TABLE I

2,6-BISHYDROXYMETHYL DERIVATIVES

p-Substituent	Solvent of crystn.	M.p., °C.	Formula	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
2-Cyclopentenyl	Toluene	106	$C_{13}H_{16}O_3$	70.89	71.18	7.32	7.56
Crotyl	Aq. methanol	77–78	$C_{12}H_{16}O_3$	69.20	68.84	7.93	7.57
3-Methylcrotyl	Aq. methanol	110–111	$C_{13}H_{18}O_3$	70.24	70.44	8.16	8.27
Isoamyl	Aq. methanol	73–74	$C_{13}H_{20}O_3$	69.61	69.85	8.99	9.13
Crotyl allyl ether[a]	Toluene–heptane	80–81	$C_{15}H_{20}O_3$	72.55	72.59	8.12	8.27

[a] Made by the reaction of the sodium salt of 2,6-bishydroxymethyl-4-crotylphenol with allyl chloride.

phenol (II), m.p. 111–112°, which was characterized by cyclization to I;[2] $\lambda_{\max}$[15] 274 mμ (log ϵ 3.35), 279 mμ (infl. log ϵ 3.32); $\lambda_{\min}$ 242.5 mμ (log ϵ 3.20).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.06; H, 9.09.

Hydrogenation of V (Adams platinum oxide catalyst, methanol, 80°) quantitatively yielded *p*-isoamylphenol (XII),[16] b.p. 103–105° (1 mm.), $n^{25}\mathrm{D}$ 1.514, which crystallized in the ice-box, m.p. 27–29°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.99; H, 10.19.

Similar hydrogenation of IV yielded *o*-**isoamylphenol** (**XI**), b.p. 85–86° (0.5 mm.), $n^{25}\mathrm{D}$ 1.510, which crystallized in the ice-box, m.p. 12–14°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.03; H, 10.10.

The phenol XI was characterized by a *p*-nitrophenylurethan which was crystallized from a mixture of heptane and toluene and melts at 90–92°.

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: N, 8.53. Found: N, 8.83.

Hydration of V.—Stirring a heptane solution of V with 80% aqueous phosphoric acid at 25° for 4 hours gave a 90% yield of VIII.

Dehydration of VIII.—A mixture of 20 g. of VIII, 400 cc. of xylene and 1 cc. of 85% phosphoric acid was refluxed with water take-off under nitrogen for one hour. The mixture was washed with water and distilled *in vacuo* to yield 16 g. of a phenol, b.p. 101–103° (0.7 mm.), the infrared and ultraviolet spectra of which indicated it to be largely V with some X. This dehydration product was characterized by its 2,6-bishydroxymethyl derivative which melted at 109–110° after several crystallizations, and which did not depress the m.p. of the derivative of pure V.

The tertiary alcohol can also be dehydrated by refluxing its xylene solutions with iodine. A solution of 5 g. of VIII and 50 mg. of iodine in 100 cc. of xylene yielded, after refluxing with water take-off for 6 hours, 1.9 g. of unreacted VIII and 2.1 g. of unsaturated phenol, largely V. With 100 mg. of iodine, there was no unreacted VIII, 2.7 g. of crude V and 1.7 g. of higher boiling products. With larger quantities of iodine, more polymeric products and some conjugated phenols are obtained.

The dehydration of VIII also can be effected simply by refluxing or slow distillation in the absence of catalysts. The product X a colorless liquid, b.p. 107–110° (1.5 mm.), $n^{25}\mathrm{D}$ 1.537, crystallizes in the cold, melts at 9–12° and depresses the m.p. of pure V. Hydrogenation of X also yielded XII. It does not form a crystalline 2,6-bishydroxymethyl derivative, and its infrared spectrum in CS_2 shows a strong band at *ca.* 11.3 μ absent in the spectrum of V.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.69. Found: C, 81.04; H, 8.70.

The Dehydration of IX.—Twenty grams of IX was refluxed under nitrogen for 3 hours, and distilled to yield some water and 16 g. of a colorless liquid, XIII perhaps with some XIV, b.p. 112–115° (0.5 mm.), $n^{25}\mathrm{D}$ 1.525.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.60. Found: C, 83.07; H, 9.65.

Dehydration to the same product also can be effected by stirring a solution of IX in heptane with 85% phosphoric acid at 25°. Dehydration also takes place when a xylene solution of IX is refluxed with a small amount of 85% phosphoric acid. A molecular rearrangement must take place, however, as the product has a higher refractive index and a substantially different infrared spectrum. Also hydrogenation does not yield the crystalline chroman XV.

6-Isoamyl-2,2-dimethylchroman (**XV**).—Hydrogenation (Adams platinum oxide catalyst, methanol, 80°) of the unsaturated ether prepared by refluxing IX, or by treating it with phosphoric acid at 25°, yields a colorless liquid, b.p. 119–120° (1.7 mm.), $n^{25}\mathrm{D}$ 1.510, which crystallizes on cooling and melts at 19–20°.

Anal. Calcd. for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.50; H, 10.31.

Acknowledgment.—We wish to thank Professor Martin G. Ettlinger for helpful advice.

MILWAUKEE, WISC.

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(15) The maxima at 224–225 mμ present in the spectra of V and VIII are absent in the spectra of the *o*-substituted II and IV.

(16) Z. M. Nazarova, *J. Gen. Chem. U.S.S.R.*, **8**, 1336 (1938); *C. A.*, **33**, 4214 (1939) gives b.p. 245–250°, $n^{27}\mathrm{D}$ 1.505.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Relative Rates of Side-chain Ethylation of Aromatic Hydrocarbons[1,2]

BY HERMAN PINES AND LUKE SCHAAP[3]

RECEIVED DECEMBER 30, 1957

The relative rates of side-chain ethylation of various alkylarenes in the presence of sodium–anthracene catalyst was determined by means of competitive reactions. The relative order of ethylation is: for toluene 1.0, ethylbenzene 2.8, *n*-propylbenzene 1.2, isopropylbenzene 1.9, and *sec*-butylbenzene 0.57. The relative rate of ethylation of indan is 1.35 as compared to that of toluene. Ethylation of xylenes decreases in rate in going from *o*-xylene to *m*-xylene to *p*-xylene. *Para* compounds in general show low rates of ethylation. *p*-Ethyltoluene, *p*-cymene and *p*-ethylcumene were ethylated in the presence of sodium–anthracene and potassium–anthracene catalyst. In the presence of sodium the larger alkyl groups ethylate preferentially.

The base-catalyzed side chain ethylation of aromatic hydrocarbons has been reported in several articles in recent years.[4] The ethylation products

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(1) Paper XIII of the series of Base-catalyzed Reactions. For paper XII, H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

(2) Taken in part from a dissertation submitted by L. Schaap in partial fulfillment of the requirements for the Ph.D. degree, August, 1957.

(3) Predoctoral fellow Universal Oil Products Co., 1954–1955, 1956–1957; Standard Oil Co. (Indiana), 1955–1956.

(4) (a) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955); (b) H. Hart, *ibid.*, **78**, 2619 (1956); (c) S. E. Voltz, *J. Org. Chem.*, **22**, 48 (1957); (d) R. D. Closson, J. P. Napolitino, G. C. Ecke and A. J. Holka, *ibid.*, **22**, 646 (1957).

have been studied extensively and are well defined. Little has been reported, however, concerning the relative ease of replacement of benzylic hydrogens by an ethyl group. Pines, Vesely and Ipatieff[4a] reported that *p*-cymene reacted selectively to yield *p*-*t*-pentyltoluene rather than *p*-*n*-propylcumene. It was also reported by these authors that apparently *o*-xylene reacted faster than *m*-xylene which reacted faster than *p*-xylene. The diethylated products from the xylenes were predominantly 3-tolylpentanes, which shows that *n*-propyl groups react faster than methyl groups. Hart[4b] also has demonstrated that compounds with alkyl substituted benzylic carbons such as 2-phenylpentane react very rapidly with ethylene once the benzylic carbanion is formed.

The main purpose of the present investigation was to establish: (a) relative rates of ethylation of alkyl groups in monoalkylarenes, of indan and of disubstituted arenes; (b) selectivity in the ethylation of *p*-dialkylarenes having two different alkyl groups. The ethylation reactions were made under pressure at about 185° using sodium– and in some experiments potassium–anthracene as catalysts. In each case only a small amount of ethylene was permitted to react with the arenes in order to avoid the diethylation reactions.

a. Relative Rates of Ethylation of Arenes.—The relative rates of ethylation of methyl-, ethyl-, *n*-propyl-, isopropyl- and *sec*-butylbenzene and of indan was determined using sodium–anthracene as a catalyst. It was preferred not to use potassium–anthracene for this study since this catalyst causes a cyclization reaction which results in the ultimate formation of indans.[5] Equimolar binary mixtures of the arenes were allowed to react with ethylene. Many of the mixtures were composed of toluene and another arene and the results of these competitive reactions (experiments 1–5) are reported in Table I and expressed as relative rates with respect to that of toluene (the calculations are based on experimental data given in Table V). The results obtained show that methyl substitution of a benzylic hydrogen increases the rate of ethylation even though these compounds do not metalate as readily as toluene.[6,7] The replacement of a methyl group by an ethyl group (ethyl *vs.* *n*-propylbenzene and isopropyl- *vs.* *sec*-butylbenzene) decreases the reactivity of the alkyl groups toward the ethylation. It is apparent from the results obtained that either decreasing rate of metalation or steric effects can be important because isopropylbenzene reacts more slowly than ethylbenzene, and the rate of reaction of *sec*-butylbenzene is much less than that of toluene. The rate of reaction of indan is not as great as that of ethylbenzene, but greater than that of *n*-propylbenzene.

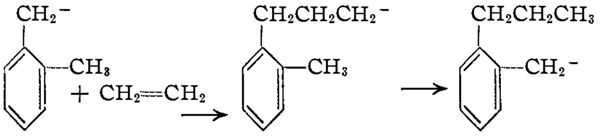
TABLE I

THE RELATIVE RATES OF REACTION OF ARENES WITH ETHYLENE

Experiment	Hydrocarbon	Relative rate toluene = 1
1[a]	Ethylbenzene	2.8
2	*n*-Propylbenzene	1.2[b]
3	Isopropylbenzene	1.9
4	*sec*-Butylbenzene	0.57
5	Indan	1.35[c]
6	*o*-Xylene	1.9
7	*m*-Xylene	1.6
8	*p*-Xylene	0.62
9	*p*-Cymene	0.75
10	*p*-*t*-Butyltoluene	0.21

[a] Experiment 1a (Table V) was not taken into consideration since the results were based on infrared spectral analysis only, and not on vapor phase chromatography. [b] This value was calculated using the relative rates of toluene and *n*-propylbenzene with respect to that of ethylbenzene. [c] Average of two values with an average deviation of ±0.08.

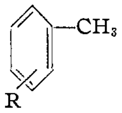
The xylenes show the order of rate of reaction that was indicated by the work reported previously.[4a] The reason for this order is not readily apparent. According to metalation data, *p*-xylene metalates much more readily than *o*-xylene,[8] but this does not explain the slow rate of reaction of *p*-xylene. It may be that the rapid rate of reaction of *o*-xylene is partly due to the ready availability of a benzylic hydrogen to the primary carbanion which is formed on addition to ethylene so that an intramolecular proton transfer can take place.



The decreasing relative rate of reaction of *p*-dialkylbenzenes seems to follow the order of the increasing inductive effect as shown by the data given for substituted toluenes in Table II. The rate decreases with the substitution of the *p*-hydrogen with a methyl group and continues to decrease with *p*-isopropyl and *p*-*t*-butyl groups. Similar results may be calculated for substituted ethylbenzenes and cumenes using the data listed in Table V indicating that the decreasing rate on increasing *p*-alkyl substitution is a general effect.

TABLE II

THE RELATIVE RATES OF REACTION OF SUBSTITUTED TOLUENES (REACTION ONLY ON A METHYL GROUP)



Experiment	R =	Relative rate
	p-H	1.00
6	*o*-CH_3	0.96
7	*m*-CH_3	.80
8, 8a	*p*-CH_3	.31
9[a]	*p*-*i*-C_3H_7	.22
10, 10a	*p*-*t*-C_4H_9	.21

[a] This value was calculated using the data obtained in experiment 13 to allow for the contribution of the methyl group toward the total alkylate.

b. Selectivity in Ethylation of *p*-Dialkylarenes.—*p*-Ethyltoluene *p*-cymene and *p*-ethylcumene were treated separately with ethylene in the presence of sodium– and potassium–anthracene cata-

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[5] L. Schaap and H. Pines, THIS JOURNAL, **79**, 4967 (1957).

[6] A. A. Morton, *Chem. Revs.*, **35**, 1 (1944).

[7] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

[8] A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., THIS JOURNAL, **65**, 1343 (1943).

lysts. The results, which are summarized in Table III, show that higher alkyl groups, especially in the presence of sodium–anthracene catalyst, ethylate more readily than methyl groups although metalation of *p*-cymene was reported to occur exclusively on the methyl group,[9,10] and metalation is presumably an intermediate step in the alkylation reaction.[4a] The reason for the more rapid addition of the group which forms the less stable carbanion probably is that the addition of the benzylic carbanion to alkenes is energetically unfavorable as discussed previously.[11] The reaction is less unfavorable for the less stable secondary (*p*-tolylethyl-) or tertiary (*p*-tolylisopropyl-) carbanions, so their rate of additions is greater. This means that, for these reactions, the rate of addition of the carbanions is more important than the rate of metalation or chain propagation.

TABLE III

THE ETHYLATION OF *p*-DISUBSTITUTED AROMATIC HYDROCARBONS

Experiment	Hydrocarbon[a]	Catalyst[b]	Monoethylated product: Yield mole %	Compounds	Mole %
11	*p*-Ethyltoluene[c]	Na	73[d]	*p*-Ethyl-*n*-propylbenzene	26
				p-*sec*-Butyltoluene	74
12	*p*-Ethyltoluene[c]	K	55[e]	*p*-Ethyl-*n*-propylbenzene	36
				p-*sec*-Butyltoluene	64
13	*p*-Cymene	Na	55	*p*-*n*-Propylcumene	28
				p-*t*-Pentyltoluene	72
14	*p*-Cymene	K	46[f]	*p*-*n*-Propylcumene	55
				p-*t*-Pentyltoluene	45
15	*p*-Ethylcumene	Na	39	*p*-*sec*-Butylcumene	48
				p-*t*-Pentylethylbenzene	52
16	*p*-Ethylcumene	K	30[g]	*p*-*sec*-Butylcumene	73
				p-*t*-Pentylethylbenzene	27

[a] One mole of the hydrocarbon was used with 0.10 mole of ethylene for each experiment. [b] The catalyst was composed of 0.044 g. at. of an alkali metal (1.7 g. of potassium or 1.0 g. of sodium) with 1.0 g. (0.0056 mole) of anthracene. [c] The material contained 3.2% of *m*-ethyltoluene. [d] This value includes an 8% yield of *m*-*sec*-butyltoluene. [e] This value includes a 6% yield of *m*-*sec*-butyltoluene. [f] An additional 7% of monoadduct was obtained which probably consisted of indans. [g] An additional 9% of monoadduct was obtained which probably consisted of indans.

The difference in selectivity of the potassium-catalyzed reactions from the sodium-catalyzed reactions can be explained by the greater reactivity of the potassium carbanions produced.[5]

It is also evident that the *m*-ethyltoluene which was present as an impurity in the *p*-ethyltoluene (expt. 11 and 12) reacted much faster with ethylene than did the *p*-isomer, which is in agreement with the data presented in Tables I and II.

Experimental

General Procedure.—The ethylation reactions were carried out at 185 ± 4° using a 250-ml. capacity Magne-Dash[12] autoclave which was charged with one mole of aromatic hydrocarbon and 0.1 mole of ethylene. A catalyst composed of 1 g. of sodium (0.044 g. atom) or 1.4 g. of potassium (0.044 g. atom) and 1 g. (0.0056 mole) of anthracene was used. The reactions were carried out in a manner similar to that reported previously. For experiments 1a, 3a and 11–17 the monoalkylated fractions were isolated by means of distillation using either a Piros-Glover spinning band column[13] or a Podbielniak whirling band column.[14] These fractions were determined quantitatively by means of infrared spectral analysis using a double beam recording spectrophotometer equipped with rock salt optics.[15] Cells

TABLE IV

ANALYTICAL WAVE LENGTHS

Compound	Wave length, microns
p-*sec*-Butyltoluene	13.80
p-Ethyl-*n*-propylbenzene	11.86
m-Ethyltoluene	14.32
m-*sec*-Butyltoluene	14.18
p-Ethyl-*t*-pentylbenzene	8.35, 12.65
p-*sec*-Butylcumene	11.20, 12.40
n-Propylbenzene	11.25, 12.12
Cumene	7.80
sec-Butylbenzene	10.47
t-Pentylbenzene	9.90, 10.7, 12.72

TABLE V

ETHYLATION OF MIXTURES OF ALKYLBENZENES

Experiment	Hydrocarbons[a]	Monoethylated product: Yield[b] mole %	Monoethylated product: Distribution mole %[f]
1(1a)[c]	Toluene	61(65)	26(24)
	Ethylbenzene		74(76)
2	Ethylbenzene	64(64)	70
	n-Propylbenzene		30
3(3a)[c]	Toluene	73	35(34)
	Cumene		65(66)
4	Toluene	63	64
	sec-Butylbenzene		36
5	Toluene	32	44
	Indan		56
6	Toluene	82	34
	o-Xylene		66
7	Toluene	71	38
	m-Xylene		62
8(8a)[c]	Toluene	70(69)	61(61)
	p-Xylene		39(39)
9	Toluene	74	56
	p-Cymene		44
10(10a)[c]	Toluene	68(66)	82(82)
	p-*t*-Butyltoluene[d]		18[e](18)
17	Ethylbenzene	64	59
	Cumene		41
18	Cumene	74	79
	sec-Butylbenzene		21
19	Ethylbenzene	66	68
	p-Ethyltoluene		32
20	Ethylbenzene	81	64
	p-Ethylcumene		36
21	Cumene	70	73
	p-Cymene		27

[a] In each experiment a mixture of 0.50 mole of each aromatic compound was used with 0.10 mole of ethylene. Sodium (1.0 g., 0.044 g. atom) with 1.0 g. (0.0056 mole) of anthracene was used as a catalyst. [b] Yields are based on ethylene charged. [c] Figure in parentheses indicates a duplicate experiment. [d] This compound contained some of the corresponding *m*-isomer. [e] This value does not include the *m*-isomer in the product. [f] The composition of the product indicated by parentheses is based on infrared spectral analysis. At the time the experiments were made, vapor phase chromatographic procedure was not available in our laboratory.

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(9) A. A. Morton and E. L. Little, Jr., THIS JOURNAL, **71**, 487 (1949).

(10) C. E. Claff, Jr., and A. A. Morton, *J. Org. Chem.*, **20**, 981 (1955).

(11) H. Pines and V. Mark, THIS JOURNAL, **78**, 4318 (1956).

(12) Autoclave Engineers, Inc., Erie, Pa.

(13) H. S. Martin and Co., Evanston, Ill.

(14) Podbielniak, Inc., Chicago, Ill.

(15) Baird Associates, Inc., Cambridge, Mass.

of 0.04 (and 0.094) mm. thickness were used. Calculations of percentage composition were made using the base-line technique from spectra of pure reference compounds and synthetic mixtures. Table IV lists the analytical wave lengths used.

For experiments 1–10 and 18–21 the total of unreacted hydrocarbons and products was analyzed by means of gas chromatography. A Podbielniak Chromacon[14] series 9475 apparatus was used. Sample volumes of 0.04 ml. were used with 6- and 12-ft. columns containing tricresyl phosphate on Celite or paraffin wax on 20–60 mesh firebrick; nitrogen was used as a carrier gas. Calibration runs were made for each analysis using synthetic mixtures of the starting materials and expected products in amounts which closely approximated the product composition. Calculations of composition and yield were made by comparing peak areas of the calibration and reaction product chromatograms. The results of experiments 1–10 and 17–21 are listed in Table V; good agreement between the two methods of analysis and good reproducibility of experiments is demonstrated by these results.

The Synthesis of Reference Compounds and *p*-Dialkylbenzenes.—Most of the monoalkylbenzenes and *n*-propyltoluene which were used as reference samples were prepared by means of side-chain alkylation of the appropriate alkylbenzene or xylene as described previously.[4a]

Most of the *p*-dialkylbenzenes which were used as reactants and reference compounds were prepared by means of hydrogenolysis of the appropriate substituted phenones using a copper–chromite catalyst at 210–250°. *p*-Ethyltoluene was prepared from *p*-methylacetophenone, *p*-ethylcumene from *p*-isopropylacetophenone, *p*-*n*-propylcumene from *p*-isopropylpropiophenone, *p*-*n*-propylethylbenzene from *p*-ethylpropiophenone and *p*-*t*-pentylethylbenzene from *p*-*t*-pentylacetophenone. These phenones were prepared in yields of 70–80% on a 0.25 to 1 molar scale using Friedel–Crafts acylation except for the *p*-methylacetophenone which was purchased (Eastman catalog no. 158).

Other dialkylbenzenes were prepared by means of hydrogenolysis of the appropriate benzyl alcohols using conditions similar to those used for the hydrogenolysis of phenones: *m*-ethyltoluene was prepared from 1-*m*-tolylethanol, *m*-*sec*-butyltoluene from 2-*m*-tolyl-2-butanol, *p*-*sec*-butyltoluene from 2-*p*-tolyl-2-butanol, *p*-*sec*-butylcumene from 2-*p*-cumyl-2-butanol. The *m*-isomers of these alcohols were prepared by Grignard reactions of *m*-bromotoluene with the appropriate aldehyde or ketone run on a 0.25-mole scale. The *p*-isomers were prepared by reaction of ethylmagnesium bromide with the appropriate *p*-substituted acetophenone on a 0.10-mole scale. The details of the hydrocarbon syntheses are listed in Table VI. The reference sample of *p*-*t*-pentyltoluene was kindly supplied by M. J. Schlatter of The California Research Corporation. Photographs of the spectra of these compounds may be found in the Ph.D. thesis of L. A. Schaap, Northwestern University, 1957.

Table VI

The Syntheses of Aromatic Hydrocarbons

Compound	Yield,[a] mole %	B.p. °C.	Mm.	n^{20}D
p-Ethyltoluene[b]	86	161.5–162.8	752	1.4942
p-Ethylcumene[c]	89	197.7–197.9	748	1.4914
p-*n*-Propylcumene	77	209–210	748	1.4895
p-Ethyl-*n*-propylbenzene	72	197–198		1.4915
p-Ethyl-*t*-pentylbenzene[d]	84	228.6		1.4960
m-Ethyltoluene	69	159		1.4961
m-*sec*-Butyltoluene	79	189.5	747	1.4919
p-*sec*-Butyltoluene	66	192–193		1.4900
p-*sec*-Butylcumene[e]	92	218		1.4890
p-*n*-Propyl-*t*-butylbenzene[f]	..	229		1.4909

[a] Based on the alcohol or ketone used. [b] The distilled material contained 3.2% of *m*-ethyltoluene. [c] The pure *p*-isomer was obtained by purification of *p*-isopropylacetophenone *via* the oxime (m.p. 72–73°) or by distillation of the hydrocarbon from the crude ketone on a Podbielniak Hypercal column.[14] Of the hydrocarbon charged, 37% was obtained as the pure *p*-isomer. [d] d^{20}_4 0.8572. *Anal.* Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; *MR*D, 58.63. Found: C, 88.67; H, 11.36; *MR*D, 60.23. [e] d^{20}_4 0.8361. *Anal.* Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; *MR*D, 58.63. Found: C, 88.92; H, 11.57; *MR*D, 59.64. [f] d^{20}_4 0.8582. *Anal.* Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; *MR*D, 58.63. Found: C, 88.50; H, 11.33; *MR*D, 60.51.

The commercially available *p*-*t*-butyltoluene which was used for experiment 17 contained some of the corresponding *m*-isomer, according to the infrared spectrum, so the sample which was used for experiment 10a was prepared from *p*-*t*-butylphenol using the method which was described previously[4a] for *p*-*t*-pentyltoluene. The reference sample of *p*-*n*-propyl-*t*-butylbenzene was a fraction which was distilled from the product of a reaction of the Eastman *p*-*t*-butyltoluene with ethylene and was not completely free of the *m*-isomer. The properties of this material are listed in Table VI.

Acknowledgment.—The authors wish to express their appreciation to Miss H. Beck for the elemental analyses reported in this paper.

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[Contribution from the Department of Chemistry of the University of Wisconsin]

The Synthesis of *dl*-Protolichesterinic Acid[1]

By Eugene E. van Tamelen and Shirley Rosenberg Bach

Received June 24, 1957

The synthesis of *dl*-protolichesterinic acid (II) involves (i) conversion of methyl 2-hexadecenoate to methyl 3-tridecylglycidate (XVIII), (ii) ring-opening of XVIII with the anion of dimethyl malonate yielding α,β-dicarbomethoxy-γ-tridecyl-γ-butyrolactone (XVII), (iii) conversion of this lactonic diester to the monopotassium salt of the corresponding lactonic diacid XIX, and (iv) treatment of the salt with formaldehyde and diethylamine, resulting in direct formation of the natural product in the racemic form. Tentative stereoformulas for protolichesterinic acid, alloprotolichesterinic acid, as well as nephromopsinic acid and its diastereomers, are developed.

As demonstrated during recent years, the α-methylenecarbonyl group I serves as a structural feature common to certain natural products of strikingly diverse origins, for example: the antibiotic sarkomycin,[2] the amino acid γ-methyleneglutamic acid,[3] and the sesquiterpenoids alantolactone[4] and helenalin.[5] The appearance of the members in this group was prefigured by the well-known fatty acid variant present in *Cetraria islandica* (Iceland moss), protolichesterinic acid, first isolated in 1902, and assigned the currently accepted

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[1] The results detailed herein were first reported in *Chemistry & Industry*, 1308 (1956).

[2] I. R. Hooper, L. C. Cheney, M. J. Cron, O. B. Fardig, D. A. Johnson, D. L. Johnson, F. M. Palermiti, H. Schmitz and W. B. Wheatley, *Antibiotics & Chemotherapy*, **5**, 585 (1955).

[3] P. C. Wailes, M. C. Whiting and L. Fowden, *Nature*, **174**, 130 (1954).

[4] L. Ruzicka and P. Pieth, *Helv. Chim. Acta*, **14**, 1090 (1931).

[5] G. Büchi and D. Rosenthal, This Journal, **78**, 3860 (1956).