3α,16-Diacetoxy-15-methyl-5β-androstane-11,17-dione (XXI).—A solution of the enol acetate XX (250 mg.) in 12 ml. of ethyl acetate was hydrogenated at 25° and 1 atm. over 150 mg. of 10% palladium on charcoal catalyst. Uptake of one molar equivalent of hydrogen was complete in 2 hr. The mixture was filtered, the filtrate taken to dryness, and the residue crystallized from ether–petroleum ether to give the saturated diacetate XXI, m.p. 176–178°; $\lambda_{\max}^{\text{chf}}$ 5.70, 5.78, 5.83 μ; positive tetrazolium test.

Anal. Calcd. for $C_{24}H_{34}O_6$: C, 68.87; H, 8.19. Found: C, 68.72; H, 8.38.

3α-Hydroxy-5β-androstane-11,16,17-trione (XXII).—A stirred mixture of ketol VIIa (150 mg.), cupric acetate monohydrate (440 mg.) in 20 ml. of methanol was refluxed for 3 hr., cooled, and the methanol removed under vacuum. Dilute hydrochloric acid was added and the mixture extracted with 1:1 benzene–ether. The latter extract was washed with dilute sodium bicarbonate and 1 *N* sodium hydroxide. The sodium hydroxide extract was washed with 1:1 benzene–ether, acidified with dilute hydrochloric acid, and extracted with 1:1 benzene–ether. The latter extract was washed with saturated salt solution, dried over magnesium sulfate and concentrated to dryness to give the base soluble 11,16,17-trione XXII, which on trituration with ether was obtained as an amorphous yellow solid, 60 mg., m.p. 127–130°; ultraviolet in methanol, no maximum; in methanol containing 0.1% sodium hydroxide, $\lambda_{\max}$ 300 mμ (1500); $\lambda_{\max}^{\text{chf}}$ 2.75, 2.8–2.9, 5.72, 5.85 μ; negative tetrazolium test.

An analytically pure specimen was not obtained.

Acetylation of XXII (20 mg.) in 0.5 ml. of acetic anhydride and 1 ml. of pyridine overnight at room temperature gave the noncrystalline **3α,16-diacetoxy-5β-androst-15-ene-11,17-dione** (XXIII); $\lambda_{\max}^{\text{MeOH}}$ 236 mμ (5000).

Conversion of 3α,17β-Diacetoxy-5β-androstane-11,16-dione (VIIb) to 40:60 Mixture of 3α-Acetoxy-5β-androstane-11,17-dione (XI) and 3α-Acetoxy-5β-androstane-11,16-dione (Xa).—The ketol acetate VIIb (360 mg.) in 10 ml. of dimethylformamide was treated with 70 mg. of sodium borohydride in 3.5 ml. of water as described above for the reduction of VIIa. The amorphous product [XXIV and XXV (350 mg.) negative tetrazolium test; $\lambda_{\max}^{\text{chf}}$ 2.75, 5.75, 5.84 μ] in 2 ml. of pyridine at 0°] was treated with 0.3 ml. of methanesulfonyl chloride for 17 hr. Iced water was added and the mixture extracted with chloroform. The latter extract was washed successively with dilute hydrochloric acid, dilute aqueous potassium bicarbonate, saturated salt solution, dried over magnesium sulfate and concentrated to dryness under vacuum to give an amorphous mixture of 16,17-acetate–mesylates XXVI and XXVII (430 mg.) as evidenced by paper chromatography [two spots $R_f \sim 0.3$ and ~ 0.7; benzene–cyclohexane (1:1)–formamide system]. The acetate–mesylate mixture in 20 ml. of ethanol and 20 ml. of 1 *N* aqueous potassium hydroxide was refluxed for 1 hr. The ethanol was removed under vacuum, water added, and the mixture extracted with chloroform. The chloroform extract was washed with saturated salt solution, dried over magnesium sulfate, and concentrated to dryness. The residue (340 mg.) crystallized slowly from ether to yield 14 mg. of **3α-hydroxy-5β-androstane-11,17-dione,** m.p. 182–187°, identical infrared spectrum and undepressed mixture melting point with authentic sample, m.p. 186–189°. Remainder of product was acetylated (2 ml. of pyridine, 1 ml. of acetic anhydride at 25° overnight). Paper chromatography (ligroin–formamide) along with samples of the individual compounds, showed the acetylation product to consist of a nearly equivalent mixture of 3α-acetoxy-5β-androstane-11,17-dione (XI) and 3α-acetoxy-5β-androstane-11,16-dione (Xa). Infrared spectroscopy *vs.* known mixtures of XI and Xa indicated the mixture to consist of 40% XI and 60% Xa.

In a second run the sodium borohydride reduction product (350 mg.) of VIIb was in part acetylated to give in good yield the triacetate XVIb, m.p. 204–206°, and in part saponified (dilute aqueous methanolic sodium hydroxide, 25° for 40 min.) to give a good yield of the triol XVIa, m.p. 265–270°, indicating the reduction product to be a clean mixture of 16β,17β-glycol monoacetates.

Acknowledgment.—The authors are grateful to Dr. N. R. Trenner and B. Arison for n.m.r. determinations, to R. W. Walker for infrared spectra, to A. Kalowsky for ultraviolet spectra, and to R. N. Boos and associates for microanalyses.

Synthesis of 2,2-Diarylpropanes by Hydride Transfer[1]

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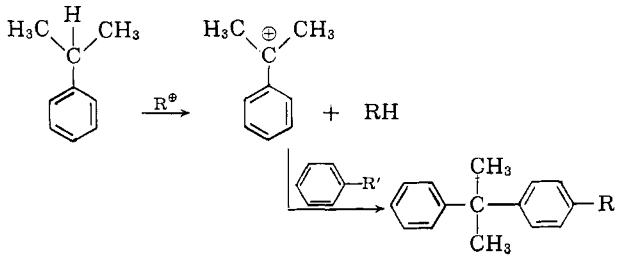
2,2-Diarylpropanes were prepared by hydride transfer reactions of 2-arylpropanes, arenes, and hydride ion acceptors. Hydride ion transfer and alkylation by the cumyl carbonium ion compete with alkylation by the hydride ion acceptors, isomerization, and transalkylation. Conversions of 2-arylpropanes to 2,2-diarylpropanes were surprisingly good in view of all these competing reactions.

Introduction

2,2-Diarylpropanes were needed in this laboratory as intermediates in oxidation studies. This led to a study of their synthesis as they are difficult to prepare by known methods. Most methods depend on alkylation of arenes with a cumyl cation formed from such reagents as α-methylstyrenes,[2] 2-chloro-2-phenylpropanes,[3] or 2-phenylpropanol-2.[4] Unfortunately these reagents readily dimerize to indanes and, except for one reaction,[3] give only a small amount of the alkylation products. Furthermore, ring-substituted α-methyl styrenes, 2-phenyl-2-chloropropanes, or 2-phenyl-2-propanols are not readily available, whereas a large number of ring-substituted cumenes can be easily prepared.

We wished to form the cumyl cations directly from 2-arylpropanes by hydride transfer to another carbonium ion in the following way.



The formation of many types of hydrocarbons by hydride transfer reactions has been reported, such as alkylation of arenes with paraffins,[5] formation of diaryl-

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[1] Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

[2] R. R. Hiatt, U. S. Patent 2,719,871 (October 4, 1955).

[3] A. T. Coscia, J. T. Penniston, and J. C. Petropoulos, *J. Org. Chem.*, **26**, 1398 (1961).

[4] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, **73**, 4766 (1951).

[5] J. T. Kelly and R. J. Lee, *Ind. Eng. Chem.*, **47**, 757 (1955).

TABLE I

REACTION OF CUMENE AND BENZENE[a]

Reactants				Products: 2,2-Diphenylpropane			Products: Other	
Cumene, moles	Benzene, moles	Hydride ion acceptors	Moles	Moles	Mole %[b]	Mole % on recovered cumene		
0.5	2.5	*t*-Butyl chloride	0.5	0.0535	10.7	28.0	*t*-Butylbenzene	0.3 mole
1.0	1.0	*t*-Butyl chloride	.5	.0590	12.0	12.5	*t*-Butylbenzene	.26 mole
0.5	2.5	*t*-Butyl chloride	1.0	.0865	17.0	37.0	*t*-Butylbenzene	.91 mole
.5	2.5	*t*-Butyl chloride	2.0	.117	24.0	34.0	*t*-Butylbenzene	1.02 moles
.5	2.5	*t*-Butyl chloride[c]	0.5	.059	12.0	35.0	*t*-Butylbenzene	0.24 mole
.5	2.5	*t*-Butyl chloride[d]	.5	.020	4.0	11.0		
.5	2.5	*t*-Butyl chloride[e]	.5	.040	8.0	18.5		
.5	2.5	*t*-Butyl chloride[f]	.5	.039	7.8	17.5	*t*-Butylbenzene	0.16 mole
.5	2.5	*n*-Propyl chloride	.5	None			Propylbenzene	.03 mole
.5	2.5	Benzhydryl chloride	.5	0.107	21.4	37.0	Diphenylmethane	.145 mole[g]
							Triphenylmethane	.28 mole
.5	2.5	Benzhydryl chloride[f]	.5	.0873	17.4	29.0	Diphenylmethane	.18 mole
.25	1.3	Trityl chloride	.25	None				
.5	2.5	2-Methylbutene-2[h]	.5	0.030	6.0	22.2		

[a] Conditions: except as noted all reactions at 20–25° using 0.05 mole of aluminum chloride as catalyst. [b] Mole % yield based on cumene. [c] Using 1.0 mole of cyclohexane as a diluent. [d] Using 0.05 mole of anhyd. ferric chloride as catalyst. [e] At 0°. [f] At 55°. [g] 29% of theory for hydride transfer. [h] With a slow stream of dry hydrogen chloride gas.

TABLE II

REACTIONS OF ARENES AND 2-ARYLPROPANES[a]

Reactants				Products					
2-Aryl-propane	Moles	Arene	Moles	2,2-Diarylpropane	Moles	Mole %[b]	Mole % on recovered 2-aryl-propane	Other products	
p-Cymene	0.5	Toluene	2.5	2,2-Ditolylpropanes[c]	0.038	7.6	29	*t*-Butyltoluene	0.375 mole
p-Cymene	0.5[d]	Toluene	2.5[d]	2,2-Ditolylpropanes	.065	13.0	27	Diphenylmethane	.20 mole
								Triphenylmethane	.2 mole
Cumene	0.5	Toluene	2.5	2,2-Diphenylpropane	.004	0.8	[e]	*t*-Butyltoluene	.26 mole
				2-Phenyl-2-tolylpropane	.014	2.8	[e]	Cymenes	.25 mole
				2,2-Ditolylpropanes	.047	9.4	[e]		
p-Cymene	0.5	Benzene	2.5	2,2-Diphenylpropane	.036	7.2	17.0	*t*-Butylbenzene	.3 mole
				2-Phenyl-2-tolylpropane	.0095	1.9	4.5		
				2,2-Ditolylpropanes	.0155	3.1	7.4		

[a] Condition: except as noted all runs at 20–25° using 0.05 mole of aluminum chloride as catalyst and 0.5 mole of *t*-butyl chloride. [b] Based on 2-arylpropane. [c] 35% *p,p'*; 28% *p,m'*; 37% *m,m'*. See Experimental. [d] Using 0.5 mole of benzhydryl chloride instead of *t*-butyl chloride. [e] Most of the unchanged cumene was transalkylated to cymene isomers.

methanes,[6–8] formation of indans[9] and 1,1-diarylethanes,[9,10] and alkylation of arenes with cycloalkanes.[11] The preparation of 2,2-diarylpropanes by hydride transfer has been reported in the patent literature[12]; however, only one reaction, the formation of 2,2-diphenylpropane was actually described. The object of the present work, then, was to make a more thorough study of the preparation of 2,2-diarylpropanes by hydride transfer reactions involving 2-arylpropanes and arenes.

Discussion

Tables I and II summarize the reactions for the preparation of 2,2-diarylpropanes by hydride transfer. While we obtained low yields of 2,2-diarylpropanes with ferric chloride, aluminum chloride was a much more effective catalyst, and was used in most reactions. The effect of changing other reaction variables for the preparation of 2,2-diphenylpropane from benzene and cumene are summarized in Table I. Optimum conditions so far determined are equimolar amounts of cumene and hydride ion acceptor in a five-mole excess of benzene at 20–25°. Conversions to 2,2-diphenylpropane were increased by increasing the *t*-butyl chloride; however, a fourfold increase in *t*-butyl chloride gives only a twofold increase in 2,2-diphenylpropane, and the yield based on recovered cumene is approximately the same as reactions using equimolar amounts of *t*-butyl chloride and cumene. The best hydride ion acceptor was benzhydryl chloride. The second hydride transfer product, diphenylmethane, was also isolated in this reaction.

Reaction of toluene and *p*-cymene (Table II) gave the expected 2,2-ditolylpropane isomers. The yield of these ditolylpropanes was slightly lower than the yield of 2,2-diphenylpropane from the benzene–cumene reaction; however, the yield of 2,2-diarylpropanes from either reaction is about the same when based on reacted 2-arylpropane. Use of benzhydryl chloride instead of *t*-butyl chloride as the hydride ion acceptor also increased the conversion to 2,2-ditolylpropanes.

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(6) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **81**, 2718 (1959).

(7) B. S. Friedman, F. L. Morritz, C. J. Morrissey, and R. Konos, *ibid.*, **80**, 5867 (1958).

(8) S. P. Malchick and R. B. Hannan, *ibid.*, **81**, 2219 (1959).

(9) H. Pines and J. T. Arrigo, *ibid.*, **80**, 4369 (1958).

(10) A. Schneider, U. S. Patent 2,742,516 (April 17, 1956).

(11) L. Schmerling, R. W. Welch, and J. P. Luvisi, *J. Am. Chem. Soc.*, **79**, 2636 (1957).

(12) A. Schneider, U. S. Patent 2,742,512 (April 17, 1956).

Reaction of cumene with toluene and *p*-cymene with benzene are summarized in Table II. Both reactions should yield 2-phenyl-2-tolylpropane. This product was found but was not the major product in either reaction. The *p*-cymene–benzene reaction gave mostly 2,2-diphenylpropane, whereas the cumene–toluene reaction gave more of the 2,2-ditolylpropanes. These unexpected products appear to arise mainly by transalkylation of the expected 2-phenyl-2-tolylpropanes in one case with benzene to yield the 2,2-diphenylpropane, or with the excess toluene in the toluene–cumene reaction to yield ditolylpropanes. Most of the unchanged cumene in the latter reaction also was converted to cymene by transalkylation with toluene.

However, the total yields of 2,2-diarylpropanes from both the toluene–cumene and *p*-cymene–benzene reactions were approximately the same as the yield of 2,2-diarylpropanes from the benzene–cumene and *p*-cymene–toluene reactions. The yields of 2,2-diarylpropanes from all the reactions studied are the same when based on changed cumene or cymene.

Steric hindrance to normal alkylation was the main driving force for many of the hydride transfer reactions previously reported.[4,11] In our study, steric hindrance is not so important, as it is as easy for the hydride ion acceptor to alkylate benzene and toluene as to undergo hydride transfer with cumene or cymene. The main driving force for the reactions described in Tables I and II may be that with the *t*-butyl and benzhydryl cations the main alkylation reaction is the most readily reversible; therefore, equilibria favorable for at least some hydride transfer are established.

Concerning the actual hydride transfer step apparently the tertiary hydrogen of the cumene or cymene is extracted exclusively, for no diarylmethanes or 1,2-diarylpropanes were found. No indanes were found.

Conclusion

In the preparation of 2,2-diarylpropanes by hydride transfer reactions, the number and complexity of possible over-all alkylation reactions is great and the driving force for the desired reactions is small. In addition, 2,2-diarylpropanes containing aryl methyl groups undergo isomerization and transalkylation, so that yields of pure single isomer are quite low. In light of this situation, it is surprising that diarylpropanes are actually obtained, albeit in rather low yields. However, the reaction gives sufficiently high yields to be of preparative value for 2,2-diphenylpropane. This compound as well as certain mixtures of the tolylpropanes can be obtained in 20–25% yields when using benzhydryl chloride as the hydride ion acceptor.

Experimental

Alkylation of Benzene with Cumene.—A typical hydride transfer reaction involving benzene and cumene was run by adding 46 g. (0.5 mole) of *t*-butyl chloride dropwise over 0.5 hr. at 22° to a rapidly stirred mixture of 195 g. (2.5 moles) benzene, 60.0 g. (0.5 mole) cumene, and 6.5 g. (0.05 mole) of anhydrous aluminum chloride. The mixture was stirred another hour after addition and hydrolyzed with water. The hydrocarbon mixture was water-washed, dried over sodium sulfate, then fractionated through a 10-plate Oldershaw column. Fraction 1 was taken from 75–230° at 1.0 atm. (wt. 91.5 g.) and fraction 2 was the remaining undistilled pot residue (wt. 12.5 g.). Both fractions were analyzed directly by gas chromatography.

Fraction 1 contained seven components; only three of the most interest (comprising 94% of the fraction) were identified. These components and their concentration as calculated from the gas chromatogram were: unchanged cumene 37.0 g. (0.31 mole), *t*-butylbenzene 40.0 g. (0.3 mole, 60 mole % of theory for simple *t*-butylation), and *t*-butylcumene 9.0 g. (0.05 mole). The other components, although not separated and identified, may be the various isomerization, de-alkylation, and/or disproportionation products expected by reaction of alkylarenes with aluminum chloride.

Fraction 2 was 86% of the desired 2,2-diphenylpropane. The remaining 14% was composed of four higher boiling unidentified components. The yield of 2,2-diphenylpropane was 10.5 g. (0.0535 mole, 10.7 mole % based on cumene). The yield based on recovered cumene (0.31 mole) was 28 mole %. The identity of this product was established by comparison of physical properties, and infrared and mass spectra with authentic 2,2-diphenylpropane. Authentic 2,2-diphenylpropane was prepared in 30% yield from α-methylstyrene and benzene by a modification of the method reported for the preparation of 2,2-ditolylpropane[3] and had m.p. 28–29°, b.p .74–76° (0.15 mm.) [280° (1 atm.)] and $n^{20}{}_{\mathrm{D}}$ 1.5705. 2,2-Diphenylpropane has been synthesized by two different methods[4,13] with reported physical properties identical to the preceding values.

Alkylation of Toluene with *p*-Cymene.—Reaction of 230 g. (2.5 moles) of toluene, 67.0 g. (0.5 mole) *p*-cymene, 46 g. (0.5 mole) of *t*-butyl chloride, and 0.05 mole of aluminum chloride at 20° gave six simple alkyl–arene components boiling at 107–240° atmospheric pressure. Among these components were 49.5 g. (0.37 mole) of cymene isomers and 55.5 g. (0.375 mole) of *t*-butyltoluene isomers. The next highest boiling product came over at 300° and was the first of the desired hydride transfer products. The following high boiling hydride transfer products were found by gas chromatography (250°, apiezon L columns).

Component	Estimated b.p. at 1 atm., °C.	%	Calcd. wt., g.
m,m'-Ditolylpropane	300	21	2.4
m,p'-Ditolylpropane	310	27	3.1
p,p'-Ditolylpropane	320	26	3.0
Unknown (4 components)	325–350	26	3.0

Fractional distillation through a 100-plate spinning band column gave only gradual enrichment of the components but not complete separation. Pure components were obtained directly from the gas chromatograph by trap-out procedures. The total yield of the three ditolylpropane isomers was 8.5 g. (0.038 mole, 7.6 mole % based on cymene). The yield was 29.3% based on recovered cymene.

The *p,p'*-ditolylpropane was identified by comparison of its physical properties and infrared and mass spectra with authentic *p,p'*-ditolylpropane, which was obtained by low temperature crystallization of mixed ditolylpropane isomers prepared from toluene, 2,2-dichloropropane, and aluminum chloride as previously described.[14] The pure *p,p'*-ditolylpropane had m.p. 76–78°. The reported m.p. is 78–80°.[1,2] Oxidation[15] of this pure *p,p'*-isomer gave a 90 mole % yield of 2,2-di(*p*-carboxyphenyl)propane, neutral equivalent, 142 (calcd., 142), melting at 313–314° (reported[3,14] 313–315°). The *m,m'*- and *m,p'*-ditolylpropane isomers are only tentative assignments of structure; no comparison was made with authentic materials. However, mass spectra show they are 2,2-ditolylpropane isomers and infrared analysis and method of formation strongly indicate the *m,m'*- and *m,p'*-isomers. These two isomers are also identical to the two isomers (in addition to the *p,p'*-ditolylpropane) produced by reaction of toluene and 2,2-dichloropropane described previously.

The highest boiling products (325–350°) from the hydride transfer reaction have not been identified. At least four components were obtained; however, mass spectra show none is a 2,2-ditolylpropane isomer.

Alkylation of Toluene with Cumene. A mixture of 230 g. (2.5 moles) of toluene, 60.0 g. (0.5 mole) of cumene, 46 g. (0.5 mole) of *t*-butyl chloride, and 6.5 g. (0.05 mole) of aluminum

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(13) R. Silva, *Bull. soc. chim. France*, (2) **34**, 674 (1880).

(14) C. E. Schweitzer, U. S. Patent 2,794,822 (June 4, 1957).

(15) A. Saffer and R. S. Barker, U. S. Patent 2,833,816 (May 6, 1958).

chloride was treated and the products were worked up in the same way as the p-cymene–toluene reaction. The low-boiling simple alkylarenes contained 7 g. (0.058 mole) of cumene, 47 g. (0.35 mole) of cymene isomers, and 38 g. (0.26 mole) of t-butyltoluene isomers. The following high boiling hydride transfer products were determined by gas chromatography and mass spectrometry. The total conversion to identified 2,2-diarylpropanes was 0.065 mole (13.0 mole % on cumene).

Component	Estimated b.p. at 1 atm., °C.	%	Calcd. wt., g.	Moles
2,2-Diphenylpropane	280	4.7	0.75	0.004
2-Phenyl-2-tolylpropane	290	18.8	2.9	.014
m,m'-Ditolylpropane	300	32.5	5.0	.022
m,p'-Ditolylpropane	310	25.5	3.9	.018
p,p'-Ditolylpropane	320	10.5	1.6	.007
Unknown	325–350	8.0	1.2	

Authentic 2-phenyl-2-tolylpropane was prepared in 75% yield from α-methylstyrene and toluene using a modification of the method reported for the preparation of 2,2-ditolylpropane.[3] It had b.p. 92–94° (0.15 mm.), n^{20}_D 1.5643.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.42; H, 8.58. Found: C, 91.02; H, 8.42.

Oxidation[15] gave fine white needles (from 1:1 ethanol–water) of 2-(p-carboxyphenyl)-2-phenylpropane, m.p. 147–148°, and neutral equivalent, 238 (calcd., 240).

Alkylation of Benzene with p-Cymene.—Benzene, 195 g. (2.5 moles), p-cymene 67 g. (0.5 mole), t-butyl chloride, 46 g. (0.5 mole), and aluminum chloride (0.05 mole) were treated and the products worked up as described. The lower boiling alkylarenes contained 34.5 g. (0.29 mole) of unchanged cymene and 40.0 g. (0.3 mole, 60 mole %) of t-butylbenzene. The following hydride transfer products were found by gas chromatography.

Components	Estimated b.p. at 1 atm., °C.	%	Calcd. wt., g.	Moles
2,2-Diphenylpropane	280	50.5	7.0	0.0360
2-Phenyl-2-tolylpropane	290	14.5	2.0	.0095
m,m'-Ditolylpropane	300	13.0	1.8	.0080
m,p'-Ditolylpropane	310	12.2	1.7	.0075
Unknown	330–350	9.8	1.2	

The total conversion to 2,2-diarylpropanes was 0.061 mole (12.2 mole % on cymene).

Polynuclear Aromatic Hydrocarbons. XI.[1] The Synthesis of Molecularly Overcrowded Benzo(c)phenanthrenes. I

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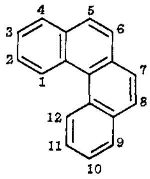
The reaction between β-methallylsuccinic anhydride and p-xylene has been examined as a means of obtaining molecularly overcrowded benzo(c)phenanthrenes. The synthesis of 1,4,5,5-tetramethyl-5,6-dihydrobenzo(c)phenanthrene (XXII) from these starting materials is described.

In an earlier communication,[4] the preparation of benzo(c)phenanthrene derivatives (I) from the Friedel–Crafts reaction products of β-methallylsuccinic anhydride (II) and benzene was outlined. In this paper, the feasibility of using p-xylene to prepare 1- and/or 12-substituted derivatives is discussed. The latter are of interest for resolution studies as well as for testing as carcinogens.



I

The starting material, β-methallylsuccinic anhydride (II), was prepared conveniently from maleic anhydride and isobutylene according to the method described by Alder and co-workers[5] and revised by Phillips and Johnson.[4] When the anhydride (II) was condensed with p-xylene in the presence of aluminum chloride, a mixture of three acids[6] (see Chart 1) and a hydrocarbon[7] was obtained. The tetralone acid (IV) usually crystallized from the acid mixture as the major product, while the other two acids (III and V) remained as an oil. However, these acids were separated easily by fractional distillation of their methyl esters. While the intramolecular acylation product (V) is of no use for the synthesis of benzo(c) phenanthrenes, III has all the carbons necessary to prepare 1,12-substituted derivatives of benzo(c)phenanthrene and IV provides a means of preparing either the 1-substituted or the 1,12-substituted derivatives.

As illustrated in Chart 1, catalytic reduction of IIIa afforded methyl α-(β-p-xylylethyl)-γ-methyl-γ-(p-xylyl)valerate (VIa), which in turn was saponified to the corresponding acid (VI). The same acid, VI, was prepared in 15% yield by condensation of p-xylene with α-(β-p-xylylethyl)-γ-methyl-γ-valerolactone (VIII), which in turn was obtained through catalytic reduction of the corresponding lactone (VII). The lactone (VII) was prepared by condensation of the anhydride (II) with p-xylene in the presence of antimony pentachloride. However, VII was obtained in a maximum yield of only 19% and consequently was a less convenient precursor to VI than was III.

Cyclization of VI with anhydrous hydrogen fluoride gave a mixture of tetralones (IX) which was subsequently reduced with lithium aluminum hydride to give a mixture of tetralols. Treatment of the tetralol

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[1] Paper X, D. D. Phillips and D. N. Chatterjee, *J. Am. Chem. Soc.*, **80**, 4364 (1958).

[2] To whom inquiries regarding this article should be sent; Shell Development Co., Modesto, Calif.

[3] From the thesis submitted by M. F. Bruno to Cornell University in partial fulfillment of the requirements for the Ph.D. degree, September, 1959.

[4] D. D. Phillips and A. W. Johnson, *J. Am. Chem. Soc.*, **77**, 5977 (1955).

[5] K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76B**, 47 (1943).

[6] A. W. Johnson, thesis, Doctor of Philosophy, Cornell University, 1957.

[7] Almost invariably, hydrocarbons were obtained in the neutral fraction when catalysts such as aluminum chloride or antimony pentachloride were used in the presence of benzene or p-xylene. These hydrocarbons will be the subject of a forthcoming publication.