1404

the conformation having the less polarized carbonyl group.^{2,3}

EXPERIMENTAL

a-Cyclohexyl-p-phenylacetophenone (VIII). Over a period of 20 min. at room temperature 2.2 g. (0.017 mole) of aluminum chloride was added with stirring to a mixture of 2.2 g. (0.014 mole) of cyclohexylacetyl chloride⁸ and 2.2 g. (0.014 mole) of biphenyl dissolved in 10 ml. of methylene chloride. After standing for 1 hr. at room temperature the reaction mixture was poured into ice cold dilute hydrochloric acid and extracted with ether. After the ether layer was washed with water, dried over anhydrous sodium sulfate and concentrated, the crude ketone dissolved in benzene was passed through an alumina column. Concentration of the eluates followed by crystallization from methanol provided 1.1 g. (28%) of α -cyclohexyl-p-phenylacetophenone, m.p. 97-99°. Crystallization from methanol and then from ethyl acetate followed by sublimation under reduced pressure produced an analytical sample, m.p. 101.5-102.5°

Anal. Calcd. for C₂₀H₂₂O: C, 86.28; H, 7.97. Found: C, 86.39; H, 8.37.

Neopentyl p-biphenylyl ketone (X). Reaction of t-butylacetyl chloride⁹ with biphenyl was carried out in the manner

(8) E. Hope and W. H. Perkin, J. Chem. Soc., 1360 (1909).

(9) A. H. Homeyer, F. C. Whitmore, and V. H. Walling-

ford, J. Am. Chem. Soc., 55, 4209 (1933).

described for the ketone VIII providing, after chromatography and crystallization from methanol, a 29% yield of *neopentyl p-biphenylyl ketone*. An analytical sample, m.p. 88-89°, was prepared by recrystallization from methanol followed by sublimation under reduced pressure.

Anal. Calcd. for C₁₈H₂₀O: C, 85.67; H, 7.99. Found: C, 85.18; H, 8.01.

 α -Morpholino-p-phenylpropiophenone (XIV). A mixture of 0.30 g. (0.00104 mole) of α -bromo-p-phenylpropiophenone¹⁰ and 0.7 ml. of morpholine dissolved in 10 ml. of ether was allowed to stand at room temperature for 0.5 hr. The reaction mixture was washed with water and extracted with dilute hydrochloric acid. The acid extracts were washed with ether and neutralized with sodium carbonate. The crude amine was dissolved in ether, washed with water, and dried over anhyd. sodium sulfate. Crystallization from pentane-ether provided 0.15 g. (49%) of α -morpholino-pphenylpropiophenone, m.p. 90–91.5°.

Anal. Calcd. for C₁₉H₂₁NO₂: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.65; H, 7.29; N, 4.83.

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(10) See Ref. j, Table I.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Reaction of the Triphenylmethyl Radical with the Isomeric Xylenes

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It has been found that the triphenylmethyl radical attacks the *side chain* of all *three* of the isomeric xylenes. These findings are quite contrary to an early report [Ann., 401, 233 (1913)] which claims: (1) that only o- and p-xylene react with triphenylmethyl radicals and (2) that the products are tetraphenylmethane derivatives resulting from a *ring* attack by the radical.

Recently we disclosed that the triphenylmethyl radical, in the presence of benzoyl peroxide, attacked various aromatic substrates in a seemingly statistical fashion to form substituted tetraphenylmethanes.¹ In general, the solvent substrates we

$$(C_{b}H_{b})_{3}C + \langle -R \xrightarrow{benzoyl} R - \langle -R \rangle$$

 $C(C_{b}H_{b})_{3}C + \langle -R - R - \langle -R \rangle$

chose for this earlier study (e.g. chlorobenzene, benzotrifluoride, etc.) were such as to preclude any attack by the triphenylmethyl group on the side chain.

Of particular interest to us, was an early report by Wieland and Müller,² that, when the triphenylmethyl radical was refluxed with either o- or pxylene, ring substitution occurred, resulting in the formation of a xylyltriphenylmethane. The structure of neither xylene product was rigorously estab-



lished; the tetraphenylmethane formulations were based solely on elemental analyses, molecular weights, and a yellow coloration which each compound produced with dichromate. Particularly puzzling was the report² that *m*-xylene failed to react like the *ortho* and *para* isomers. From the orange-yellow oil which was formed in the *m*xylene reaction, only *p*-benzhydryltetraphenylmethane could be isolated. Since this material had been shown previously to result from an irreversible dimerization of triphenylmethyl radicals,³ it was concluded that the *m*-xylene had not entered into the reaction.

In order to resolve this anomalous situation, wherein only two of the three xylene isomers

(3) F. Ullmann and W. Borsum, Ber., 35, 2877 (1902).

⁽¹⁾ R. A. Benkeser and W. Schroeder, J. Am. Chem. Soc., 80, 3314 (1958).

⁽²⁾ H. Wieland and C. Müller, Ann., 401, 233 (1913).

supposedly react with triphenylmethyl radicals, it was decided to repeat the reaction with all three xylene isomers, and to characterize the products by comparing their properties with samples made by independent methods.

Unlike the earlier report, we have found that all three xylenes react with the triphenylmethyl radical in a similar fashion. Unfortunately the tenuous characterization of the earlier workers led them into an additional error, since we have found, that, in every case, the triphenylmethyl radicals attack *the side chain* of the xylenes rather than the *ring* as was originally claimed. As shown

in Equation 2, in every case, the product of the reaction was a tolyltriphenylethane rather than a xylyltriphenylmethane (Equation 1).

The structure of our products was rigorously established by an independent synthesis. We found that a good yield of the tolyltriphenylethanes could be obtained by treating the isomeric xylyl chlorides with triphenylmethylsodium, in liquid ammonia. In every case, the products obtained by

$$\underbrace{\bigvee}_{CH_2} CH_2Cl \xrightarrow{(C_6H_5)_2CNa}_{liq.NH_3}} \underbrace{\bigvee}_{CH_2} CH_2(C_6H_5)_3 \quad (3)$$

Reaction 3 agreed exactly in physical properties (melting point, infrared spectrum) with those obtained from Reaction 2. It was clear, that in the case of o- and p-xylene, we were dealing with the same materials which were isolated by the previous workers, since the melting points and general properties of our products agreed well with theirs.

We desired to gain some assurance that the syntheses we employed for our authentic samples (Equation 3) were valid and had not resulted in any rearrangements. Toward this end, we treated benzyl chloride with triphenylmethylsodium in liquid ammonia and isolated *unsym*-tetraphenylethane in good yield. It was clear from the melting

$$\underbrace{ \begin{array}{c} \\ \\ \end{array} \\ - CH_2Cl \begin{array}{c} (C_0H_0)_3CN_8 \\ \hline \\ liq. NH_3 \end{array} } \underbrace{ \begin{array}{c} \\ \\ \end{array} \\ - CH_2(C_0H_5)_3 \end{array} (4)$$

point of this product (144°) that it could not be any of the tolyltriphenylmethanes. All three of the latter isomers had been prepared in our laboratory previously,⁴ and melted at widely different temperatures from the material we obtained from Reaction 4. In addition we found that the *unsym*tetraphenylethane was also formed when toluene was refluxed with triphenylmethyl radicals. Thus, this reaction parallels that which we observed with the xylenes.

(4) R. B. Gosnell, Ph.D. Thesis, Purdue University, 1957.

In summary, the present work tends to unify the commonly accepted picture of free radicals having a preference for *alpha* hydrogen substitution. It leaves unanswered the reason for ring attack in the peroxide-catalyzed tritylation reaction⁵⁻⁷ of aromatic hydrocarbons like toluene. It should be borne in mind, however, that no effort has yet been made to discover whether the peroxide-catalyzed reaction also result in some side chain products. Such a study might well be profitably undertaken.

EXPERIMENTAL

The reactions of the triphenylmethyl radical with the three isomeric xylenes were all carried out in a similar fashion. The direction given below for the o-xylene reaction can be taken as typical of all. Table I lists the physical properties of the various tetraphenylethanes which were obtained.

Reaction of o-xylene with triphenylmethyl. A three-necked flask, fitted with a reflux condenser, mechanical stirrer, and a tube for the addition of solids was charged with 22.0 g. (0.079 mole) of triphenylchloromethane⁸ (m.p. 111-113°) and 200 ml. of o-xylene (Eastman). The system was purged of air by a stream of nitrogen, and a nitrogen atmosphere was maintained throughout. The solution was stirred and refluxed and then 20 g. (0.34 g. atom) of zinc dust was added na the addition tube. The solution turned red in color as the metal was added; but became light yellow as the reaction progressed. After 6 hr., it was filtered to remove the excess zinc and zinc chloride. The xylene was removed under reduced pressure leaving a thick yellow oil. This oil was distilled, and 8.2 g. (85%) of a solid identified as triphenylmethane was collected, boiling at 132°/0.1 mm. It was necessary to wrap the Vigreux column with heating tape, and to heat the adapter and receiving flask with infrared lamps to prevent clogging of the apparatus during this distillation. The dark, solid residue in the distillation flask was dissolved in a few milliliters of benzene, and placed on a 12-inch alumina-packed chromatogram column. Benzene was used as both the developer and eluant. A red and a yellow solution were obtained upon elution. From the latter, after two crystallizations from a benzene-ethanol solution, 9.05 g. (65%) of 1,1,1-triphenyl-2-(o-tolyl)ethane was obtained as a white crystalline solid (m.p. 170-171°). The red solution yielded a small amount of a red oil which resisted solidification.

Preparation of authentic samples. Authentic samples of all the compounds listed in Table I were prepared by the reactions depicted in Equations 3 and 4. Since the details of these preparations were all similar, the directions given below for the preparation of 1,1,1-triphenyl-2(o-tolyl)ethane can be taken as typical of all.

1,1,1-Triphenyl-2(o-tolyl)ethane. A three-necked flask was fitted with a Dry Ice condenser, mechanical stirrer, and an ammonia inlet tube. About 200 ml. of liquid ammonia was introduced into the flask, followed by 0.92 g. (0.04 g.-atom) of sodium and a crystal of ferric nitrate. The solution first turned blue in color and then a dark gray. Then 9.48 g. (0.04 mole) of triphenylmethane in 200 ml. of ether was added slowly to the sodium amide suspension via a dropping funnel. An immediate blood-red color developed.

(5) S. S. Medwedew and E. N. Alexejewa, Ber., 65, 137 (1932).

(6) H. Wieland, T. Ploetz, and H. Indest, Ann., 532, 179 (1937).

(7) H. Wieland and A. Meyer, Ann., 551, 249 (1942).

(8) C. R. Hauser and B. E. Hudson, Jr., Org. Syntheses, Coll. Vol. III, 842 (1955).

THISICAL FROPERTIES OF THE TETRAPHENYLETHANES						
Compound	M.P.	Yield, %	Calcd.		Found	
			C	H	C	Н
1,1,1,2-Tetraphenylethane	143-144°	$74 (78)^a$	See footnote ^b			
1,1,1-Triphenyl-2(o-tolyl)ethane	170–171°	$65 (80)^a$	93.05	6.95	93.04	7.00
1,1,1-Triphenyl-2(m-tolyl)ethane	94-95°	70 (73) ^a	93.05	6.95	92.85	6.94
1,1,1-Triphenyl-2(p-tolyl)ethane	159–160°	$78(90)^a$	93.05	6.95	93.13	7.09

TABLE I

^a The value in parenthesis is the yield obtained in the preparation of the authentic samples. ^b See C. B. Wooster and N. W. Mitchell, J. Am. Chem. Soc., 52, 688 (1930) where this compound is reported.

After the solution was stirred for 0.5 hr., an ethereal solution containing 5.6 g. (0.04 mole) of *o*-xylyl chloride⁹ was added. The red color of the solution disappeared after the addition of the chloride was complete. The ammonia was evaporated, and 10 ml. of water was then added to the ether solution. The ether layer was separated, dried, and the solvent removed. The resulting white crystalline solid,

(9) M. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 2142 (1939).

(10.9 g.; 80%) after crystallization from a benzene-absolute ethanol solution melted at 170-171°. A mixed melting point and infrared spectrum showed this material was identical with that isolated from the reaction of *o*-xylene with triphenylmethyl.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. XXIV. The Reimer-Tiemann Reaction with Two p-Substituted Phenols¹

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The Reimer-Tiemann reactions of *p*-cresol and *p*-hydroxybenzaldehyde have been studied. It is found that a *p*-metnyl group increases and a *p*-formyl group decreases the rate of attack of dichloromethylene on the carbon atom *ortho* to the $-O^-$ group. Attack at the *para* position of the *p*-cresolate anion is slower than at the *para* position of the phenoxide ion, perhaps because of steric factors.

In a previous paper evidence has been summarized that the Reimer-Tiemann reaction involves the combination of the phenoxide ion with a dichloromethylene molecule generated by the action of base on chloroform.² The relative rates of attack of dichloromethylene on the three centers of nucleophilicity of the phenoxide ion, namely the oxygen atom and the *ortho* and *para* carbon atoms, were also determined. In the present investigation we have studied two *p*-substituted phenols, *p*-hydroxybenzaldehyde and *p*-cresol, one with an electron-withdrawing substituent and the other with an electron-donating substituent.

RESULTS AND DISCUSSION

If it is assumed that, in the relatively dilute solutions with which we have worked, the attack of dichloromethylene on the *ortho* and *para* carbons and the oxygen atom of the *p*-cresolate anion leads inevitably to the 2-formyl-4-methylphenoxide ion, 4-dichloromethyl-4-methylcyclohexa-2,5-dienone and unchanged *p*-cresolate anion, respectively, the reaction paths open to dichloromethylene may be written:

$$CCl_{2} + p-RC_{6}H_{4}O^{-} \xrightarrow{k_{0}} \overset{R}{\longrightarrow} \overset{R}{\longrightarrow} \overset{O^{\ominus}}{\longrightarrow} \overset{CHO}{\longrightarrow} CHO$$

$$CCl_{2} + p-RC_{6}H_{4}O^{-} \xrightarrow{k_{0z}} p-RC_{6}H_{4}O^{-} + CO \text{ or } HCO_{2}^{-}$$

$$CCl_{2} + H_{2}O \xrightarrow{k_{0z}} CO \text{ or } HCO_{2}^{-}$$

$$CCl_{2} + OH^{-} \xrightarrow{k_{0z}} CO \text{ or } HCO_{2}^{-}$$

where $R = CH_3$. A derivation like that used previously² shows

$$\frac{1}{f_o} = 1 + \frac{(k_p/k_w) + (k_{oz}/k_w)}{(k_o/k_w)} + (k_w/k_o) \frac{[\text{H}_2\text{O}] + (k_h/k_w)[\text{O}\text{H}^-]}{[\text{RC}_6\text{H}_4\text{O}^-]}$$
(1)

⁽¹⁾ For part XXIII in this series see J. Hine and J. J. Porter, J. Am. Chem. Soc., 82, 6178 (1960).

⁽²⁾ J. Hine and J. M. van der Veen, J. Am. Chem. Soc., 81, 6446 (1959). For a recent review on the Reimer-Tiemann reaction see H. Wynberg, Chem. Revs., 60, 169 (1960).