ammonia, was recrystallized from aqueous ethanol to give fine white needles, m.p. 151.5–152°.

Anal. Calcd. for $C_{14}H_{13}O_4SN$: C, 57.73; H, 4.50. Found: C, 57.44; H, 4.77.

Ditosylate of *p*-Hydroxybenzyl *p*-Hydroxybenzoate.—A solution containing 48.0 g. (0.173 mole) of crude *p*-methylolphenyl tosylate, 60.0 g. (0.193 mole) of the tosylate of *p*-hydroxybenzoyl chloride and 100 ml. of pyridine was heated at reflux temperature for 2 hr. The product was a yellow oil which solidified when triturated with ether. The solid was recrystallized from ethanol to give 65.9 g. (69%) of white crystals, m.p. 118–121°. Further recrystallization from ethyl acetate–ethanol mixtures afforded flat white crystals, m.p. 120–121°.

Anal. Calcd. for $C_{28}H_{24}O_8S_2$: C, 60.84; H, 4.38. Found: C, 60.67; H, 4.54.

Reaction of the Ditosylate of *p*-Hydroxybenzyl *p*-Hydroxybenzoate with Methylmagnesium Iodide; *p*-Isopropenylphenyl Tosylate.—Methylmagnesium iodide, prepared from 5.45 g. (0.224 gram atom) of magnesium turnings and 35.5 g. (0.250 mole) of methyl iodide dissolved in 150 ml. of absolute ether, was added dropwise with stirring, to a slurry of 61.9 g. (0.112 mole) of the ditosylate of *p*-hydroxybenzyl *p*-hydroxybenzoate and 200 ml. of ether; the addition was complete at the end of 1 hr. The reaction mixture was treated in the same fashion as in the anomalous reaction. Distillation of the crude product gave a pale yellow distillate, b.p. 210–222° (1.5 mm.), with the major fraction distilling at 218–220°. The distillate, which solidified on cooling, was recrystallized from aqueous ethanol to give 13.3 g. (41%) of *p*-isopropenylphenyl tosylate, m.p. 87–89°.

Isolation of *p*-Methylolphenyl Tosylate from the Products of the Anomalous Reaction.—Another reaction of *p*-tosyloxybenzaldehyde with methylmagnesium iodide was performed as described above, and the reaction mixture was treated in exactly the same manner up to the distillation. A solution containing 24.3 g. of the brown oil, 22.5 g. of 3,5-dinitrobenzoyl chloride and 100 ml. of pyridine was heated on a steam-bath for 8 hr. and then poured on a mixture of 200 g. of ice and 10 g. of sodium carbonate. The solid which separated was collected and dried in air to give 5.71 g. of pale brown amorphous solid, m.p. 128–147°. The product was recrystallized once from ethanol, once from a mixture of benzene and petroleum ether (b.p. 60–68°) and once again from ethanol to give 2.44 g. of white crystalline solid, m.p. 140–148°.

Further crystallizations from ethyl acetate–ethanol mixtures gave white leaflets, m.p. 165–166°. Repeated recrystallizations were not completely successful in freeing this product from the last traces of tenacious impurities.

Anal. Calcd. for $C_{21}H_{16}O_9N_2S$: C, 53.39; H, 3.41. Found: C, 54.19; H, 3.51.

The 3,5-Dinitrobenzoate of *p*-Methylolphenyl Tosylate.—The derivative was prepared by heating a solution of 9.45 g. (0.0340 mole) of *p*-methylolphenyl tosylate, 9.2 g. (0.040 mole) of 3,5-dinitrobenzoyl chloride and 50 ml. of pyridine at the reflux temperature for 4 hr. The product was recrystallized from an ethyl acetate–ethanol mixture to give 4.9 g. (26%) of white crystalline compound, m.p. 163–165°. Further recrystallization from the same solvent gave white leaflets, m.p. 166–167°.

Anal. Calcd. for $C_{21}H_{16}O_9N_2S$: C, 53.39; H, 3.41. Found: C, 53.38; H, 3.63.

An intimate mixture (1:1) of this compound with the compound isolated above as the 3,5-dinitrobenzoate derivative from the reaction mixture of *p*-tosyloxybenzaldehyde with methylmagnesium iodide melted at 165–166.5°. The infrared absorption spectra of the two compounds, scanned from 1110 to 1850 cm.^{-1}, were essentially identical.

Tosylate of *p*-Hydroxycinnamic Acid.—A mixture of 75.0 g. (0.272 mole) of the tosylate of *p*-hydroxybenzaldehyde, 42.5 g. (0.407 mole) of malonic acid and 7 ml. of pyridine was heated for 1 hr. during which time the mixture melted, evolved carbon dioxide and solidified. The product was recrystallized from ethanol to give 79.9 g. (92%) of white solid, m.p. 201–202°.

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[8] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1941).

Anal. Calcd. for $C_{16}H_{14}O_5S$: C, 60.36; H, 4.43. Found: C, 60.53; H, 4.63.

The amide was prepared in the usual manner using thionyl chloride and aqueous ammonia. The product was recrystallized from aqueous ethanol to give fine white needles, m.p. 151–151.5°.

Anal. Calcd. for $C_{16}H_{14}O_4NS$: C, 60.52; H, 4.76. Found: C, 60.61; H, 4.55.

p-Vinylphenyl Tosylate.—A mixture containing 100 ml. of freshly distilled quinoline and 5 g. of copper powder was heated to 220°. With stirring, 50.0 g. (0.157 mole) of the tosylate of p-hydroxycinnamic acid was added, in small portions; the addition was complete in 15 minutes. Stirring and heating were continued for 1 hr. The crude reaction mixture was distilled, and the fraction boiling at 90–180° (1 mm.) was retained. This fraction solidified when cooled and was recrystallized from aqueous ethanol to give 12.7 g. (30%) of white crystalline product, m.p. 67–68°. A second experiment gave a 33% yield of product. Further recrystallization from aqueous ethanol gave flat white needles, m.p. 68–68.5°.

Anal. Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.40; H, 5.26.

The dibromide derivative was prepared by dissolving the compound in chloroform, adding bromine until the bromine color persisted; evaporation of the solvent left a pale yellow solid. Recrystallization from aqueous ethanol gave fine white needles, m.p. 74–75°.

Anal. Calcd. for $C_{15}H_{14}O_3SBr_2$: C, 41.48; H, 3.25. Found: C, 41.45; H, 3.44.

The Addition of the Tosylate of p-Hydroxybenzaldehyde to Methylmagnesium Iodide.—To 0.203 mole of methylmagnesium iodide was added dropwise with stirring an ethereal solution of 56.0 g. (0.203 mole) of the tosylate of p-hydroxybenzaldehyde. No sludge formed during this addition, in marked contrast to the behavior of the inverse addition. The reaction mixture was purified in the same manner as the anomalous reaction. Distillation of the crude product under diminished pressure gave a trace of yellow solid distillate before sudden decomposition occurred, leaving a non-distillable purple tar.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF BRYN MAWR COLLEGE AND THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Allyl Groups in Three-carbon Systems. VI. Benzene and Phenanthrene Derivatives

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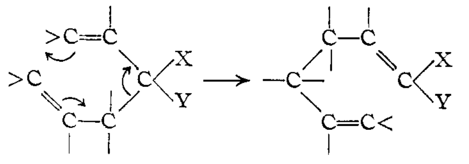
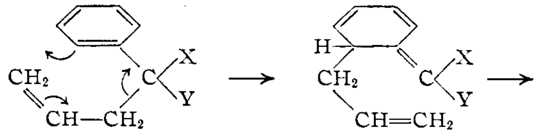
Compounds III–VI and VIII containing an allyl group and a benzenoic ring attached to a carbon atom substituted by two electron-attracting groups failed to rearrange on heating with migration of the allyl group to an *ortho* position. Such rearrangements do occur with migration of an allyl group to the β-carbon atom of an aliphatic vinyl group (*i.e.* I → II). Diethyl α-allyl-9-phenanthrenemalonate (IX) was observed to rearrange on heating, and evidence has been obtained indicating that the rearrangement product is the diethyl ester of 1-carboxy-2,3-dihydro-1H-cyclopenta(*l*)phenanthrene-2-acetic acid (XI).

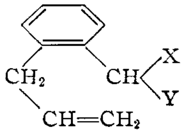
Earlier papers in this series[1] have described the thermal intramolecular rearrangement of allyl groups in three-carbon systems. The allyl group has been shown to migrate with inversion from a carbon atom which in most instances was attached to one or more electron-attracting groups to the β-carbon atom of an aliphatic vinyl group, as shown in the equation


I II

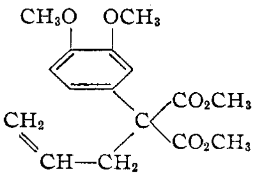
This paper reports an investigation of the behavior on heating of a number of similar compounds in which the two carbon atoms comprising the vinyl group form part of an aromatic ring. Rearrangement of such compounds would be similar to the Claisen rearrangement of allyl aryl ethers[2] and would be expected to occur with a shift of hydrogen to reform the aromatic nucleus as shown in the equation



III, $X = Y = CO_2C_2H_5$
IV, $X = CO_2C_2H_5$, $Y = CN$
V, $X = Y = CN$
VI, $X = Y = C_6H_5$


VII

When the compounds III–VI were heated at temperatures of 190–290° in an atmosphere of nitrogen, partial decomposition occurred, but no evidence of rearrangement was obtained, for only the unchanged compounds III–VI could be isolated after heating. The absence of any substantial amount of a rearrangement product corresponding to VII was shown by oxidation with potassium permanganate of the samples of III, IV and V recovered after heating, which yielded benzoic acid but no o-phthalic acid. Dimethyl (3,4-dimethoxy-


VIII

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[1] Preceding paper: A. C. Cope and L. Field, THIS JOURNAL, **71**, 1589 (1949).

[2] D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.