[CONTRIBUTION NO. 157 FROM THE CENTRAL RESEARCH LABORATORIES OF THE MINNESOTA MINING AND MANUFACTURING CO.[1]]

The Chemistry of Xylylenes. III. Some Reactions of *p*-Xylylene that Occur by Free Radical Intermediates[2]

BY L. A. ERREDE AND JOHN M. HOYT

RECEIVED MAY 5, 1959

The high reactivity of *p*-xylylene is found to be consistent with the calculations of Coulson on the electronic structures of singlet and triplet states of this molecule. *p*-Xylylene is diamagnetic at low temperature and yet is extremely reactive toward mono- and diradicals forming α,α'-disubstituted derivatives of *p*-xylylene and linear copoymers, respectively. The reactivity of *p*-xylylene is so much greater than that of olefinic monomers that copolymerization does not occur at −78°. However, copolymers can be formed if a solution of *p*-xylylene kept at −78° is added to the less reactive monomer or its solution maintained at *ca.* 100°. In the presence of excess mercaptan, chain transfer is observed even at low temperature yielding high molecular weight telomers. Less active chain transfer agents react very inefficiently.

Introduction

Coulson, *et al.*,[3] have calculated by the molecular orbital method the singlet and triplet states of *p*-xylylene and their results are shown in Fig. 1. They indicate that the molecule in its lower energy state is diamagnetic and is described conveniently by a quinonoid structure while its higher energy state is paramagnetic and corresponds to a benzenoid structure. A calculated energy difference of 12 kcal. separates the two energy states implying that at low temperatures virtually all the molecules are in the singlet form. The calculated free valence values indicate that centers 1 and 6 of both forms have high electron availability comparable to that of a benzyl radical.[4] On the other hand, the electron availability at carbon atoms within the ring is very similar to those found in "normal" molecules such as diphenyl. These data imply that *p*-xylylene even in its singlet state should be extremely reactive and that 1,6-addition by free radical mechanism should occur readily at the two terminal methylene groups. The resonance energy of the molecule in its ground state was calculated to be *ca.* 38 kcal. implying high stability of an isolated molecule.

The publications of Szwarc[5,6] and subsequently of others[7-10] attest to the extreme reactivity of *p*-xylylene. They reported that *p*-xylylene produced pyrolytically was stable in the gas phase at low pressure, but polymerization to poly-*p*-xylylene occurred on condensation, even at −190°. Although their experiments were limited to reactions occurring in the gas phase or at the moment of condensation, their results demonstrated clearly that addition to *p*-xylylene involves the two terminal methylene groups.

It has been shown recently that relatively stable solutions of *p*-xylylene could be prepared by quenching a fast flowing low pressure stream of pyrolyzed *p*-xylene in a solvent kept at −78°.[11] This discovery afforded a convenient method to study the chemistry of *p*-xylylene and to test the conclusions inferred by theoretical considerations.

Results and Discussion

It was reported in our first publication[11] that monomeric *p*-xylylene can be kept indefinitely when immobilized in a solid matrix of crystalline *p*-xylene and that dilute solutions of this compound are reasonably stable at low temperature. These results, as well as Szwarc's earlier observation indicating stability of the species in gas phase at low pressure, are consistent with the calculated high resonance energy[3] of *p*-xylylene. Moreover, as anticipated from Coulson's calculations, the molecule is diamagnetic at low temperature. Its 0.03 molar solution of *p*-xylylene frozen at −190° did not produce a signal when placed in an electron spin spectrometer.[12]

p-Xylylene in solution is, however, a very reactive molecule even at −78°. It reacts readily with monoradicals and halogen molecules, and decolorizes quickly solutions of diphenyl picryl hydrazyl. The addition occurs inevitably at the two terminal methylene groups.

Thus, *p*-xylylene diiodide was isolated in pure form in about 20 to 30% of theory[13] when a solution of *p*-xylylene was added at −78° to an excess of iodine.[11] The low yield realized is attributed to the instability of the resulting diiodide which decomposes partially during the purification procedure, since in another experiment *p*-xylylene dithiocyanate was isolated in 80% yield when the

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[1] This work was carried out in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Co. with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Co. in March, 1957.

[2] Presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] C. A. Coulson, D. P. Craig, A. MacColl and A. Pullman, *Disc. Faraday Soc.*, **2**, 36 (1947).

[4] C. A. Coulson, *ibid.*, **2**, 9 (1947).

[5] M. Szwarc, *ibid.*, **2**, 46 (1947).

[6] M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

[7] M. H. Kaufman, H. F. Mark and R. B. Mesrobian, *ibid.*, **13**, 3 (1954).

[8] R. S. Corley, H. C. Haas, M. W. Kane and D. I. Livingston, *ibid.*, **13**, 137 (1954).

[9] (a) L. A. Auspos, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. P. Speck, *ibid.*, **15**, 9 (1955); (b) L. A. Auspos. C. W. Burman, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R, Schaefgen and S. B. Speck, *ibid.*, **15**, 19 (1955).

[10] J. R. Schaefgen, *ibid.*, **15**, 203 (1955).

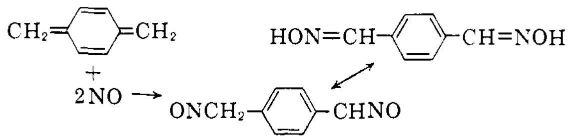
[11] L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

[12] The authors are indebted to Dr. John Wertz who graciously supervised the performance of this experiment by his students at the University of Minnesota.

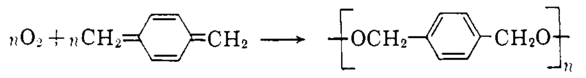
[13] Theoretical yields were based on titration of an aliquot with iodine solution. The yields observed do not represent the amount of desired product actually produced but rather the amount isolated in pure form from the very complex reaction mixture.[14]

[14] L. A. Errede, R. S. Gregorian and J. M. Hoyt, unpublished results.

originally formed solution of *p*-xylylene diiodide was treated with KCNS. Similarly, purified *p*-xylylene dichloride and *p*-xylylene dibromide were isolated in 40 to 60% yield when solutions of *p*-xylylene were added to excess chlorine and bromine, respectively. Addition of *p*-xylylene to an ethereal solution of thiocyanogen afforded *p*-xylylene dithiocyanate in good yield. However, a considerable amount of polymeric material was also obtained. Its infrared spectrum indicated the presence of some *p*-xylylene units, but it was not determined whether or not these were present as a copolymer or as a mixture of two polymers. Linear telomers of *p*-xylylene are obtained when solutions of the monomer are added to monoradicals such as NO_2 and NO; the degree of polymerization, depending on the concentration of monoradical, being usually less than 10. A small amount of terephthalaldoxime was isolated when *p*-xylylene in methanol was saturated at −78° with nitric oxide at atmospheric pressure. Similarly, *p*-chloromethylbenzaldoxime and O-(*p*-chloromethylbenzyl)-*p*-chloromethylbenzaldoxime were isolated from the reaction mixture obtained on adding a solution of *p*-xylylene to excess NOCl.



Poly-*p*-xylylene peroxide is formed[15] in almost 100% yield when a vigorous stream of oxygen is bubbled through a solution of *p*-xylylene at −78°.

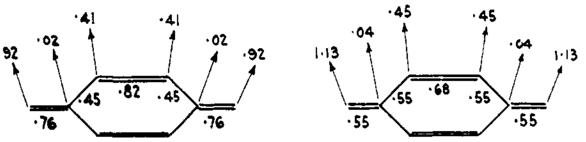


The structure of the resulting polymeric peroxide was verified by controlled thermal rupture of the O–O bonds to afford terephthalaldehyde, *p*-hydroxymethylbenzaldehyde, *p*-xylylene gycol and hydrogen as the only products of decomposition.

p-Xylylene is particularly prone to undergo homopolymerization even at −78° to afford linear poly-*p*-xylylene.[11] The polymerization is first order with respect to monomer and has an activation energy of about 9 kcal./mole.[14] The half-life of a *p*-xylylene solution was observed to be about 22 hours at −78° and about 22 minutes at −36°.

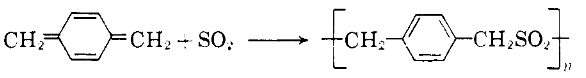
Derivatives of *p*-xylylene, such as 2-chloro-*p*-xylylene, 2-methyl-*p*-xylylene, 2-aza-*p*-xylylene and 2,5-diaza-*p*-xylylene, copolymerize readily with *p*-xylylene forming linear copolymers. Their composition is identical, within experimental error, with that of the charge. The properties of the copolymers are intermediate between those reported for the corresponding homopolymers.[6,7,9]

As is known, SO_2 reacts with olefinic monomers by a free radical mechanism to form the corresponding linear polysulfones.[16,17] This type copolymer is obtained also with *p*-xylylene, and the infrared



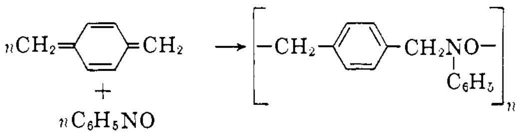
Ground state (singlet). Fig. 1. Ground state (triplet.)

spectrum of the polymer is consistent with the structure

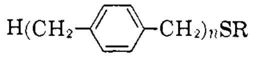


In presence of excess *p*-xylylene the composition of the polymer is identical, within experimental error, with the monomer's composition in the original solution. Apparently, the addition of a *p*-xylyl radical to SO_2 is considerably faster than the corresponding addition to *p*-xylylene monomer. The poly-*p*-xylylene sulfone polymers are insoluble in the usual solvents although they can be molded at 200° and 500 atm. pressure into translucent sheets.

p-Xylylene forms copolymers with nitroso compounds such as nitrosobenzene, *p*-nitroso-N,N-dimethylaniline and α-nitroso-β-naphthol. The polymers are soluble in organic solvents and they melt or soften at about 200°. The copolymer with *p*-nitrosodimethylaniline is soluble in concentrated HCl and is reprecipitated by dilution with water. Presumably these reactions take place according to the equation



p-Xylylene does not react readily with most of the usual chain transfer agents. Thus, polymerization of *p*-xylylene at −78 to 23° in a 50–50 solution of chloroform and carbon tetrachloride results in a formation of unmodified poly-*p*-xylylene free of chlorine. Unmodified poly-*p*-xylylene is also obtained when polymerization is carried out in a one-to-one solution of *p*-cymene in toluene and in saturated toluene solutions of diphenylmethane, triphenylmethane, phenol, benzoquinone, hydrobenzoquinone, nitrobenzene and anilines. Chain transfer was observed when mercaptan was present in the polymerization medium. Thus 1.52% sulfur, corresponding to a *p*-xylylene to thiophenol ratio of 21 to 1, was found in the insoluble polymer when *p*-xylylene was polymerized in the presence of a threefold excess of thiophenol. Similar results were obtained with *n*-octyl mercaptan. The infrared spectrum was consistent with the linear structure



p-Xylylene does not react appreciably with olefinic monomers under the usual experimental conditions. Virtually unmodified poly-*p*-xylylene was produced when polymerization was carried out in a one-to-one solution of hexane and the following

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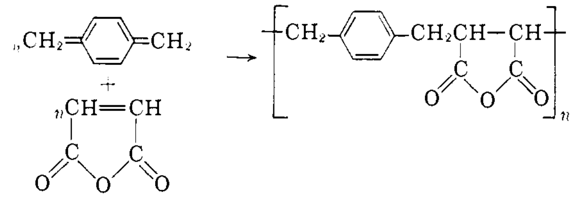
[15] L. A. Errede and S. L. Hopwood, THIS JOURNAL, **79**, 6507 (1957).

[16] R. D. Snow and F. Frey, *Ind. Eng. Chem.*, **30**, 176 (1938).

[17] W. G. Barb, *J. Polymer Sci.*, **10**, 49 (1953).

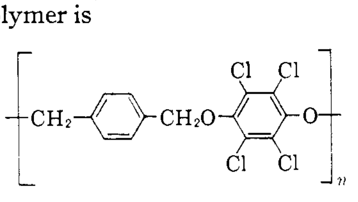
investigated olefinic monomers: vinyl ethyl ether, vinyl acetate, vinyl chloride, acrylonitrile, acrylamide, methyl acrylate, methyl methacrylate, styrene, *p*-chlorostyrene, butadiene, diethyl maleate, diethyl fumarate, maleic anhydride, terpene-B and ketene. Similar results were obtained in polymerizations proceeding in the presence of quinones and of $\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-*p*-xylylene. Apparently the reactivity of *p*-xylylene is much greater than that of any of these compounds and hence the former is consumed predominantly by homopolymerization.

It is possible, however, to copolymerize the less reactive monomers with *p*-xylylene by slowly adding its solution, kept at −78°, to the olefinic monomer or its solution maintained at about 100°. Under these conditions the concentration of *p*-xylylene is always very low, and this favors copolymerization. Using this procedure it was possible to produce the one-to-one copolymer with maleic anhydride. This product is soluble in warm dilute aqueous NaOH and is reprecipitated by acidification with strong mineral acid. Its oxidation with $KMnO_4$ produces terephthalic acid as the only major product. Apparently the addition occurs as



Similar results were obtained with diethyl maleate, diethyl fumarate, acrylonitrile, *n*-butyl acrylate and styrene. All these copolymers form thermoplastic materials.

The method described above is also applicable to the preparation of copolymers of quinones and *p*-xylylene. For example, under the above conditions a highly swollen gelatinous product was obtained with chloranil. The molar ratio of *p*-xylylene to chloroanil, calculated on the basis of its chlorine content (32.9%), was 1.8 to 1. The infrared spectrum indicated the presence of benzenoid rings, but showed no evidence for quinoid units or carbonyl groups. Therefore, it is believed that the structure of the copolymer is



Experimental

General Procedure for Reactions of *p*-Xylylene at −78° with Various Compounds.—The desired volume of standardized *p*-xylylene solution was added at −78° to a known excess amount of the compound in question or its solution. The resulting solution was warmed to room temperature. Any insoluble material was removed by filtration. The soluble products were recovered from the mother liquor by evaporation and the desired *p*-xylylene derivative was isolated from the insoluble and soluble non-volatile residue as indicated below.

(a) **With Iodine.**—The crude product was recrystallized twice from hexane and then from methanol to afford pure *p*-xylylene diiodide (m.p. 176–177°) in 34% yield. *Anal.* Calcd. for $C_8H_8I_2$: I, 70.91. Found: I, 70.9.

In another experiment the non-volatile residue was digested with KCNS in acetone, and *p*-xylylene dithiocyanate (m.p. 132–134°) was isolated in 80% yield indicating that the diiodide was produced initially in very high yield but that partial decomposition occurred during the isolation procedure.

(b) **With Bromine.**—*p*-Xylylene dibromide (m.p. 137–140°) was isolated from the non-volatile reaction mixture as described above. The yield of pure product was 40%.

(c) **With Chlorine.**—*p*-Xylylene dichloride (m.p. 95–97°) was isolated in 54% yield after recrystallization from hexane, sublimation under vacuum and final recrystallization from methanol.

(d) **With Thiocyanogen.**—The non-volatile products of the reaction were recrystallized from hot hexane and then from acetic acid to afford white needle-like crystals of *p*-xylylene dithiocyanate (m.p. 133.5–134.5°) in 38% yield. *Anal.* Calcd. for $C_{10}H_8S_2N_2$; S, 29.1. Found: S, 28.6. A considerable amount of yellow insoluble polymeric material was also obtained. This was identified by infrared analysis as polymeric thiocyanate. A small amount of *p*-xylylene was also detected. It was not established whether or not this was a copolymer or a mixture of two polymers.

(e) **With Nitrogen Dioxide.**—The non-volatile residue was recrystallized from methanol to afford a mixture of linear telomeric products in 90% yield. This was separated into three fractions of decreasing solubility containing 5.11, 3.03 and 2.35% nitrogen, respectively.

(f) **With Nitric Oxide.**—The reaction mixture obtained as residue was leached with dilute aqueous NaOH. The alkaline extract was acidified with mineral acid to afford telomeric oximes in 80% yield. This material contained 7.97% N which corresponds to a ratio of *p*-xylylene to two nitroso groups of 2.8 to 1. A small amount of terephthalaldoxime (m.p. 212–213°) was isolated from the mixture by repeated crystallization from hot water.

(g) **With Nitrosyl Chloride.**—The non-volatile products were dissolved in toluene and reprecipitated by dilution with hexane. The precipitate was purified further by sublimation under vacuum and subsequent recrystallization from hot hexane. White crystals (m.p. 45–46°) of a compound, whose infrared spectrum was consistent with the structure of O-(*p*-chloromethylbenzyl)-*p*-chloromethylbenzaldoxime, was isolated in 10% yield. *Anal.* Calcd. for $C_{16}H_{15}ONCl_2$: Cl, 23.02; N, 4.54. Found: Cl, 23.3; N, 4.58. Crude *p*-chloromethylbenzaldoxime was recovered from the toluene–hexane mother liquor. This was purified by sublimation under vacuum and then by recrystallization from hexane. The compound was isolated in 7% of theory in the form of small white needles (m.p. 101.5–102.5°). *Anal.* Calcd. for C_8H_8NOCl: C, 56.64; H, 4.73; Cl, 20.91; N, 8.26. Found: C, 57.0; H, 4.35; Cl, 20.8; N, 8.18.

(h) **With Thiophenol.**—A mixture of insoluble telomeric products was obtained in almost quantitative yield. This was removed by filtration and then leached with refluxing xylene. The insoluble material contained 1.51% S corresponding to an average degree of polymerization of 21, whereas the telomeric product that reprecipitated from the hot xylene extract contained 4.06% S corresponding to an average degree of polymerization of 7. Both fractions softened at 190–250°.

(i) **With SO_2.**—Poly-*p*-xylylene sulfone was obtained in about 90% of theory as an insoluble powder. The polymer contained 17.2% S corresponding to a ratio of *p*-xylylene to SO_2 of 1.2-to-1. The experiment was repeated using excess *p*-xylylene. Under these conditions, the ratio of *p*-xylylene units to SO_2 in the polymer was about the same as that of the charge.

(j) **With Nitrosobenzene.**—The non-volatile residue was reprecipitated from a minimum amount of hot toluene to afford low molecular weight linear copolymer that melted at 200–250°. This polymer, which contained 5.04% N corresponding to a ratio of *p*-xylylene to nitrosobenzene of 1.7 to 1, was isolated in about 50% of the theory. Similar results were obtained with *p*-nitrosodimethylaniline. The product contained 11.5% N indicating that it was almost the one-to-one copolymer. It softened at 175–210° and it was soluble in concentrated HCl.

Copolymerization of *p*-Xylylene with Maleic Anhydride.—*p*-Xylylene (0.26 mole) in toluene (2.5 liters) was added at −78° over a period of 2 hours to maleic anhydride (700 g.) kept at 130°. The excess maleic anhydride was removed by vacuum distillation and the brittle brown glassy solid residue was reprecipitated from tetrahydrofuran as an amorphous powder (31 g.). The powder softened at about 60–70° and dissolved slowly in warm 10% aqueous KOH to form a somewhat viscous solution. The polymer was reprecipitated by the addition of HCl. The infrared spectrum of this material was similar to that obtained *via* co-condensation of maleic anhydride and pyrolyzed *p*-xylene.[10]

Anal. Calcd. for the 1:1 copolymer of *p*-xylylene with maleic acid, $C_{12}H_{12}O_4$: C, 65.41; H, 5.49. Found: C, 66.2, 66.3; H, 5.62, 5.74.

A small sample was converted in good yield to terephthalic acid by oxidation with $KMnO_4$ in aqueous NaOH to confirm the assigned linear configuration of the polymer.

Copolymers of *p*-xylylene with diethyl maleate, diethyl fumarate, acrylonitrile, *n*-octyl acrylate and styrene were also prepared using this procedure to afford thermoplastic polymers that softened in the range 60–150°.

Copolymerization of *p*-Xylylene and Chloranil.—*p*-Xylylene (0.04 mole) in toluene (500 cc.) at −78° was added slowly to 0.1 mole of chloranil dissolved in 400 cc. of *p*-xylene kept at 95–100°. A highly swollen, gelatinous solid (2.5 g.) was obtained. After continuous extraction with hot *p*-xylene for 3 hours, the white insoluble residue contained 32.9% chlorine corresponding to a molar ratio of *p*-xylylene:chloranil of 1.8:1. The material softened at 195–200° and was completely soluble in tetrachloroethane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Action of Alkali on 3,4-Phenacylidene-3-acetylcoumarin

BY S. WAWZONEK AND C. E. MORREAL[1,2]

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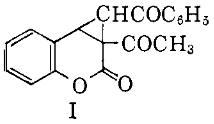
The structure of 3,4-phenacylidene-3-acetylcoumarin prepared by the alkaline condensation of 3-acetylcoumarin with phenacyl bromide has been confirmed by its synthesis from 3-acetylcoumarin and diazoacetophenone. Alkaline treatment of this compound gave 3-phenyl-4-*o*-hydroxybenzal-2-cyclopenten-1-one as reported by Widman. Proof of this structure is the conversion of its methyl ether to 5-*o*-methoxybenzal-4-phenyl-3-cyclopenten-1,2-dione. Cleavage of this diketone gave β-phenyl-α-*o*-methoxybenzalglutaconic acid which was identical with a sample prepared by the alkaline condensation of β-phenylglutaconic acid with *o*-methoxybenzaldehyde.

3,4-Phenacylidene-3-acetylcoumarin (I), which has been prepared by the reaction of 3-acetylcoumarin with phenacyl bromide in the presence of sodium ethoxide[3] is converted by 10% sodium hydroxide into a new compound to which structure II was first assigned and then later structure III.[3] Since the only evidence offered for structure III was the formation of salicylic acid in the oxidation with potassium permanganate, compound III was considered worthy of further investigation.



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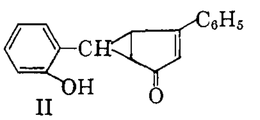
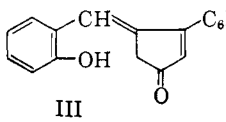
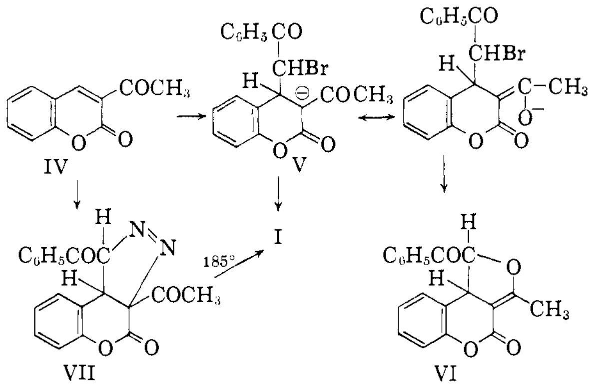


II



III

3,4-Phenacylidene-3-acetylcoumarin (I) was prepared successfully according to Widman's directions.[3] This reaction probably proceeds by a Michael addition of the phenacyl bromide anion directly to 3-acetylcoumarin (IV) followed by an intramolecular alkylation of the resultant ion (V) rather than by the alkylation of the ethyl α-acetylcoumarinate anion as proposed by Widman. Cyclization of the ion V can proceed in two ways; C-alkylation would give 3,4-phenacylidene-3-acetylcoumarin (I), whereas O-alkylation would form the dihydrofuran VI. The latter possibility was eliminated by the infrared spectra, which gave an absorption peak at 9.85μ in the region reported for cyclopropane rings,[4] and by synthesis from 3-acetylcoumarin and diazoacetophenone. The intermediate pyrazoline VII gave the desired product upon heating at 185°.



Treatment of 3,4-phenacylidene-3-acetylcoumarin (I) with alkali gave a product which from its reactions proved to be 3-phenyl-4-*o*-hydroxybenzal-2-cyclopenten-1-one (III) as reported by Widman. To facilitate further study this compound was converted into its methyl ether VIII with dimethyl sulfate and alkali. This ether (VIII) added two moles of hydrogen and gave 4-*o*-methoxybenzyl-3-phenylcyclopentanone (IX) which formed an oxime. Condensation of the methylene group in VIII with *o*-methoxybenzaldehyde to a di-*o*-methoxybenzal derivative was not successful. 3-Phenyl-4-*o*-methoxybenzal-2-cyclopenten-1-one (VIII), however, could be oxidized to 5-*o*-methoxybenzal-4-phenyl-3-cyclopenten-

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(1) Abstracted in part from the Ph.D. Thesis of C. E. Morreal, June, 1959.

(2) Allied Chemical Corporation Fellow, 1957–1958.

(3) O. Widman, *Ber.*, **51**, 533, 907 (1918).

(4) F. J. Piehl and W. G. Brown, THIS JOURNAL, **75**, 5023 (1953).