

and then held at this temperature for 15 minutes more. A dark red color developed during the reaction. Hydrolysis yielded a greenish-brown, sticky solid. It was washed well with water and then digested with 300 ml. of 10% sodium hydroxide solution. The insoluble residue was filtered, washed with water and air-dried. Further purification was effected by digesting the dry solid with 100 ml. of hot ethanol, filtering and then washing with another 100 ml. of hot ethanol. Recrystallization of the solid from dimethylformamide gave, as a first fraction, 8.6 g. of a yellow crystalline solid, m.p. 241–243°. Reworking of the mother liquor yielded an additional 1.5 g. of yellow crystals of the same melting point, and 9.0 g. of very impure mixture (m.p. 130–235°). This mixture could not be further separated into its components. The total yield of product, m.p. 241–243°, was 10.1 g. (15%). Recrystallization from dimethylformamide raised the melting point to 244°.

Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.73; H, 5.07; N, 3.71. Found: C, 82.79; H, 4.91; N, 3.61.

Infrared absorption maxima: 3305, 1652, 1640, 1610, 1600, 1582, 1505, 1339, 1285, 840, 740 and 696 cm^{-1} .

The amine (m.p. 244°) reacted with acetic anhydride to give an amide, melting point 142°.

Anal. Calcd. for $C_{28}H_{21}NO_3$: C, 80.17; H, 5.05; N, 3.34. Found: C, 80.41; H, 5.31; N, 3.35.

In the presence of hydroxylamine a mixture of solid oximes was obtained, which resisted attempts at purification.

p-Toluic acid and diphenylamine react in an analogous manner, giving yellow crystals, melting point 206°.

Anal. Calcd. for $C_{28}H_{23}NO_2$: C, 82.94; H, 5.72; N, 3.45. Found: C, 82.79; H, 5.47; N, 3.47.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

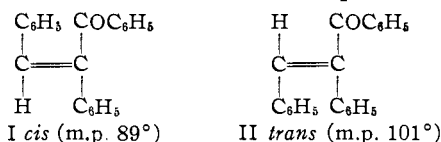
The Action of Lithium Aluminum Hydride and Phenyllithium on Phenylated Chalcones¹

BY ROBERT E. LUTZ AND EVERETT H. RINKER, JR.

RECEIVED AUGUST 12, 1954

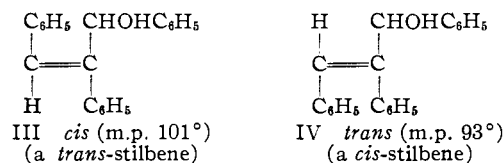
Aluminum isopropoxide in normal fashion reduces the carbonyl of *trans*- but not of *cis*- α -phenylchalcone; lithium aluminum hydride reduces the carbonyls of both, and also the carbonyl of α,β -diphenylchalcone. Phenyllithium adds 48% 1,2 and 33% 1,4 to the *trans* isomer but chiefly 1,4 to the *cis*; and it adds only 1,2 to the carbonyl of α,β -diphenylchalcone. These results are shown to fit a consistent pattern.

The configurations and conformations of the *cis*- and *trans*- α -phenylchalcones (I and II) have been demonstrated.² In certain nucleophilic 1,4-addi-



tions it has been shown that the *trans* isomer has the more effectively conjugated α,β -unsaturated ketone system. In the *cis* isomer the *cis*-stilbene is the more planar and more effectively conjugated system and the benzoyl group is forced out of the plane of conjugation; the carbonyl, while freer from the influence of conjugation with the ethylene double bond, is at the same time more seriously shielded sterically than in the *trans* isomer because it is boxed in by both the α - and β -phenyls. Examples of favored attack on the α,β -unsaturated ketone system of the *trans* isomer are addition of hydrogen chloride, base-catalyzed addition of desoxybenzoin and addition of methoxide ion; an example of hindrance at the carbonyl group is the failure of the *cis* compound to give a phenylhydrazone.² It is of particular interest in this connection that phenyl- and ethylmagnesium bromides add predominantly 1,4 to both *cis* and *trans* isomers,³ and the present investigation was undertaken to confirm and to extend the work in this field.

Aluminum isopropoxide reduction of *trans*- α -phenylchalcone (II) (a repetition of an earlier experiment⁴) gave the corresponding alcohol IV



in almost quantitative yield. The structure assigned to the product was confirmed by its stilbene-like ultraviolet absorption at 260 $m\mu$, by its infrared hydroxyl band at 2.86 μ , and by the absence of either ultraviolet or infrared bands typical of the benzoyl or carbonyl groups. Chromic acid oxidized the alcohol to the *trans*- α -phenylchalcone (II), but this fact does not demonstrate retention of configuration during these transformations because the *cis*-alcohol III (to be described below) is oxidized similarly to the same *trans*-ketone II.

cis- α -Phenylchalcone (I) was recovered unchanged under reducing conditions comparable to those employed successfully to reduce the *trans* isomer.

These results are consistent with expectations based on the carbonyl-specificity of the reagent, and on the high degree of steric hindrance at the carbonyl in the *cis* compound⁵ which would be expected adversely to affect its reducibility.

Lithium aluminum hydride reduction of *trans*- α -phenylchalcone (II) also gives the corresponding 1,2-reduction product IV in excellent yield. This result is of a special interest because, unlike aluminum isopropoxide, lithium aluminum hydride does on occasion react 1,4 with an α,β -unsaturated ketone in which the carbonyl group is sterically hindered as it is in vinyl mesityl ketones.⁶

As was anticipated this reagent, which is much

(1) This work was supported by a research grant from the Office of Ordnance Research.

(2) W. B. Black and R. E. Lutz, *THIS JOURNAL*, **75**, 5990 (1953); cf. also references cited therein.

(3) E. P. Kohler, *Am. Chem. J.*, **36**, 177, 511 (1906).

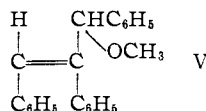
(4) (a) F. Bergmann, *J. Org. Chem.*, **6**, 443 (1941); (b) F. Bergmann, D. Shapiro and H. E. Eschinazi, *THIS JOURNAL*, **64**, 559 (1942).

(5) Cf. "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 187.

(6) Cf. R. E. Lutz and D. F. Hinkley, *THIS JOURNAL*, **72**, 4091 (1950).

more powerful than aluminum isopropoxide, reduced *cis*- α -phenylchalcone also 1,2 at the carbonyl group in spite of the severe steric hindrance involved, and gave the *cis*-alcohol III. The structure of this product III (new) was shown by analysis, its stilbene-type ultraviolet absorption at 259 m μ , its infrared hydroxyl absorption at 2.86 μ , and the lack of infrared benzoyl-type absorption in the 6 μ region; and the configuration is evident from the mode of formation coupled with its difference from the *trans* isomer IV.

Chromic acid oxidation of the *cis*-alcohol III while successful gave *trans*- α -phenylchalcone (II) rather than the *cis* isomer I. Since acids cause *cis*-*trans* equilibration to mixtures of the α -phenylchalcones, and because just the one *trans* isomer is obtained in this oxidation, it is clear that stereochemical rearrangement has occurred prior to or during, but not after, the oxidation. In this connection it is therefore of particular interest to note that both of the alcohols III and IV react with methanolic hydrogen chloride to give the same methyl ether V (known⁴) the structure of which is shown by analysis and by the lack of the 2.86 μ infrared hydroxyl band. The compound is tentatively assigned the *trans* configuration V for the following reasons:



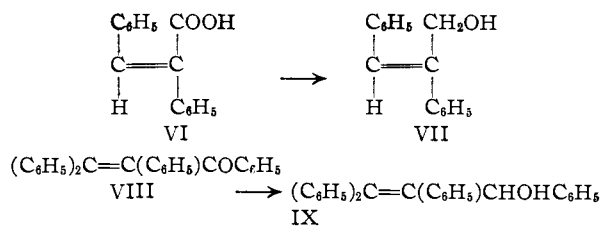
presumably, because it is formed from both III and IV, it corresponds to the more stable type of configuration in this series; the oxidation of both isomeric alcohols to the same *trans*- α -phenylchalcone (II) indicates that the more stable alcohol IV and the ether must have the *trans* configuration (an argument which by itself is weak because it assumes that difference in the rate of oxidation of the two alcohols is not important); and finally the ultraviolet absorption curve of the methyl ether is almost identical with that of the alcohol IV and slightly but nevertheless appreciably different from that of the alcohol III.

It has been shown that the double bond of cinnamyl alcohol obtained in the analogous lithium aluminum hydride reduction of cinnamyl aldehyde or ester is reduced slowly by excess reagent,⁷ and similar results have been reported in the reduction of *trans*-chalcone.⁸ In the reduction of the α -phenylchalcones to the alcohols excess reagent was used and liberal reaction time allowed, and no secondary reduction was noted. In new experiments *cis*- α -phenylcinnamic acid VI was reduced by excess reagent to the alcohol VII, and α,β -diphenylchalcone (VIII) was reduced similarly to the alcohol IX.

The structures of these alcohols (VII and IX; new) were shown by analysis and by comparison of the ultraviolet and infrared absorption spectra with those of the parent and related compounds. The alcohol VII has a typical α -substituted-*cis*-stilbene band at 260 m μ and an infrared hydroxyl band

(7) F. A. Hochstein and W. G. Brown, *THIS JOURNAL*, **70**, 3484 (1948).

(8) W. G. Brown, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 482.

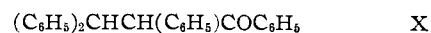


at 2.8 μ ; and the alcohol IX has shoulders of absorption at 240 and 278 m μ (ϵ 20,000 and 8,000) and an infrared hydroxyl band at 2.8 μ . The latter compound was characterized further by dehydration to triphenylindene.

These results show that the double bond in the cinnamyl system when it is phenylated is not easily reduced by excess lithium aluminum hydride. Whether this effect is steric or due to resonance is not clear, but it should be pointed out that *para* substituents in cinnamyl alcohol lower the reducibility of the double bond,⁷⁻⁹ doubtless by their resonance effects.

It should be noted that the above reduction of α,β -diphenylchalcone has gone mainly 1,2 in spite of steric hindrance at the carbonyl group, a result which was predicted on the basis of the mode of addition of the Grignard reagent (described below).

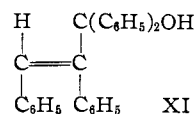
The additions of phenylmagnesium bromide to *cis*- and *trans*- α -phenylchalcones (I and II) reported by Kohler³ were repeated under controlled conditions at 0° and resulted in consistent 1,4-addition to give X as the principal reaction product. Kohler



reported also that the addition of ethylmagnesium bromide to the two isomers gave in each case the same mixture of diastereoisomers³ which would be expected of a 1,4-addition passing through a common enolate. In these latter reactions it is possible that facile isomerization precedes addition but this seems unlikely in view of the many differences in other reactions of the isomers including the addition of phenyllithium described below. It seems more likely that the dominance of 1,4-addition here is the resultant of the normal inclination of the reagent toward 1,4-addition (which can happen in both isomers, albeit more easily in the *trans* than the *cis*) and of the marked steric resistance to 1,2-addition at both carbonyls.

These additions are to be contrasted with the slower addition to α,β -diphenylchalcone which requires elevated temperature and longer time and goes mainly 1,4 involving the *o*-position of the benzoyl group, and less than 12% 1,2 at the carbonyl group.¹⁰

Addition of phenyllithium to *trans*- α -phenylchalcone (II) gave 33% of the 1,4-addition product X and 48% of the 1,2-addition product XI which is new. This latter compound has been characterized by analysis and dehydration by formic acid to



(9) K. Freudenberg and G. Gehrke, *Ber.*, **84**, 443 (1951).

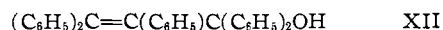
(10) E. P. Kohler and E. M. Nygaard, *ibid.*, **52**, 4128 (1930).

1,2,3-triphenylindene; its ultraviolet absorption maximum at 260 $m\mu$ shows the presence of the substituted *cis*-stilbene function, and the infrared spectrum shows a hydroxyl band at 2.84 μ and no band in the benzoyl range at 6 μ . The configuration is presumed from the mode of formation.

cis- α -Phenylchalcone (I) reacted with phenyllithium to give the 1,4-addition product X in 67% yield; and although this yield was not high, careful study of the by-products failed to reveal the presence of a 1,2-addition product.

These results fit into a consistent pattern. Phenyllithium is known to add 84% 1,2 and 16% 1,4 to *trans*-chalcone¹¹ whereas phenylmagnesium bromide adds chiefly 1,4;³ but phenyllithium does add 1,4 when there is prohibitive hindrance to 1,2-addition as is the case in benzalacetomesitylene.¹² In *trans*- α -phenylchalcone where the more effectively conjugated α,β -unsaturated ketone system is coupled with a benzoyl group which is flanked by only one α -ethylene substituent, a successful competition between 1,2- and 1,4-addition is not unexpected. In the case of the addition of phenyllithium to the *cis*- α -phenylchalcone, however, it would seem that the carbonyl group is so completely boxed in by the α - and β -phenyls as to make 1,2-addition definitely difficult even by this highly reactive reagent, and that 1,4-addition predominates because the α,β -unsaturated ketone system, although not as effective as that of the *trans* isomer, is not seriously hindered sterically and is capable of reacting, albeit presumably more slowly than the *trans* system.

The reactions with α,β -diphenylchalcone (VIII) are of interest because here both the chalcone conjugated system and the carbonyl group are relatively unreactive, as is seen in the reactions with phenylmagnesium bromide.¹⁰ In the reaction with phenyllithium we obtained as the only product isolated a 67% yield of the 1,2-addition product XII



which was shown to be identical with that obtained in small yield by the addition of phenylmagnesium bromide¹⁰; and this compound was further characterized by its stilbene-type ultraviolet absorption (λ_{max} 275, ϵ 7,000), by the infrared hydroxyl band at 2.86 μ , and by the absence of a carbonyl band in the 6 μ region. The result here is in keeping with the high activity of the reagent and its normal preference for 1,2- over 1,4-reaction, and it was predicted on the basis of the prohibitive hindrance toward 1,4-addition of the Grignard reagent, yet ability of the carbonyl group slowly to react 1,2.

Experimental¹³

Preparation of known materials were by the methods given in references cited. *cis*³ and *trans*¹⁰- α -phenylchalcones (I and II) were made by condensations of benzaldehyde with desoxybenzoin.¹⁴

Authentic *cis*-1,2,3-triphenyl-2-propen-1-ol (having the *trans*-cinnamyl system) IV was prepared in 97% yield by reduction of *trans*- α -phenylchalcone II following Berg-

mann's procedure¹⁵ using redistilled aluminum isopropoxide, under partial reflux for 3 hr.

Preparation of IV by lithium aluminum hydride reduction of *trans*- α -phenylchalcone II (1.0 g. in 70 ml. of ether) by addition of 1.0 g. of the reagent in 30 ml. of ether (over 30 min.) and standing for an additional 30 min., gave an oil which crystallized from 60–90° ligroin upon cooling in the deep freeze; 0.95 g. (94%), m.p. 90–92°; identified as IV by mixture m.p.; recrystallized, m.p. 93°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.78; H, 6.33; λ_{max} 260 $m\mu$, ϵ 15,800; λ_{min} . 242 $m\mu$, ϵ 10,800; breadth of band at ϵ 12,000, 246.5–271.5 $m\mu$; infrared band at 2.86 μ ; none at 5.8–6.1 μ .

trans-1,2,3-Triphenyl-2-propen-1-ol (a *cis*-cinnamyl alcohol; new) III was prepared by lithium aluminum hydride reduction of *cis*- α -phenylchalcone by the above procedure; yield 79%; recrystallized from 60–90° ligroin; m.p. 100–101° (it gave a 20° mixture m.p. depression with IV).

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.15; H, 6.45; λ_{max} 262 $m\mu$, ϵ 16,000; λ_{min} . 237 $m\mu$, ϵ 10,300; breadth of band at ϵ 12,000, 247.5–271.5 $m\mu$; infrared band at 2.86 μ ; none at 5.8–6.1 μ .

An attempted reduction of *cis*- α -phenylchalcone (I) by aluminum isopropoxide by the procedure described above resulted in 92% recovery of starting material.

Chromic acid oxidation of *cis*- and *trans*-1,2,3-triphenyl-2-propen-1-ol (IV and III) in glacial acetic acid (5 min. at room temperature) gave oils which crystallized from ethanol; yields 32 and 40%, respectively, of *trans*- α -phenylchalcone (identified by mixture m.p.).

cis- α -Phenylcinnamyl Alcohol (VII).—A slurry of 8.96 g. (0.04 mole) of *cis*- α -phenylcinnamic acid (VI) in 50 ml. of ether was added to 2 g. of lithium aluminum hydride in 200 ml. of ether, and the mixture was allowed to react for an additional 10 min. The product crystallized from 30–60° petroleum ether; yield 5.6 g. (66.5%), m.p. 69–72°; after five recrystallizations from petroleum ether, m.p. 73–74°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.69; H, 6.71. Found: C, 85.78; H, 7.01; λ_{max} 222, 258 $m\mu$, ϵ 14,500; λ_{min} . 240 $m\mu$, ϵ 7,900; infrared band at 2.86 μ ; none at 5.8–6.1 μ .

A similar reduction of the methyl ester of VI on a 2-g. scale gave 72% of VII.

Aluminum isopropoxide reduction of *trans*-chalcone by the method of Truett and Moulton¹⁶ gave *cis*-1,3-diphenyl-2-propen-1-ol (a *trans*-cinnamyl alcohol), m.p. 57–58°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.54; H, 6.83; λ_{max} 243 $m\mu$, ϵ 20,400; λ_{min} . 226 $m\mu$, ϵ 5,300; infrared band at 2.86 μ , none at 5.8–6.1 μ .

Reaction of Phenyllithium with *trans*- α -Phenylchalcone (II).—To a solution of 0.041 mole of phenyllithium (from 0.84 g. of lithium and 6.4 g. of bromobenzene) in 100 ml. of ether¹⁶ was added over 45 min. an ether solution of 2.84 g. (0.01 mole) of II, with continued stirring for 15 min. The resulting product crystallized from ethanol; 1.20 g. (32%), m.p. 180–181° (identified as α,β,β -triphenylpropiofenone⁸ (X) by mixture m.p.).

cis-1,1,2,3-Tetraphenyl-2-propen-1-ol (XI) (a *trans*-cinnamyl alcohol) was obtained by evaporation of the alcohol filtrate in the above experiment and crystallizing the resulting oil from *n*-hexane; 1.74 g. (48%), m.p. 98–102° (it gave a mixture m.p. depression with starting material; recrystallized from *n*-hexane, m.p. 106–107°).

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.31; H, 6.03; λ_{max} 259 $m\mu$, ϵ 13,600; λ_{min} . 245 $m\mu$, ϵ 10,700; infrared band at 2.86 μ ; none at 5.8–6.1 μ .

Attempted oxidation by chromic acid in acetic acid gave no crystalline product.

Reaction of phenyllithium with *cis*- α -phenylchalcone (I) exactly as with II above gave 67% of X as the sole product isolated (identified by mixture m.p. with an authentic sample⁸).

Preparation of methyl ether of 1,2,3-triphenyl-2-propen-1-ol (V) was carried out essentially by Bergmann's procedure used on IV¹⁶ and applied now to III. To a solution of 1.0 g. of III in 10 ml. of hot methanol was added one drop of concd. sulfuric acid. After 20 min. and then cooling,

(15) W. L. Truett and W. H. Moulton, Jr., *ibid.*, **73**, 5913 (1951).

(16) H. Gilman, C. A. Zoellner and W. M. Selby, *ibid.*, **55**, 1251 (1933).

(11) A. Lüttringhaus, *Ann.*, **557**, 70 (1945).

(12) H. Gilman and R. H. Kirby, *THIS JOURNAL*, **63**, 2046 (1941)

(13) Microanalyses were by Miss Patricia L. Paynter.

(14) D. A. Ballard and W. M. Dehn, *THIS JOURNAL*, **54**, 3970 (1932).

1.0 g. (95%) of V crystallized (the yield using IV was 43%); recrystallized from 60–90° ligroin, m.p. 93°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.99; H, 6.71. Found: C, 87.89; H, 6.58; λ_{max} 260 $m\mu$, ϵ 15,500; λ_{min} 242 $m\mu$, ϵ 11,100; breadth of band at ϵ 12,000, 243–282 $m\mu$; no infrared bands at 2.8–3.0 μ or at 5.8–6.1 μ .

α,β -Diphenylchalcone (VIII)¹⁰: m.p. 153°. *Anal.* Calcd. for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.74; H, 5.50; λ_{max} 242 $m\mu$, ϵ 25,000; shoulder at 285 $m\mu$, ϵ 12,000.

1-Ethoxy-1,2,3-triphenylindene¹⁷ was obtained as a by-product in one preparation of α,β -diphenylchalcone (VIII) where technical (non-dried) bromine was used and the ether solution was dried, evaporated and treated with ethanol; m.p. 171–172° (K¹⁷, 172°). It was characterized by analysis and absorption spectra; λ_{max} 245, 322 $m\mu$, ϵ 25,200, 10,500; λ_{min} 277 $m\mu$, ϵ 3,500; no infrared absorption bands at 2.8–3.0 or 5.8–6.1 μ .

1,2,3,3-Tetraphenyl-2-propene-1-ol (IX).—A slurry of 2 g. of the ketone VIII in 175 ml. of ether was added to 1 g. of lithium aluminum hydride in 50 ml. of ether with continued stirring for 20 min.; crystallized from 60–90° ligroin; 2.0 g. (99%), m.p. 93–103°. Slow recrystallization gave large colorless needles of similar wide melting range.

(17) E. P. Kohler, *Am. Chem. J.*, **40**, 222 (1910).

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.31; H, 6.03. Found: C, 89.28; H, 6.22; ultraviolet absorption, decreasing from 220–340 $m\mu$ with pronounced shoulder at 270 $m\mu$, ϵ 9,600.

Dehydration of *cis*-1,1,2,3-tetraphenyl-2-propen-1-ol (a *trans*-cinnamyl alcohol) (XI) by refluxing 88% formic acid (1 hr.) gave 1,2,3-triphenylindene in 99% yield (identified by mixture m.p. with an authentic sample¹⁷).

Dehydration of 1,2,3,3-tetraphenyl-2-propen-1-ol (IX) similarly gave 67% of 1,2,3-triphenylindene (identified).

1,2,3-Triphenylindene^{17,18}: m.p. 133–134°. *Anal.* Calcd. for $C_{22}H_{20}$: C, 94.17; H, 5.85. Found: C, 93.70; H, 5.79.

Reaction of phenyllithium with α,β -diphenylchalcone (VIII), carried out exactly according to the above procedure for II, gave 67% yield of 1,1,2,3,3-pentaphenyl-2-propene-1-ol (XII)¹⁰; crystallized from chloroform–ligroin mixture, m.p. 164–169° (identified by m.p. analysis and spectral data, and the m.p. 217–218° of its acetate¹⁰).

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.38; H, 5.98. Found: C, 90.00; H, 5.89; λ_{max} 265–280 $m\mu$, ϵ 7,500; λ_{min} 255 $m\mu$, ϵ 6,200; infrared band at 2.86 μ ; none at 5.8–6.1 μ .

(18) E. P. Kohler and W. E. Mydans, *THIS JOURNAL*, **54**, 4667 (1932).

CHARLOTTESVILLE, VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

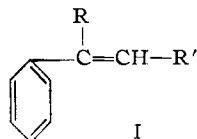
Ionic Polymerization.¹ A Convenient Synthesis of α - and β -Alkylstyrenes. The Effect of an α -Alkyl Group on the Ultraviolet Absorption Spectra

BY C. G. OVERBERGER AND DAVID TANNER²

RECEIVED MAY 28, 1954

A convenient synthesis of α - and β -alkylstyrenes by the deacetylation of the acetates from carbinols II and III is reported. Evidence is presented for the structure of the styrenes based on ozonolysis and correlation of fractional distillation data and ultraviolet absorption spectra. Steric inhibition of resonance in the case of α -alkylstyrenes is suggested based on the interpretation of the ultraviolet absorption spectra.

In order to determine quantitatively the steric effect of alkyl groups on the rate of addition of an ion pair to a vinyl group by use of the copolymerization technique, a series of pure α - and β -alkylstyrenes have been prepared. This paper reports the preparation and characterization of I, R = C_2H_5 , R' = H; R = $n-C_3H_7$, R' = H; R = iso- C_3H_7 , R' = H; R = H, R' = CH_3 ; R = H, R' = C_2H_5 and R = H, R' = $n-C_3H_7$. Copolymerization data will be reported separately.



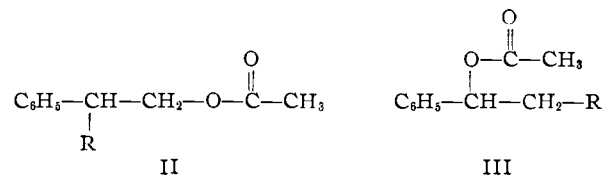
Although these styrenes have previously been prepared in a variety of ways, we wish to report a convenient preparation for the pure monomers by deacetylation of II to obtain the α -alkylstyrenes and III to obtain the β -alkylstyrenes. Furthermore, the preparation of the pure monomers by one investigator has made it possible to compare their physical properties.

Examination of the literature revealed that de-

(1) This is the fourth in a series of papers concerned with ionic catalyzed polymerization; for the third, see C. G. Overberger, R. J. Ehrig and D. Tanner, *THIS JOURNAL*, **76**, 772 (1954).

(2) A portion of a thesis submitted by D. Tanner in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

hydration³ or dehydrohalogenation⁴ of the appropriate alcohol or alkyl halide, respectively, for the preparation of α -alkylstyrenes usually gave mixtures of products, either due to double bond isomerization or rearrangement of the carbon skeleton. Reported decarboxylations of β -alkylcinnamic acids were unsatisfactory for large scale preparation due to small yields.⁵ Since deacetylation is known to proceed through a cyclic mechanism without rearrangement,⁶ this method seemed preferable for the preparation of pure α -alkylstyrenes.



The synthesis of the β -alkylstyrenes was effected by a similar procedure, although many other useful procedures are recorded in the literature (Table III).

(3) (a) Footnote a, ref. 1, Table III; (b) Mme. Ramart-Lucas and Mlle. Amagat, *Compt. rend.*, **184**, 30 (1927); (c) P. Ramart and P. Amagat, *Ann. chim.*, **8**, 263 (1927); (d) Mme. Ramart-Lucas and P. Amagat, *Bull. soc. chim.*, **15**, 108 (1932).

(4) (a) Footnote c, ref. 1, Table III; (b) C. R. Hauser, P. S. Skell, R. D. Bright and W. B. Renfrow, *THIS JOURNAL*, **69**, 589 (1947).

(5) Footnote a, ref. 2, Table III; footnote b, ref. 1, Table III.

(6) E. R. Alexander and A. Mudrak, *THIS JOURNAL*, **72**, 1810 (1950); see also reference 18 for discussion and earlier references.