TABLE II

METHYL β-ACYLOXYCINNAMATES AND 3-ACYLOXYALKENOATES, RC(OCOR')=CHCOOCH$_3$

R	R'	M.p. or b.p. (mm.), °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
C_6H_5	C_6H_5	84–85	$C_{17}H_{14}O_4$	72.33	72.21	5.00	5.05
C_6H_5	*p*-$NO_2C_6H_4$	109–110	$C_{17}H_{13}O_6N$	62.39	62.38	4.00	3.87
n-C_4H_9	*n*-C_4H_9	106(0.4)[a]	$C_{13}H_{22}O_4$	64.45	64.45	9.16	9.13
n-$C_{11}H_{23}$	*n*-$C_{11}H_{23}$	210–212(0.1)[b]	$C_{27}H_{50}O_4$	73.92	73.98	11.49	11.69

[a] n^{25}_D 1.4460, d^{25}_4 0.9853, λ_{max} 216 mμ, ε 6200 (ethanol). [b] n^{25}_D 1.4575, d^{25}_4 0.9151, λ_{max} 216 mμ, ε 7850 (ethanol).

viously cooled in a Dry Ice–acetone cold bath. The resulting mixture was treated as in the preceding experiment (c).

The reaction product, a white crystalline solid, was taken up in benzene and after the addition of petroleum ether (b.p. 60–68°) was allowed to crystallize. Upon filtration, 467 mg. of 3β-acetoxyetio-5-cholenylketene dimethylacetal (XVIII) was isolated. Its properties are shown in Table I.

Reaction of Succinyl Chloride with Ketene Acetal.—To 35.2 g. (0.40 mole) of ketene dimethylacetal was added dropwise 7.74 g. (0.05 mole) of freshly distilled succinyl chloride while the reaction mixture was magnetically stirred and heated at reflux. After completion of the addition, the mixture was refluxed for 1 hour and allowed to cool. The volatile material was removed at 50–60° under reduced pressure. The residue, under nitrogen, was placed in a refrigerator overnight. The precipitate (3.2 g.) which formed was filtered and washed with cold (Dry Ice–acetone) ether. After removal of ether, the mother liquors were allowed to cool overnight in a refrigerator. A second crop of crystals was obtained to give a total yield of 5.05 g. (65%) of **γ-carbomethoxymethylene-γ-butyrolactone (XX)**, m.p. 71–72.5°.

The material became an intractable tar when exposed to air for several minutes and could not be isolated sufficiently pure for analysis. The infrared spectrum displayed an absorption peak at 5.60 μ, characteristic of a five-membered enol-lactone carbonyl.[7]

Heat was evolved when 4.65 g. of this product was dissolved in 10 ml. of 20% hydrochloric acid. As the solution was heated to reflux for 1 hour a rather moderate evolution of gas occurred. The solution was then made just basic by addition of 10% sodium hydroxide and steam distilled. No volatile material other than water was detected in the distillate. The solution was then acidified with 10% hydrochloric acid and evaporated to dryness. The oily residue of sodium chloride was extracted with ether and after evaporation of the extracts, 2.0 g. of viscous oil remained. It had an infrared spectrum essentially identical with that of levulinic acid. Some of the oil was treated with 2,4-dinitrophenylhydrazine reagent to yield the 2,4-dinitrophenylhydrazone of levulinic acid, m.p. 204.5–206° (reported[19] 206°), which showed no depression of melting point when mixed-melted with authentic material.

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(19) H. H. Strain, THIS JOURNAL, **57**, 760 (1935).

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Vinylation. II.[1] Stereochemistry and Synthesis of β-Methoxystyrenes[2]

BY SIDNEY I. MILLER

RECEIVED MARCH 30, 1956

A rule of *trans* nucleophilic addition to acetylenes is suggested. The methoxide-catalyzed addition of methanol to phenylacetylene to give a high-boiling β-methoxystyrene is stereospecific and probably *trans*. Small quantities of the unexpected α-methoxystyrene also were found. Different routes to β-methoxystyrene from phenylacetaldehyde dimethylacetal led to a mixture of isomeric β-methoxystyrenes from which the low-boiling isomer was obtained. Certain features of the infrared spectra of the α- and β-methoxystyrenes are discussed. An infrared study of the system methanol–phenylacetylene indicated that gross interactions such as H-bonding or complexing between these molecules were absent.

As a model for the stereochemical course of reactions involved in the preparation of alkoxyalkenes, the formation of the β-methoxystyrenes (I) from phenylacetaldehyde dimethylacetal (II) and from phenylacetylene (III) was investigated. The most serious attempt to solve this general problem was that of Dufraisse and Chaux.[3] They prepared mixtures of the β-ethoxystyrenes by various methods but could isolate only one of the isomers. Their work, as well as Sigmund and Uchann's studies on the pyrolytic decomposition of acetals,[4] are background to this work.

In order to obtain the reference compounds (I), several synthetic approaches were tried; reaction sequences are given in Chart I. Ihb (hb = high boiling) was isolated pure while Ilb (lb = low boiling) was obtained almost free from Ihb. The higher boiling point and refractive index,[5] and especially the characteristic infrared bands, strongly suggest that Ihb is the *cis* isomer formed from III by *trans* addition.

β-Methoxystyrene (Ihb).—β-Alkoxystyrenes often have been prepared by the base-catalyzed addition of alcohols to III.[3,6–8] The sealed tube reactions of III with sodium methoxide in methanol gave excellent yields of Ihb. None of Ilb could be detected in the above product. In contrast to its facile isomerization at room temperature or lower on exposure to air, neither thermal nor base-catalyzed isomerization of Ihb had occurred even after one week at 149°. Taking into account the facts that Ihb was the major product and that the equilibrium mixture of I contained

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(1) For paper I see S. I. Miller and G. Shkapenko, THIS JOURNAL, **77**, 5038 (1955).

(2) Work supported by the Office of Ordnance Research, U. S. Army.

(3) C. Dufraisse and R. Chaux, *Bull. soc. chim.*, [4] **39**, 905 (1926).

(4) F. Sigmund and R. Uchann, *Monatsh.*, **51**, 234 (1929).

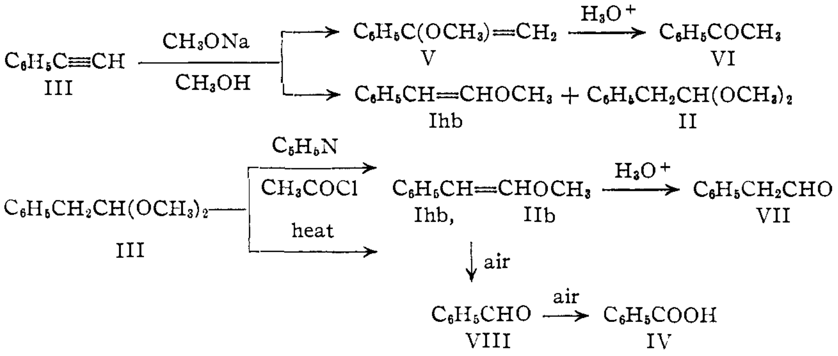
(5) A. Wasserman, "Stereochemie," K. Freudenberg, editor, Leipzig, 1933, p. 721.

(6) T. L. Jacobs and W. R. Scott, Jr., THIS JOURNAL, **75**, 5500 (1953).

(7) (a) J. U. Nef, *Ann.*, **308**, 264 (1899); (b) C. Moureu, *Bull. soc. chim.*, [3] **31**, 526 (1904).

(8) K. Auwers, *Ber.*, **44**, 3514 (1911).

CHART I



detectable quantities of both isomers, it is clear that the synthesis of Ihb from III was stereospecific.

Infrared spectra of the head fractions from some of the above preparations indicated that α-methoxystyrene (V) was present (<5%), but III and carbonyl-containing compounds were absent. (In passing it may be remarked that $C_6H_5CH(CH_3)$-CHO (IX) and $C_6H_5COC_2H_5$ (X), which could conceivably have formed from the methoxystyrenes by rearrangement,[9] were absent.) It appears that this is the first time that an α-alkoxystyrene has been found in the base-catalyzed addition of alcohols to III; it presumably arises from the type of addition of methanol to III which predominates in acid solution.[7a]

In similar systems small quantities of the corresponding acetals have been found along with the styryl ethers.[6,10] The tail fractions of the above preparations had refractive indices and infrared spectra which indicated definitely that II was a co-product of Ihb.

β-Methoxystyrene (IIb).—When II was pyrolyzed at 200–250°, or when II was heated briefly at 170° with an excess of pyridine–acetyl chloride, a mixture of I, with Ihb predominating, was obtained. (Other preparative methods from II are described in the Experimental section.) It is not clear whether there was a single product and the reaction conditions favored isomerization, or whether both isomers were primary products. However, it was shown that fractions rich in Ihb or IIb, when heated in sealed tubes at 149°, did not change appreciably, but that similar fractions, stored in stoppered tubes in a refrigerator and sampled occasionally, did isomerize and produce VIII.

When the crude products of the above preparations were distilled, the head fractions gave low refractive indices and positive Schiff aldehyde tests. The presence of VIII accounted in part for these properties; VII could not be detected. However, the composition of the first fractions from the two preparative methods differed in at least one important aspect: the infrared spectrum of the product of the pyridine–acetyl chloride reaction had a strong band in the carbonyl region whose intensity, taken with the spectral pattern as a whole, could not be attributed to IV, VII, VIII, methyl formate or methyl benzoate. This unidentified material, conceivably β-acetoxystyrene,[11] might have been formed in the pyridine–acetyl chloride medium.

The best sample of IIb, obtained in small quantity (< 0.2 ml.) by fractional distillation, still contained some Ihb. The properties of the isomers compare as follows: IIb, $n^{20}D$ 1.5574, b.p. 205°; Ihb, $n^{20}D$ 1.5683, b.p. 210°. On the basis of several preparations it was assumed that IIb was always produced in equilibrium with Ihb. It was estimated that this mixture had $n^{20}D$ 1.5650 ± 0.0010 and that at most 30% IIb was present. It also appeared that IIb was more labile: this made repetitive fractionation techniques difficult.

Infrared Data on the Alkoxystyrenes. Since the spectra of aliphatic vinyl ethers have been discussed,[12–14] it would seem useful to record the infrared data for the alkoxystyrenes (see Experimental section). IIb has a *trans* band at 937 cm.$^{-1}$ while Ihb has a *cis* band at 726 cm.$^{-1}$; indeed, the structural assignment rests on the assignment of these characteristic C–H out-of-plane deformation bands.[13–15]

The alkene C=C absorption is strong and in the expected region. It is interesting that the *cis* band, usually *ca.* 17 cm.$^{-1}$ lower than that for *trans*,[15] lies 5 and 8 cm.$^{-1}$ higher for the but-1-enyl butyl ethers[14] and the β-methoxystyrenes, respectively. Apart from the aryl C=C band at about 1600 cm.$^{-1}$, only V appears to have another medium to strong olefinic C=C band at 1608 cm.$^{-1}$ which is typical of aliphatic vinyl ethers[12,13]; it may be possible to use this band to distinguish 1,1- from 1,2-alkoxyalkenes. The bands at 1570–1580 cm.$^{-1}$ appear to be aryl in origin and intensified by conjugation.

The C–O frequencies could not be picked out unambiguously. For comparison it may be noted that in the region 1025–1275 cm.$^{-1}$ the strongest bands of ethyl and *n*-butyl vinyl ether fall close to 1200 cm.$^{-1}$ and those of 1-methoxy-2-phenylethane and 1-methoxy-1-phenylethane appear close to 1110 cm.$^{-1}$.[16]

Phenylacetylene–Methanol Interaction.—Interactions of alcohols with acetylenes have not been investigated by infrared techniques. It was felt that the regions of the acetylenic C—H and C≡C and the methanolic O—H stretching vibrations might prove interesting in solutions of phenyl-

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[9] K. B. Wiberg and B. I. Rowland, THIS JOURNAL, **77**, 1159 (1955).

[10] K. Weissbach, German Pateut 821,2 3 (Nov. 15, 1951); *C. A.*, **48**, 12172 (1954); S. J. Cristol, A. Begoon, W. P. Norris and P. S. Ramey, THIS JOURNAL, **76**, 4558 (1954).

[11] J. Böeseken and A. Kremer, *Rec. trav. chim.*, **50**, 827 (1931).

[12] A. Kirrmann and P. Chancel, *Bull. soc. chim.*, [5] **21**, 1338 (1954); W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

[13] G. D. Meakins, *ibid.*, 4170 (1953).

[14] R. H. Hall, A. R. Philpotts, E. S. Stern and W. Thain, *ibid.*, 3341 (1951).

[15] N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952); L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954.

[16] Unpublished observations.

acetylene in methanol. While the detection of any interactions would be inconclusive with regard to the vinylation mechanism, it could be suggestive.

From Table I it is clear that there have been no major shifts in the bands considered. Deviations in band intensity were also considered. Because of the difficulty of working in the region of strong methanolic absorption, only the C≡C band was examined in detail. Figure 1 is a Beer's law plot of log I_0/I *vs.* concentration in carbon tetrachloride. It is evident that negative deviations from additivity are small and, despite an apparent trend, are still close to experimental error. Clearly the effects of methanol and phenylacetylene molecules on each other even up to 4:1 mole ratio appear to be small; H-bonding or complex formation apparently do not occur to any appreciable extent.

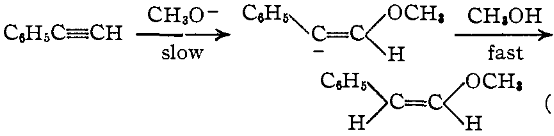
TABLE I

STRETCHING FREQUENCIES IN μ OF PHENYLACETYLENE–METHANOL IN CARBON TETRACHLORIDE

O–H	Solvent	C–H (acetylenic)	Solvent	—C≡C—	Solvent
2.721	CCl_4	3.015	...	4.737	...
		2.998	CCl_4	4.729	CCl_4
2.723	CCl_4–$C_6H_5C{\equiv}CH$	2.997	CH_3OH	4.735	CH_3OH
		2.997	CCl_4–CH_3OH	4.729	CCl_4–CH_3OH

Discussion

The methoxide-catalyzed addition of methanol to III gave Ihb, presumably the *cis* isomer, by *trans* addition



$$C_6H_5C{\equiv}CH \xrightarrow[\text{slow}]{CH_3O^-} \overset{C_6H_5}{\underset{-}{C}}{=}C\overset{OCH_3}{\underset{H}{}} \xrightarrow[\text{fast}]{CH_3OH} \overset{C_6H_5}{\underset{H}{C}}{=}C\overset{OCH_3}{\underset{H}{}} \quad (1)$$

There is independent evidence that the base-catalyzed addition should be *trans*.[17] For example, methyl β-methoxy-β-(3-bromo-2,4,6-trimethylphenyl)-acrylate,[18] *cis*-β-phenoxyacrylic acid,[19] β-ethoxycrotonic acid,[20] cyclohexylthiofumaric acid,[21] ethyl phenoxyfumarate,[22] ethyl (*o*-, *m*-, and *p*-)-cresoxyfumarate,[23] 1-ethoxybut-1-en-3-yne,[13] *cis*-ω-styryl *p*-tolyl sulfide,[24] methyl *cis*-ω-styryl sulfide,[24] 2-*p*-tolylmercapto-*trans*-2-butene,[24] *cis*-1-chloro-2-thiophenylethene[24] and *cis*-1,2-dithiophenylethene[24] are products of such nucleophilic additions. Indeed, Truce, *et al.*, "observed that base-catalyzed additions of thiols to the acetylenic compounds . . . proceed in a *trans* fashion."[24]

It would appear that the examples cited collectively amount to a general *rule of trans nucleophilic addition* for alkynes analogous to the Michael rules of *trans* addition of halogens and halogen acids.[25,26]

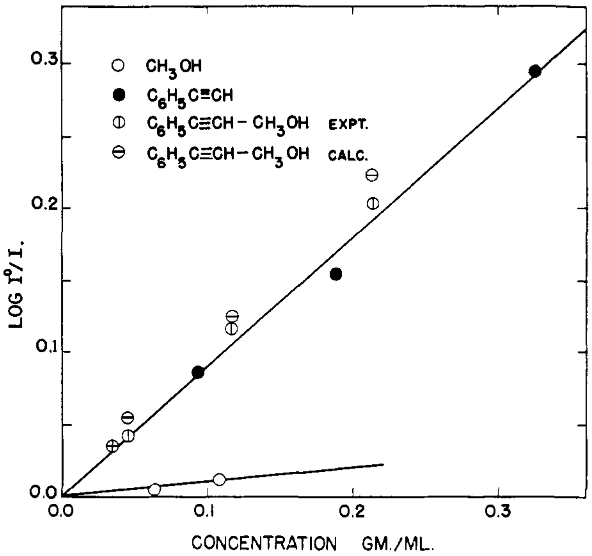


Fig. 1.—Effect of methanol on the intensity of the C≡C stretching frequency of phenylacetylene in carbon tetrachloride solvent (for points near the upper line the abscissa is the concentration of phenylacetylene).

In the first paper[1] it was shown that the methoxide-catalyzed vinylation of III at 149° was first order in methoxide ion and first order in III. A mechanism[30] was proposed in which the carbanion $C_6H_5\underline{C}{=}CHOCH_3$, formed in the rate-determining step, abstracts a proton from the solvent (see equation 1). An alternative mechanism, in which a solvated phenylacetylene molecule adds methoxide and a proton simultaneously in *trans* positions cannot be ruled out. Since no kinetic dependence on methanol was found and since no appreciable concentration of any complex between methanol and phenylacetylene could be detected, the mechanism given in equation 1 is preferred. Given this mechanism, then it may be more evidence for a sterically stable ethylenic carbanion at 149°.[31]

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(17) C. K. Ingold, *J. Chem. Soc.*, 2991 (1954). Ingold and King have recently reported that the first excited electronic state of acetylene has a flat *trans*-bent structure. Ingold has suggested that this may provide a theoretical basis for the well-known superiority of *trans* over *cis* additions or eliminations in heterolytic reactions.

(18) R. Adams and C. W. Theobald, THIS JOURNAL, **65**, 2383 (1943).

(19) E. Gottesman, *Ber.*, **66**, 1168 (1933).

(20) W. Wislicenus and K. Schöllkopf, *J. prakt. Chem.*, **95**, 269 (1917).

(21) B. Weibull, *Arkiv. Kemi*, **3**, 225 (1951).

(22) S. Ruhemann and F. Beddow, *J. Chem. Soc.*, **77**, 1119 (1900).

(23) S. Ruhemann and H. E. Stapleton, *ibid.*, **77**, 1179 (1900).

(24) W. E. Truce, *et al.*, THIS JOURNAL, **78**, 696, 2743, 2752, 2756 (1956). These articles appeared after our own manuscript had been prepared.

(25) A. Michael, *Ber.*, **34**, 4215 (1901); *J. prakt. Chem.*, **52**, 344 (1895).

(26) Other adducts to alkynes have been omitted for various reasons: only one isomer was reported or *cis–trans* structures were not assigned; the addition was probably free radical or acid catalyzed; the mechanism was complex. Adducts which subsequently underwent ring closure can be educed both for and against the rule: "favorable" products are 3-phenylpyrazole[27] and flavones[28]; "unfavorable" products are β-alkoxy-α,β-unsaturated lactones.[29] Since the isomeric adducts were not available, evidence based on these ring closures must be viewed with caution.

(27) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 953 (1946).

(28) S. Ruhemann, *Ber.*, **46**, 2188, 3384 (1913); **47**, 119 (1914).

(29) E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1423 (1949).

(30) Two papers, in which kinetic evidence was given for this mechanism, have recently come to our attention: T. Tsuruta, H. Komatsubara and J. Furukawa, *Bull. Chem. Soc. Japan*, **28**, 552 (1955); R. Rigamonti and L. Bernardi, *Chim. Ind.* (*Milan*), **34**, 561 (1952); *C.A.*, **47**, 2583 (1953).

(31) (a) See also A. A. Bothner-By, THIS JOURNAL, **77**, 3293 (1955); E. Grovenstein, Jr., and D. E. Lee, *ibid.*, **75**, 2639 (1953). (b) A referee has suggested that a stereospecific product could arise because of preferential approach of the proton donor to a non-sterically stable ethylenic curbanion.

Experimental

All melting points are corrected; boiling points on semimicro scale[32] were uncorrected. Fractional distillations were carried out in a Podbielniak Hypercal column at *ca.* 1 mm. Carbon hydrogen analyses were done by Micro-Tech Laboratories, Skokie, Ill. Refractive indices were measured at/or corrected to 20°; the temperature coefficient of a mixture of I was −0.0005 deg.$^{-1}$. The Schiff aldehyde test was performed in a standard manner: a 1% phenylacetaldehyde solution gave a visible violet color in 20 sec.; any test was considered positive if color developed in 60 sec.

Infrared spectra were taken on a Perkin–Elmer model 21 spectrophotometer with sodium chloride optics. Most of the samples were liquids; their spectra were usually measured as thin films squeezed between salt plates or in carbon tetrachloride solution. Reference spectra of II, III, IV, VI, VII, VIII, methyl formate, methyl benzoate, propiophenone, ethoxyethene, α-methylphenylacetaldehyde, *n*-butoxyethene, styrene, 1-methoxy-2-phenylethane, 1-methoxy-1-phenylethane and solvents were taken. Data on the methoxystyrenes are given in Table II. In the region 600–1700 cm.$^{-1}$ the accuracy is greater than 3 cm.$^{-1}$; above 1700 cm.$^{-1}$ the uncertainty may reach 10 cm.$^{-1}$.

TABLE II

INFRARED DATA ON THE METHOXYSTYRENES IN CM.$^{-1}$

α-Methoxystyrene	β-Methoxystyrene (high boiling)	β-Methoxystyrene[a] (low boiling)
3065w[c]	3029m	3027m
3013w	2940m	2941m
2956m	2866w	2825w
2844w	2834w	2181vw
2342vw	2085w	2085w
2261vw	1951w	1952w
2201w	1886w	1883w
2099vw	1821w	1822w
2036vw	1752vw	1731 vw
1957m	1687vw	1703vw
1891w	1650s	1642s
1807m	1602m	1601w
1760w	1574w	1576w
1727vw	1493m	1495m
1643s	1455m	1465w
1608s	1445m	1457m
1601w	1403m	1404w[b]
1576s	1318vw	1343vw
1496s	1300m	1330vw
1467m	1270vs	1313vw
1452s	1204m	1301w[b]
1382w	1183vw	1270w[b]
1314s	1152vw	1238s
1303s	⎰1100	1204vw[b]
1284s	⎱1092vs	1192m
1193m	1074s	1150s
1179vw	1030w	1126m
1151vw	1000vw	1096s
1125s	980w	1073w[b]
1079m	912w	1030vw
1043s	778vs	999w
899s	726w	937s
800m	692s	864w
767s		815w
687s		780m[b]
		750m
		692s
		648w

[a] Contains some high-boiling isomer. [b] Band assigned exclusively to the high-boiling isomer. [c] w = weak, m = medium, s = strong, v = very.

For the spectra of phenylacetylene–methanol, calcium fluoride optics were used. All solutions were scanned at least twice at slow speeds under constant operating conditions. The solutions were made up by weight, and the weight per ml. of any component was determined by assuming additivity in the volumes of the individual components.

α-Methoxystyrene (V).—The preparation of Winstein and Ingraham was used.[33] Crude 2-methoxy-2-phenylethyl iodide, n^{25}D 1.5775 (lit.[33] n^{25}D 1.5793), was converted practically quantitatively into V. On distillation a middle fraction was obtained which had b.p. 30–32° (0.4 mm.), n^{20}D 1.5429 (lit.[33] b.p. 85–89 (20 mm.), n^{20}D 1.5434).

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.30; H, 7.65.

β-Methoxystyrene (Ihb).—While the directions given here are representative of several experiments, the quantities given derive from a specific preparation. An ampule containing III and methanolic sodium methoxide was cooled in Dry Ice; its vapor space was blown out with nitrogen and its neck sealed. The solution was kept in a furnace at 145–150° for 1 week, then treated with water and ether containing hydroquinone. The extract was dried over potassium hydroxide and calcium chloride. A short path vacuum distillation gave a brown liquid which was fractionally distilled. None of the fractions gave positive Schiff tests. Infrared spectra showed that III and IIb were absent, while early fractions contained traces of V and the last fraction contained II; all of the fractions contained Ihb. The recovery of liquid was typically 60–70%, although yields of crude liquid as high as 90% could be realized. Several properties of presumably pure Ihb were obtained from a cut of refractionated material: b.p. 210°, n^{20}D 1.5683 (lit.[3] 210–213°, 99° (13 mm.), n^{20}D 1.5639).

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.46; H, 7.93.

Analyses of both I were often low in carbon. After it was pointed out to the analyst that compound I was oxygen-sensitive he returned the above analysis. It was also found that after three weeks in the refrigerator the refractive indices of Ihb had dropped and both VII (n^{20}D 1.5255) and IIb bands had appeared in their infrared spectra.

α-Methoxystyrene (V) as a Co-product of (Ihb).—To show the presence of V, 0.3 ml. was dissolved in ethanol and treated with dinitrophenylhydrazine reagent. The red-orange precipitate was filtered immediately; in the filtrate a yellow precipitate was soon formed. It was shown in another experiment that the DNP of VI is thrown down more rapidly than that of VII. After recrystallization from ethanol the DNP melted at 241–243° and 119.5–121°, respectively. The melting points of authentic DNP from VI and VII were 242–243° (lit.[34] 249–250°) and 120–121° (lit.[34] 121°), respectively. Appropriate mixed melting points were undepressed.

β-Methoxystyrene (IIb).—The procedure of Dufraisse and Chaux was modified to exclude acid washing of the product.[3] Fifty ml. of acetyl chloride and 25 ml. of ether were added dropwise to a cooled, agitated solution of 50 ml. of pyridine and 25 ml. of ether; 43 g. of II was added to the white solid. The mixture was heated 15 minutes without a condenser on the water-bath, then in an oil-bath at 170° for 15 minutes. The dark liquid was poured on ice, extracted with ether and dried over potassium hydroxide.

After the ether had been distilled, a short-path distillation at 1 mm. gave 25 g. of a light-yellow liquid, which was fractionated. Infrared spectra revealed at least some Ihb and IIb in all of the fractions; the over-all ratio of IIb/Ihb was less than $^1/_2$. The intense band at 1702 cm.$^{-1}$ found in the early fractions was presumed to arise from β-acetoxystyrene.

The best sample of IIb was obtained as follows. Several fractions of I, repeatedly refractionated, were combined over sodium. This mixture was pumped on for several hours, then distilled. The first few drops of distillate had b.p. 205°, n^{20}D 1.5574, gave only a weakly positive Schiff test and had essentially no infrared carbonyl bands. Some of the strongest infrared bands of Ihb appeared as weak bands in the IIb spectrum. After six days in the refrigerator the refractive index of this sample had dropped to n^{20}D

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(32) F. Schneider, "Qualitative Organic Microanalysis," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 93.

(33) S. Winstein and L. L. Ingraham, THIS JOURNAL, **77**, 1738 (1955).

(34) N. R. Campbell, *Analyst*, **61**, 391 (1936).

1.5538 and a carbonyl band, probably that of VIII, had appeared in the infrared spectrum. Refractionation appeared to increase the proportion of Ihb in these samples.

Pyrolyses of Phenylacetaldehyde Dimethylacetal (II).—When II was distilled slowly from a flask containing potassium hydroxide and calcium carbonate through a heated tube containing a 7″ column of nichrome helices, the conversion to I was *ca.* 40%. Twenty-one grams of the above distillate was heated for two days in the same column so that the head temperature was below 205°. The temperature was then raised and 10–11 g. of clear product was obtained while *ca.* 6 g. remained in the pot. The product was treated with sodium carbonate and calcium chloride. From its refractive index, it appeared that most of the acetal had been consumed. Both I were present. Except for traces of VIII in the head and II in the tail fractions, a high quality mixture of I was obtained on distillation.

Other preparative methods will be described briefly. Sealed tubes containing II and activated alumina or silica gel exploded at 220° (presumably dimethyl ether had formed from methanol). Sealed tubes at 220° containing II and freshly ignited calcium oxide gave I. When II was heated with quinoline or activated alumina in a nitrogen (oxygen-free) atmosphere, compound I was obtained. In all cases the products contained both isomers. The prior removal of peroxides from II with adsorption alumina appeared to have no effect on the outcome of these experiments.

Oxidation Products of β-Methoxystyrene (I).—When mixtures of I were allowed to stand exposed to light and air for several weeks the odor of VIII was apparent. In one case several crystals had formed on the walls of the flask. These were fished out singly. The highest melting point found was 121–122° of several in the range 115–122°. By a similar procedure the highest mixed melting point with an authentic sample of benzoic acid (IV) was undepressed at 120–121°.

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Alkenylphenols Related to the Poison Ivy Principle. An Improved Method of Synthesis Involving the Na–Butanol Cleavage of Benzyl Ethers

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Because of their acid labile properties, the synthesis of alkenylphenols, such as are found in the poison ivy principle, has involved the problem of developing a method of protecting the phenolic hydroxyl groups while the olefinic side chain is introduced. It has been found that benzyl ethers of phenols are cleaved readily by sodium and butanol under conditions which do not effect an isolated olefinic bond. However, the benzyl ethers of styrene-type phenols are simultaneously cleaved and reduced by sodium and butanol, a fact which is advantageous in the Grignard synthesis of both alkyl and alkenyl phenols. An improved synthesis of *o*-pentadecylphenol and 3-pentadecylcatechol (hydrourushiol) is described.

The allergenic principles of the poison ivy plant and the Japanese lac tree have both been shown to be mixtures of compounds having a normal 15 carbon chain attached in the 3-position of catechol.[2-4] In both cases, less than 5% of the mixture is 3-pentadecylcatechol (hydrourushiol). More than 95% of the mixture consists of three olefinic components,[5] differing only in the degree and positions of unsaturation in the 15 carbon side chain.[3,4]

Whereas the minor and saturated component, 3-pentadecylcatechol, has for several years been available (synthetically) for clinical study,[6] the individual olefinic components of the poison ivy principle have only recently been separated in the form of their dimethyl ethers.[3] In the methylated form the components are clinically inactive, and demethylation is not possible in the case of the olefinic components. Thus to make the major poison ivy components available for clinical study, either a new method of separation must be developed which will yield the olefins in their active and free phenolic form, or a method of synthesis must be devised. This communication is concerned with one of the problems in the synthesis.

Hydrourushiol has been synthesized by methods involving, as the final step, aluminum chloride[7] or hydrochloric acid[8] cleavage of the hydrourushiol dimethyl ether. Such methods, however, cannot be used in the synthesis of the olefinic components of urushiol, because alkenylphenols are sensitive to heat and to acids,[9] *i.e.*, they undergo extensive and rapid polymerization. Mason[10] has considered this aspect of the problem of synthesizing alkenylcatechols and has advocated the use of the diphenylmethylene ether as a means of protecting the phenolic groups during synthesis. He found that the diphenylmethylene ether of model alkylcatechols could be cleaved under mildly acidic conditions, but he apparently did not investigate the stability of alkenylcatechols under these same conditions. No one has reported the synthesis of an alkenylphenol utilizing the diphenylmethylene ether derivative, and experience in this Laboratory with olefinic phenols would indicate that even mild acidic conditions should be avoided. For this reason, it has seemed advisable to consider other means of protecting the phenolic hydroxyl groups.

It has been found in the present investigation that benzyl ethers of phenols can be cleaved readily by treatment with sodium and butyl alcohol. Thus benzylhydrocardanol (I) has been converted into hydrocardanol (II), and dibenzylhydrourushiol (XIII) has been converted into hydrourushiol (XIV).

Although the catalytic hydrogenolysis of benzyl

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[1] This paper is based on a portion of the thesis submitted by Bernard Loev in 1952 to Columbia University in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

(2) R. Majima and co-workers, *Ber.*, **55**, 172 (1922), and preceding papers.

(3) W. F. Symes and C. R. Dawson, THIS JOURNAL, **76**, 2959 (1954).

(4) S. V. Sunthankar and C. R. Dawson, *ibid.*, **76**, 5070 (1954).

(5) For nomenclature see B. Loev and C. R. Dawson, *ibid.*, **78**, 1180 (1956).

(6) H. Keil, D. Wasserman and C. R. Dawson, *J. Allergy*, **16**, 275 (1945).

(7) C. R. Dawson, D. Wasserman and H. Keil, THIS JOURNAL, **68**, 534 (1946).

(8) H. S. Mason, *ibid.*, **67**, 1538 (1945).

(9) R. Majima, *Ber.*, **42**, 1418 (1909).

(10) H. S. Mason, THIS JOURNAL, **66**, 1156 (1944).