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# Sodium-Catalyzed Reactions of *o*-, *m*- and *p*-Methylstyrene in the Presence of Toluene[1,2]

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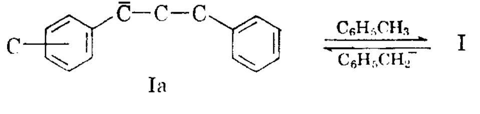
**The sodium-catalyzed reactions of *o*-, *m*- and *p*-methylstyrene in the presence of toluene were studied at 110°. The monoadducts formed were: 1-*o*-tolyl-3-phenylpropane, 17.4%; 1-*m*-tolyl-3-phenylpropane, 34.2%; and 1-*p*-tolyl-3-phenylpropane, 40.8% by weight of the corresponding total products. These concentrations include small amounts of the skeletally identical diarylpropenes. Part of the methylstyrenes underwent hydrodimerization leading to the formation of 1,3-ditolylbutanes. A second type of dimer, preserving a free vinyl group and resulting from the competitive metalation of methylstyrene, was observed in the products of *o*- and *p*-methylstyrene only. The reactions were accompanied by considerable polymer formation, especially in the case of *o*-methylstyrene. The mechanism of the reactions is discussed.**

It was reported previously that styrene reacts with alkylbenzenes in the presence of sodium or sodium-organosodium catalysts to form mono- and diaddition products.[4] As an extension of this work the sodium-catalyzed reactions of the isomeric methylstyrenes in the presence of toluene were investigated with the purpose of obtaining information on the influence of ring substitution in the styrene molecule upon the mode and extent of reaction. The experiments were carried out at the reflux temperature of toluene in the presence of the previously used sodium-benzylsodium catalyst.[4] The composition of the products obtained is summarized in Table I.

The data show that like styrene itself the methyl-substituted styrenes react with toluene to form the corresponding 1-phenyl-3-tolylpropanes as well as some quantities of the skeletally identical 1-phenyl-3-tolylpropenes.

The reaction is probably initiated by a benzyl carbanion which adds to the methylstyrene to form Ia. The latter is converted into stable products either by abstraction of a proton from another toluene molecule, thus forming monoadduct I, or by hydride transfer reaction resulting in the formation of the phenyl conjugated olefins II and III:



Ia (1)

$$\mathrm{Ia} + CH_3C_6H_4CH{=}CH_2 \rightleftharpoons \underset{\substack{\uparrow\downarrow\\ \mathrm{III}}}{\mathrm{II}} + CH_3C_6H_4\bar{C}HCH_3 \quad (2)$$

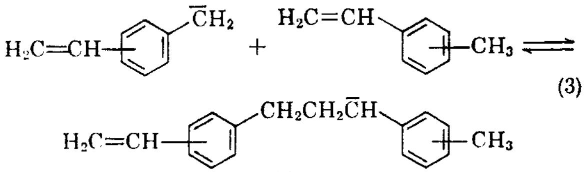
(For I–III see Table I).

The carbanion formed in (2) can abstract a proton from a toluene molecule to give ethyltoluene.

*o*-Methylstyrene interacts with toluene to a much lower extent than the *meta* and *para* isomers. This was confirmed by repeating several times the experiment with *o*-methylstyrene in order to exclude the possibility of differences in the activity of the catalyst.

The secondary carbanion formed in reaction (2) can interact with a second monomer molecule to form a dimeric carbanion from which the 1,3-ditolylbutanes (IV) and the small amounts of skeletally related 1,3-ditolylbutenes are derived.

The formation of vinyl containing dimers (V) is attributed to the metalation of the methyl group in the monomer molecule followed by addition of the carbanion formed to the vinyl group of a second molecule:



(3)

V

The proposed mechanism would require a quantitative relationship between the total amount of unsaturation of the products (excluding the vinyl group content) and the amount of hydride transfer products, namely 1,3-ditolylbutane and ethyltoluene. It was found in the experiment with *p*-methylstyrene that the amount of diarylalkenes formed accounts for about 80% of the total amount of hydride transfer products. The difference is probably due to a certain extent of hydride transfer reactions accompanying the formation of polyalkylated products. In the case of *m*- and *o*-methylstyrene, which form larger amounts of polymeric products, the agreement is somewhat less satisfactory.

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(1) Paper XX of the series "Base-catalyzed Reactions." For paper XIX, see B. Notari and H. Pines, *J. Am. Chem. Soc.*, 82, 2945 (1960).

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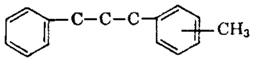
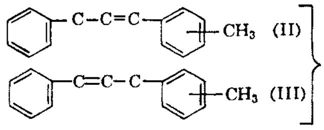
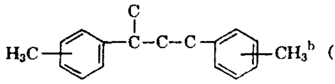
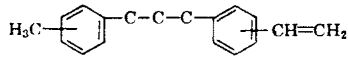
(4) H. Pines and D. Wunderlich, *J. Am. Chem. Soc.*, 80, 6001 (1958).

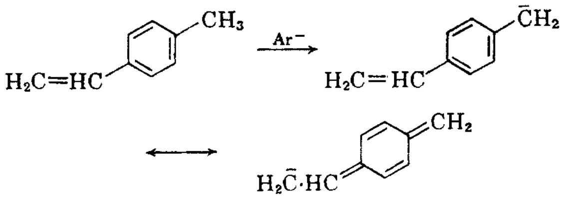
TABLE I

COMPOSITION OF PRODUCTS OBTAINED IN THE SODIUM-CATALYZED REACTIONS OF *o*-, *m*- AND *p*-METHYLSTYRENE IN THE PRESENCE OF TOLUENE[a]

| | *o*-Methylstyrene | *m*-Methylstyrene | *p*-Methylstyrene |
|---|---|---|---|
| Conversion of methylstyrene, % | 83.1 | 86.7 | 100 |
| Product component, wt. % | | | |
| Ethyltoluene | 3.9 | 4.0 | 0.7 |
|  (I) | 14.7 | 29.8 | 36.1 |
|  (II) (III) | 2.7 | 4.4 | 4.7 |
|  (IV) | 6.4 | 19.1 | 16.0 |
|  (V) | 3.8 | | 11.9 |
| Polymer | 68.5 | 42.7 | 30.6 |

[a] Twelve grams (0.1 g., mole) of methylstyrene and 60 g. (0.65 g., mole) of toluene were used in each experiment; 0.05 g.-atom of sodium and 0.006 g., mole of promoter (*o*-chlorotoluene) were taken per mole of toluene; reaction temp., 110 ± 2°; time, 2 hr. [b] Includes skeletally identical ditolylbutenes. [c] Includes skeletally identical diarylpropenes (see Experimental).

If metalation is assumed to be the rate-controlling step of reaction (3) then the differences in the concentration of the vinyl containing dimer could supply information on the relative acidity of the isomeric methylstyrenes. It can be expected that the metalation of *o*- and *p*-methylstyrene should be easier than that of toluene because the resulting benzylic carbanion will be stabilized by an additional resonance structure, for example:



No additional resonance stabilization of this type can be operative in the case of *m*-methylstyrene.

In order to compare the rate of metalation of toluene with that of *o*- and *p*-methylstyrene one should consider the molar concentration of the products derived from Ia *vs.* that of the products of reaction (3). By multiplying these concentrations with the proper factor derived from the molar dilution ratio of methylstyrene in toluene (1:6.4) one could calculate that the relative rate of metalation of *p*-methylstyrene to toluene is 2.1:1 and that of *o*-methylstyrene to toluene about 1.6:1. The actual relative rates are, however, much higher and probably of a completely different order of magnitude because the slow dropwise addition of methylstyrene to an excess of toluene results in a very high operative dilution ratio. This assumption is supported by the fact that in the case of *m*-methylstyrene, which has probably an acidity comparable to that of toluene, no detectable amounts of a vinyl-containing dimer were found. The observed phenomenon of increased acidity of *p*-methylstyrene points to a difference in the effect of a *p*-vinyl as compared to a *p*-methyl substituent, because in the case of *p*-xylene the reverse phenomenon of decreased alkylation was reported.[5]

## EXPERIMENTAL

*Apparatus and procedure.* The sodium-benzylsodium catalyst was prepared in a three necked flask of 125-ml. capacity, equipped with a high-speed stirrer. A mixture of 1 g. of freshly cut sodium, 0.8 g. of *o*-chlorotoluene and 10 g. of toluene was introduced in the flask and stirred at reflux temperature for a period of 3-4 hr. under a slow stream of helium.

The reactants (see Table I, footnote a) were then added dropwise over a period of 30 min. The catalyst was decomposed with ethanol. The solution was filtered, washed and distilled. The product was subjected to the following analytical treatment:

*Catalytic hydrogenation.* The degree of unsaturation of the fractions was determined by semimicro hydrogenation using 5% palladium on carbon powder as the catalyst.

*Gas-liquid chromatography.* Low-boiling fractions which contained mainly methylstyrene and ethyltoluene were analyzed on a tricresyl phosphate column. Fractions boiling in the 120-165°/1 mm. range and composed mainly of monoaddition products were analyzed on a silicon column (Dow-Corning 550 Fluid). Cuts composed of pure compounds (95% or more) were subjected to complemental infrared analysis. The identity of components in composite fractions was determined by comparison of their retention volumes with those of pure synthetic samples. Quantitative analyses of such fractions were carried out generally after subjecting them first to catalytic hydrogenation by which procedure the small amounts of olefins were converted into the corresponding skeletally identical diarylalkanes.

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(5) H. Pines and L. Schaap, *J. Am. Chem. Soc.*, **80,** 3076 (1958).

TABLE II

Preparation of Methylstyrenes

| Intermediate Carbinol | Yield, %[a] | B.P. | Mm. | $n_D^{20}$ | Styrene Derivative | Yield, %[a] | B.P. | Mm. | $n_D^{20}$ |
|---|---|---|---|---|---|---|---|---|---|
| *o*-Tolylmethylcarbinol[b] | 67 | 107–108 | 20 | 1.5300 | *o*-Methylstyrene[c] | ~100 | 80–81 | 25 | 1.5449 |
| *m*-Tolylmethylcarbinol[d] | 61 | 100–100.5 | 5 | 1.5227 | *m*-Methylstyrene[e] | ~100 | 50 | 4 | 1.5414 |
| *p*-Tolylmethylcarbinol[f] | 68 | 97–98 | 7 | 1.5223 | *p*-Methylstyrene[g] | ~100 | 46–47 | 5 | 1.5420 |

[a] Based on carbinol charged. [b] F. Eisenlohr and L. Schulz, *Ber.*, **57,** 1808 (1924); b.p. 107.8–108° at 20 mm. [c] A.P.I. Res. Project 44, Table 13a, b.p. 171° at 760 mm., $n_D^{20}$ 1.5450. [d] C. Marvel *et al.*, *J. Am. Chem. Soc.*, **68,** 736 (1946); b.p. 103–105 at 6 mm., $n_D^{20}$ 1.5240. [e] C. Marvel *et al.*, *J. Am. Chem. Soc.*, b.p. 50–51° at 3 mm., $n_D^{20}$ 1.5410. [f] D. Mowry *et al.*, *J. Am. Chem. Soc.*, **68,** 1105 (1946); b.p. 105–106° at 13 mm., $n_D^{20}$ 1.5203. [g] D. Mowry *et al.*, *J. Am. Chem. Soc.*, b.p. 65–66° at 18 mm., $n_D^{25}$ 1.5402.

*Spectroscopic analysis.* The concentration of dimeric olefins having a free vinyl group was estimated by using the 990-cm.$^{-1}$ absorption band. The absorbances of dilute carbon disulfide solutions of the pure monomer were first measured. Subsequently the absorbances of carbon disulfide solutions of the examined dimeric fractions were measured at the same key band and the concentration of the vinyl-containing dimer estimated on assumption that its absorptivity (specific extinction) is twice lower than that of the monomer. The estimations were in good agreement with the results obtained by gas chromatography. The presence in some fractions of addition products having phenyl-conjugated double bonds was shown by ultraviolet analysis.

*o-Methylstyrene-toluene.* Part of the toluene-free product, 12.4 g., was distilled as follows:

| No. | B.P. | Wt. % |
|---|---|---|
| 1 | 30–32/2 mm. | 19.3 |
| 2 | 134–136/1.5 mm. | 13.7 |
| 3 | 160–162/1.5 mm. | 9.7 |
| 4 | Residue and hold up | 57.3 |

Fraction 1 was identified as a mixture of 84.5% of unconverted *o*-methylstyrene and 15.5% of *o*-ethyltoluene. Fraction 2 contained 88.5% of 1-phenyl-3-*o*-tolylpropane (I) and its related olefins, 6.3% of unchanged *o*-methylstyrene and 5.2% of the higher boiling *o*-methylstyrene dimers. In an experiment on a larger scale compound I was obtained in a pure form (98%).

*Anal.* Calcd. for $C_{16}H_{18}$: C, 91.43; H, 8.57, mol. wt., 210. Found: C, 91.44; H, 8.48, mol. wt. (Beckmann's method), 207.

Two types of *o*-methylstyrene dimers were found in fraction 3. One, representing about 55% of the fraction, was identified as 1,3-di-*o*-tolylbutane. The second dimer, which represented about 33% of the fraction, was shown to contain a free vinyl group by infrared analysis of the nonhydrogenated fraction. The structure of 1-*o*-tolyl-3-*o*-vinylphenylpropane was assigned to this isomer by analogy with the corresponding vinyl-containing dimer obtained from *p*-methylstyrene, the identity of which was established by synthesis.

*m-Methylstyrene-toluene.* After removing the excess of toluene the residual liquid (14.3 g.) was fractionated as follows:

| No. | B.P. | Wt. % |
|---|---|---|
| 1 | 26–30/1.5 mm. | 12.6 |
| 2 | 122–123/1.3 mm. | 30.1 |
| 3 | 168–174/1.2 mm. | 20.2 |
| 4 | Residue and hold up | 38.4 |

Fraction 1 contained 80.2% of unconverted *m*-methylstyrene and 19.8% of *m*-ethyltoluene. Fraction 2 contained 71.6% of 1-phenyl-3-*m*-tolylpropane and 13.4% of skeletally related propenes.

Fraction 3 was composed of 70% of 1,3-di-*m*-tolylbutane and 30% of its related olefins. No evidence was found for the presence of a vinyl-containing dimer.

*p-Methylstyrene-toluene.* The product, 14.6 g., was fractionated as follows:

| No. | B.P. | Wt. % |
|---|---|---|
| 1 | 131–132/2 mm. | 27.4 |
| 2 | 133–159/2 mm. | 1.4 |
| 3 | 160–174/2 mm. | 40.4 |
| 4 | Residue and hold up | 30.8 |

Fraction 1 was composed of 90% of 1-phenyl-3-*p*-tolylpropane and 10% of the related olefins.

The hydrogenated fraction 3 contained 32.0% of 1-phenyl-3-*p*-tolylpropane, 38.7% of 1,3-di-*p*-tolylbutane and

TABLE III

Frequencies of Infrared Absorption Maxima[a] of the Methylstyrenes (Cm.$^{-1}$)

| *o*-Methylstyrene | *m*-Methylstyrene | *p*-Methylstyrene |
|---|---|---|
| 730 (s) | 652 | 697 |
| 772 (s) | 713 (s) | 712 |
| 826 | 790 (s) | 731 (s) |
| 867 | 826 | 796 |
| 910 (s) | 882 | 820 |
| 938 | 908 (s) | 905 (s) |
| 990 (s) | 993 (s) | 990 (s) |
| 1025 | 1031 | 1020 |
| 1036 | 1043 | 1034 |
| 1063 | 1099 | 1116 |
| 1109 | 1158 | 1182 |
| 1163 | 1169 | 1205 |
| 1185 | 1250 | 1262 |
| 1224 | 1272 | 1273 |
| 1285 | 1291 | 1310 |
| 1377 | 1378 | 1373 |
| 1445 | 1446 | 1449 |
| 1464 (s) | 1453 | 1509 (s) |
| 1491 (s) | 1490 (s) | 1565 |
| 1575 | 1585 (s) | 1608 |
| 1603 | 1605 (s) | 1629 (s) |
| 1627 (s) | 1634 (s) | 1677 |
| 1713 | 1693 | 1810 |
| 1804 | 1784 | 1896 |
| 1833 | 1822 | 2850 |
| 1881 | 1873 | 2900 |
| 1912 | 1938 | 3000 (s) |
| 1947 | 2868 | |
| 2860 | 2923 | |
| 3018 (s) | 3025 (s) | |

[a] Absorption bands denoted by (s) correspond to a transmittance equal or lower than 10% when the pure compound is examined in a cell of 0.04-mm. width.

TABLE IV

SYNTHESIS OF INTERMEDIATE 1,3-DIARYLPROPANOLS

| Reactants | | | | | | |
|---|---|---|---|---|---|---|
| Halide | Aldehyde | Carbinol | Yield, % | B.P. | Mm. | $n_D^{20}$ |
| β-Phenylethyl bromide | *o*-Tolualdehyde | 1-*o*-Tolyl-3-phenylpropanol | 78 | 177 | 5 | 1.5676 |
| β-Phenylethyl bromide | *m*-Tolualdehyde | 1-*m*-Tolyl-3-phenylpropanol | 68 | 184–185 | 5 | 1.5631 |
| β-Phenylethyl bromide | *p*-Tolualdehyde | 1-*p*-Tolyl-3-phenylpropanol | 69 | 180–181 | 5 | 1.5673 |
| β-*p*-Tolylethyl bromide[a] | *p*-Ethylbenzaldehyde[b] | 1-*p*-Ethylphenyl-3-p-tolylpropanol | 40 | 170–171 | 0.6 | 1.5535 |

[a] B.p. 96° at 5 mm., $n_D^{20}$ 1.5505, prepared in 68% yield by bromination of *p*-tolylethanol with phosphorus tribromide; *p*-tolylethanol, b.p. 85° at 1.2 mm., $n_D^{20}$ 1.5293, was obtained in 70% yield by Grignard reaction of *p*-tolylmagnesium bromide with ethylene oxide. [b] B.p. 112–113° at 20 mm., $n_D^{20}$ 1.5018, prepared from benzaldehyde by the Gattermann-Koch method [*Org. Syntheses*, **Coll. Vol. II,** 583 (1943)].

TABLE V

SYNTHESIS OF 1,3-DIARYLPROPANES

| Intermediate Olefin | Yield, %[a] | B.P. | Mm. | $n_D^{20}$ | Diarylpropane | B.P. | Mm. | $n_D^{20}$ | C, %[b] | H, % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-*o*-Tolyl-3-phenyl-x-propene[c,d] | 81 | 130–131 | 1 | 1.5917 | 1-*o*-Tolyl-3-phenylpropane | 134 | 1.3 | 1.5606 | 91.30 | 8.55 |
| 1-*m*-Tolyl-3-phenyl-x-propene[c,d] | 82 | 133–134 | 1 | 1.5867 | 1-*m*-Tolyl-3-phenylpropane | 124–125 | 1.0 | 1.5562 | 91.25 | 8.58 |
| 1-*p*-Tolyl-3-phenyl-x-propene[c,d] | 81 | 132 | 1.2 | 1.5876 | 1-*p*-Tolyl-3-phenylpropane | 130–131 | 1.0 | 1.5509 | 91.28 | 8.47 |
| 1-*p*-Tolyl-3-*p*-ethylphenyl-x-propene[c,d] | 85 | 158–160 | 0.8 | 1.5744 | 1-*p*-Tolyl-3-*p*-ethylphenylpropane | 160–161 | 0.6 | 1.5435 | 90.54 | 9.20 |

[a] Based on corresponding propanol (Table IV) charged. [b] Calcd. for $C_{16}H_{18}$: C, 91.37, H, 8.63; Calcd. for $C_{18}H_{22}$: C, 90.69, H, 9.31. [c] Infrared spectrum shows the presence of a phenyl-conjugated double bond (absorption in the vicinity of 1630 cm.$^{-1}$); *trans* isomers are predominant (strong absorption at 960 cm.$^{-1}$). [d] Gas chromatography shows the presence of the two possible double bond isomers.

TABLE VI

SYNTHESIS OF 1,3-DITOLYLBUTANES

| Intermediate Dypnone | Yield, %[a] | B.P. | Mm. | $n_D^{20}$ | C, %[b] | H, % | Ditolylbutane | Yield, %[c] | B.P. | Mm. | $n_D^{20}$ | C, %[d] | H, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *o,o'*-Dimethyldypnone | 58 | 171–172 | 1 | 1.5925 | 86.80 | 7.29 | 1,3-Di-*o*-tolylbutane | ~100 | 156 | 1 | 1.5528 | 90.52 | 9.22 |
| *m,m'*-Dimethyldypnone | 64 | 179–180 | 1 | 1.6114 | 86.46 | 7.17 | 1,3-Di-*m*-tolylbutane | ~100 | 163–164 | 1 | 1.5455 | 90.58 | 9.15 |
| *p,p'*-Dimethyldypnone | 62 | 182–184 | 0.8 | [e] | 86.38 | 7.17 | 1,3-Di-*p*-tolylbutane | ~100 | 159–160 | 1 | 1.5449 | 90.60 | 9.24 |

[a] Based on methylacetophenone taken. [b] Calcd. for $C_{18}H_{18}O$: C, 86.35; H, 7.25. [c] Based on dimethyldypnone taken. [d] Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. [e] M.p. 62.5–63°.

29.3% of 1-*p*-tolyl-3-*p*-ethylphenylpropane. The vinyl-containing dimer in the nonhydrogenated fraction accounted for 82% of the total 1-*p*-tolyl-3-*p*-ethylphenylpropane found in the hydrogenated fraction. The total amount of olefins, excluding the vinyl group content, was 24.9%.

*Materials. Preparation and properties.* The methylstyrene isomers were prepared through the Grignard reaction of acetaldehyde with the corresponding tolylmagnesium bromides, followed by dehydration of the tolylmethylcarbinols formed. The dehydrations were carried out at 310° over activated alumina (Harshaw, 1/8" tablets) in admixture with an equal amount of *tert*-butyl alcohol, by which method the styrenes were obtained in practically quantitative yields. It should be noted that dehydration according to the method of Brooks[6] or by refluxing over potassium bisulfate in the presence of benzene gives much poorer (50–60%) yields. Table II summarizes the yields and the physical properties of the methylstyrenes, as well as those of the intermediate carbinols. The infrared spectra of the isomers are given in Table III. Examination of the 1650–2000-cm.$^{-1}$ (5 to 6 $\mu$) region of the three spectra reveals the presence of groupings of absorption bands specific for an *ortho-*, *meta-* and *para*-disubstituted benzene ring, correspondingly.[7]

*Synthesis of diarylalkanes.* The isomeric 1-tolyl-3-phenylpropanes (Table V) were synthesized through the Grignard reaction of β-phenylethyl bromide with the corresponding tolualdehydes, followed by dehydration of the resulting carbinols at 310° over alumina and hydrogenation of the propenes thus formed at 160° and 110–115 atm. pressure in the presence of a copper chromite catalyst. The 1-*p*-tolyl-3-

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[6] L. A. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944).

[7] C. W. Young, R. B. Du Vall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

TABLE VII

FREQUENCIES OF INFRARED ABSORPTION MAXIMA[a] OF DIARYLALKANES (CM.$^{-1}$)

| 1-*o*-Tolyl-3-phenyl-propane | 1-*m*-Tolyl-3-phenyl-propane | 1-*p*-Tolyl-3-phenyl-propane | 1-*p*-Tolyl-3-*p*-ethyl-phenyl-propane | 1,3-Di-*o*-tolyl-butane | 1,3-Di-*m*-tolyl-butane | 1,3-Di-*p*-tolyl-butane |
|---|---|---|---|---|---|---|
| 697 (s) | 698 (s) | 697 (s) | 696 | 728 (s) | 703 (s) | 704 |
| 745 (s) | 747 (s) | 746 (s) | 751 | 743 (s) | 742 | 722 |
| 764 | 764 | 773 | 773 | 758 (s) | 783 (s) | 754 |
| 800 | 784 (s) | 806 | 806 (s) | 863 | 879 | 791 |
| 843 | 803 | 834 | 830 | 937 | 897 | 808 (s) |
| 867 | 841 | 870 | 873 | 987 | 920 | 816 (s) |
| 907 | 881 | 906 | 897 | 1032 | 966 | 839 |
| 936 | 903 | 1024 | 935 | 1058 | 1040 | 897 |
| 1033 | 1033 | 1033 | 961 | 1089 | 1072 | 937 |
| 1054 | 1079 | 1079 | 1023 | 1129 | 1095 | 960 |
| 1077 | 1096 | 1112 | 1042 | 1158 | 1157 | 1022 |
| 1111 | 1158 | 1156 | 1060 | 1176 | 1169 | 1042 |
| 1157 | 1172 | 1184 | 1116 | 1215 | 1306 | 1073 |
| 1179 | 1348 | 1348 | 1160 | 1286 | 1340 | 1117 |
| 1348 | 1374 | 1373 | 1185 | 1347 | 1369 | 1154 |
| 1378 | 1449 (s) | 1449 (s) | 1217 | 1371 | 1445 (s) | 1181 |
| 1450 (s) | 1489 (s) | 1488 | 1245 | 1452 (s) | 1482 (s) | 1214 |
| 1457 (s) | 1586 | 1508 | 1313 | 1480 (s) | 1583 | 1302 |
| 1487 (s) | 1602 | 1583 | 1346 | 1577 | 1598 | 1341 |
| 1582 | 1758 | 1600 | 1373 | 1598 | 1685 | 1368 |
| 1600 | 1783 | 1747 | 1456 (s) | 1700 | 1762 | 1412 |
| 1750 | 1818 | 1800 | 1520 (s) | 1730 | 1783 | 1445 (s) |
| 1815 | 1884 | 1874 | 1577 | 1803 | 1870 | 1499 (s) |
| 1880 | 1946 | 1898 | 1618 | 1838 | 1941 | 1576 |
| 1920 | 2862 | 1941 | 1795 | 1880 | 2870 | 1604 |
| 1950 | 2933 (s) | 2845 (s) | 1898 | 1913 | 2940 (s) | 1650 |
| 2875 (s) | 3022 (s) | 2922 (s) | 2872 | 1946 | 3020 (s) | 1750 |
| 2920 (s) |  | 3020 | 2936 (s) | 2866 |  | 1798 |
| 3035 (s) |  |  | 3010 | 2945 (s) |  | 1900 |
| 3080 |  |  |  | 3012 |  | 2866 |
|  |  |  |  | 3060 |  | 2945 (s) |
|  |  |  |  |  |  | 3000 |

[a] Absorption bands denoted with (s) correspond to a transmittance lower than 30%, when the pure compound is examined in a cell of 0.025-mm. width; 50% solutions of the compounds in carbon tetrachloride and cells of 0.094-mm. width were used in examining the 1650–2000-cm$^{-1}$ (5–6 $\mu$) region.

*p*-ethylphenylpropane was prepared similarly through the Grignard reaction of $\beta$-*p*-tolylethyl bromide with *p*-ethylbenzaldehyde. The synthesis and physical properties of the intermediate diarylpropanols are summarized in Table IV. The properties of the intermediate olefins as well as those of the final products are given in Table V. Data on the infrared spectra of the diarylpropanes are given in Table VII.

The ditolylbutanes (Table VI) were prepared by the Claisen-Schmidt condensation[8] of *o*-, *m*-, and *p*-methylacetophenone, respectively, followed by hydrogenation of the resulting dimethyldypnones at 240–250° and a hydrogen pressure of 125–130 atm. in the presence of copper chromite catalyst. The methylacetophenones were prepared by oxidation of the corresponding tolylmethylcarbinols (Table II) with sodium dichromate in glacial acetic acid. The preparation and properties of the ditolylbutanes are summmarized in Table VI. The infrared spectra of the compounds are given in Table VII.

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