[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Alkylbenzenes. VIII.[1] Rearrangements Accompanying Friedel–Crafts Alkylations with Propyl and Butyl Chlorides

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The products from the alkylation of benzene in the presence of aluminum chloride with *n*-propyl, *n*-butyl, *sec*-butyl and isobutyl chlorides have been determined qualitatively and quantitatively by infrared spectrophotometry and/or vapor-phase chromatography. The expectation that *sec*-butyl chloride gives a mixture of *sec*-butylbenzene and isobutylbenzene was confirmed. No *t*-butylbenzene was produced, even at 80°. *n*-Butyl chloride gave a mixture of *n*-butylbenzene and (predominantly) *sec*-butylbenzene at 0°; at 80° some isobutylbenzene was also produced. Isobutyl chloride gave only *t*-butylbenzene at temperatures from −18° to 80°. A surprisingly small temperature effect on the proportion of *n*-propylbenzene and isopropylbenzene produced from *n*-propyl chloride was found in contrast to earlier data. The mechanism of Friedel–Crafts alkylations is discussed in the light of the fact that extensive or complete rearrangement accompanies the reaction of even primary alkyl halides.

Introduction

The recent observation[2] that *sec*-butylbenzene is isomerized to isobutylbenzene by heating with aluminum chloride led us to suspect that a mixture of *sec*-butylbenzene and isobutylbenzene may be produced whenever alkylations are carried out with a *sec*-butyl halide and aluminum chloride at elevated temperatures. The presence of the isobutylbenzene would have been unexpected in earlier work, and it would have been difficult to detect or separate from *sec*-butylbenzene due to the almost identical boiling points of the two isomers.

With the advent of infrared spectrophotometry, mass spectrometry and vapor phase chromatography it has become possible to analyze mixtures such as these very accurately and very conveniently. Although these quantitative methods have been applied in a number of recent investigations of Friedel–Crafts reactions,[2–4] the conclusions regarding the occurrence and extent of rearrangements of *n*-propyl, *n*-butyl, *sec*-butyl and isobutyl groups during alkylations are based on earlier data, all of which are less quantitative and some of which are clearly open to question.

Alkylation of benzene by *sec*-butyl chloride and aluminum amalgam at 0° was found by Estreicher,[5] in 1900, to produce *sec*-butylbenzene. Diuguid,[6] in 1941, reported that the same treatment at 25° gave *t*-butylbenzene as the principal product.

n-Butyl halides with aluminum chloride (or amalgam) and benzene have been reported to produce a mixture of *n*- and *sec*-butylbenzene,[5–7] *sec*-butylbenzene[5,8] and *t*-butylbenzene,[9] depending on the halide or the temperature.

Isobutyl chloride has been reported to yield only *t*-butylbenzene[8,10,11] even at −18°.[11]

The production of both *n*-propylbenzene and isopropylbenzene by alkylation of benzene with *n*-propyl halides is well documented.[6,11,12–17] Some investigators[11,14,16] reported *n*-propylbenzene to be the exclusive or principal product at low temperatures.

This paper describes a reinvestigation of the alkylation of benzene with *n*-propyl, *n*-butyl, *sec*-butyl and isobutyl chlorides, using infrared spectrophotometry and/or vapor chromatography for qualitative and quantitative analysis of the alkylbenzenes produced.

Experimental

Analytical Procedures.—A Baird double beam recording infrared spectrophotometer, model 4-55, was used. Starting materials and products were analyzed qualitatively as the pure liquids. Quantitative analysis of binary product mixtures was accomplished in 2,2,4-trimethylpentane (spectroscopic grade) solutions as described previously.[2] The absorption peaks used in the optical density *vs.* composition plots were: *sec*-butylbenzene (13.1 μ)–isobutylbenzene (13.5 μ); *sec*-butylbenzene (13.1 μ)–*n*-butylbenzene (13.4 μ); isopropylbenzene (13.1 μ)–*n*-propylbenzene (13.5 μ). Quantitative analysis of ternary mixtures of *n*-butylbenzene, *sec*-butylbenzene and isobutylbenzene was complicated by the overlap of the strongest characteristic absorption peaks of the three isomers. However, the proportion of *n*-butylbenzene could be determined by vapor phase chromatography, and standard solutions containing this proportion of *n*-butylbenzene and varied proportions of the other two isomers in 2,2,4-trimethylpentane were prepared and compared with a solution of the reaction product mixture.

For vapor phase chromatography, a Perkin–Elmer Vapor Fractometer, model 154-B, was used, equipped with a 2-m. Celite-packed column impregnated with di-2-ethylhexyl sebacate. This column separated completely all of the alcohols, alkyl chlorides and alkylbenzenes encountered in this study, with the exception of *sec*-butylbenzene and isobutylbenzene, which appeared as a single peak. (Fortunately mixtures of these two are easily resolved by infrared spectrophotometry.)

Materials.—The alkyl chlorides were prepared from the redistilled commercial alcohols by one of the two following methods. Both the alcohols and the alkyl chlorides were analyzed for purity before use by infrared spectrophotometry and vapor phase chromatography.

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[1] Preceding papers in this series: VI, R. M. Roberts and J. E. Douglass, *Chemistry & Industry*, 926 (1959); VII, R. M. Roberts and Y. W. Han, *Tetrahedron Letters*, **6**, 5 (1959).

[2] R. M. Roberts, Y. W. Han, C. H. Schmid and D. A. Davis, THIS JOURNAL, **81**, 640 (1959).

[3] L. Schmerling, R. W. Welch and J. P. Luvisi, *ibid.*, **79**, 2636 (1957), and preceding papers.

[4] (a) A. Streitwieser, Jr., D. P. Stevenson and W. D. Schaeffer, *ibid.*, **81**, 1110 (1959); (b) A. Streitwieser, Jr., W. D. Schaeffer and S. Andreades, *ibid.*, **81**, 1113 (1959).

[5] T. Estreicher, *Ber.*, **33**, 436 (1900).

[6] L. T. Diuguid, THIS JOURNAL, **63**, 3527 (1941).

[7] A. M. Petrova, *Zhur. Obshchei Khim.*, **24**, 491 (1942); *C. A.*, **49**, 6150i (1955).

[8] J. Schramm, *Monatsh.*, **9**, 613 (1888).

[9] N. O. Calloway, THIS JOURNAL, **59**, 1474 (1937).

[10] M. Senkowski, *Ber.*, **23**, 2412 (1890).

[11] M. I. Konowalow, *J. Russ. Phys.-Chem.*, **27**, 456 (1895); *Bull. soc. chim.* **16**, 864 (1896).

[12] G. Gustavson, *ibid.*, **30**, 22 (1878); *Ber.*, **11**, 1251 (1878).

[13] R. D. Silva, *Bull. soc. chim.*, **43**, 317 (1885).

[14] R. Heise, *Ber.*, **24**, 768 (1891).

[15] P. Genvresse, *Compt. rend.*, **116**, 1065 (1893).

[16] V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

[17] B. A. Krentsel, A. V. Topchiev and L. N. Andreev, *Doklady Akad. Nauk S.S.S.R.*, **98**, 75 (1954); *C. A.*, **49**, 11574c (1955).

sec-Butyl chloride and *n*-butyl chloride were prepared by treatment of the corresponding alcohols with concd. hydrochloric acid and anhydrous zinc chloride.[18] The *n*-butyl chloride prepared in this way contained about 17% *sec*-butyl chloride and it was necessary to redistil it several times through a 100-cm. Nichrome spiral column until the last traces of the *sec*-isomer were removed (vapor phase chromatography). When this method was applied to the preparation of *n*-propyl chloride, isopropyl chloride was also produced (11–15%). It was more satisfactory to use the method described below than to fractionate this mixture.

Isobutyl chloride and *n*-propyl chloride were prepared from the alcohols by means of thionyl chloride and pyridine.[19] The products prepared in this way contained no isomeric chlorides (infrared and vapor phase chromatography).

The alkylbenzenes used as standards for the analyses were: *sec*-butylbenzene, Phillips pure grade (99 mole % minimum); *n*-butylbenzene and isopropylbenzene, Eastman Kodak Co. white label. Isobutylbenzene,[2] *t*-butylbenzene[2] and *n*-propylbenzene[20] were synthesized by methods described previously. Their infrared spectra were identical with those recorded in the reports of A.P.I. Project No. 44.

Aluminum chloride was B. and A., anhydrous sublimed, reagent, used as received.

Alkylations. (A) Butyl Chlorides.—The general procedure followed in all alkylations is illustrated by the reaction of *sec*-butyl chloride at 80°.

Benzene (195 g., 2.50 moles), which had been dried first by calcium chloride and then by azeotropic distillation, and anhydrous aluminum chloride (6.0 g., 0.045 mole) were placed in a three-necked flask equipped with a reflux condenser, mechanical stirrer, and dropping funnel. The flask was heated in an oil-bath at 80 ± 1°. *sec*-Butyl chloride (46.3 g., 0.50 mole) was added dropwise to the stirred mixture during 0.5 hr. Stirring and heating were maintained for an additional 0.5 hr. The reaction mixture was allowed to cool to room temperature and poured into a mixture of 200 g. of cracked ice and 100 g. of water. After decomposition was complete, the layers were separated and the organic layer was washed twice with 100-ml. portions of 5% sodium bicarbonate solution, then with water until the washings were neutral. After drying over calcium chloride, the organic solution was distilled through a short glass helices-packed column to remove the excess benzene. The remaining liquid was transferred to a smaller flask and distilled through a 100-cm. Nichrome spiral column. Arbitrary distillation cuts were taken: (I) 165–170°, (II) 170–175°, (III) 175–180° and (IV) 180–185°. The yield and composition of the product is given in Table I. Different temperatures in other expts. were maintained within ±1° by using water-baths, ice-baths or ice–salt-baths, as appropriate.

The same amounts of butyl chloride, benzene and aluminum chloride were used in all experiments with butyl chlorides except the last ones of Tables I and II, in which larger amounts of catalyst were used.

The fourth and fifth entries in Table I represent experiments which duplicate those of Diuguid.[6] Aluminum amalgam (0.1 mole) was used as catalyst in these experiments, with *sec*-butyl chloride (1 mole) and benzene (6 moles). The *sec*-butyl chloride was added at room temperature during 4 hr. and the reaction mixture was allowed to stand an additional 14 hr. before work-up.

The other times listed in the tables represent the total of the period of addition (a.) of the alkyl halide and an additional period of continued stirring (s.) at the same temperature, divided as follows: 1 hr. (0.5a. + 0.5s.); 2 hr. (1a. + 1s.); 5 hr. (2.5a. + 2.5s.); 6 hr. (2a. + 4s.).

(B) *n*-Propyl Chloride.—The proportions of *n*-propyl chloride (1 mole), benzene (2 moles) and aluminum chloride (0.08 mole) used by Ipatieff, Pines and Schmerling[16] were employed in all these expts. The reaction mixtures were worked up in the same way as those from butyl chlorides, except that in the final distillation two arbitrary cuts were taken: (I) 150–155° and (II) 155–160°. The average n^{25}D of I cuts was 1.4888 and of II cuts was 1.4893. These cuts were analyzed separately by infrared spectrophotometry and vapor phase chromatography. The I cuts were richer in isopropylbenzene and the II cuts were richer in *n*-propylbenzene, as expected, but separation was far from complete, the difference in composition of the two cuts being only 15–20%. The analytical values reported in Table IV are calculated for the total propylbenzene fraction, *i.e.*, cuts I and II combined.

TABLE I

ALKYLATION OF BENZENE (2.5 MOLES) WITH *sec*-BUTYL CHLORIDE (0.5 MOLE) AND ALUMINUM CHLORIDE (0.045 MOLE)

Temp., °C.	Time,[a] hr.	Products Yield, %[b]	$n^{24.5}$D	s-BuPh, %[c]	i-BuPh, %[c]
0	6	71	1.4877	100	0
30	2.5	70	1.4875	100	0
30	6	72	1.4875	95	5
25[d]	18	78	1.4875	92	8
25[d]	18	77	1.4873	92	8
80	1	68	1.4855	35	65
80	2.5	67	1.4852	35	65
80[e]	2.5	34	1.4856	36	64

[a] See Experimental section. [b] Product from cut II only; other cuts were negligible; see Experimental section. [c] Infrared analysis of 2,2,4-trimethylpentane solutions. [d] Aluminum amalgam catalyst; see Experimental section. [e] 0.119 mole of aluminum chloride used in this experiment.

Discussion of Results

The results of the alkylations with *sec*-butyl chloride are summarized in Table I. At 0 and at 30°, with a short reaction time, the product was pure *sec*-butylbenzene. At 80° the product was a 2:1 mixture of isobutylbenzene and *sec*-butylbenzene. Increasing the amount of catalyst did not alter the composition of the butylbenzene but did decrease the yield. Reactions carried out at 25 or 30° with a long period of contact with aluminum chloride or aluminum amalgam catalyst gave *sec*-butylbenzene as the principal product, accompanied by 5–8% of isobutylbenzene. There was no trace of *t*-butylbenzene, which was reported by Diuguid[6] to be the principal product under these conditions.

Alkylation with *n*-butyl chloride at low temperature gave a mixture of *n*- and *sec*-butylbenzene in a ratio of *ca.* 1:2 (Table II). One possible source of error which should be considered in comparing the compositions of alkylation products of various workers is illustrated by our experience in the preparation of *n*-propyl and *n*-butyl chlorides. When concd. hydrochloric acid and zinc chloride were used, rearrangement (11–17%) to the *sec*-alkyl chloride accompanied the replacement reaction in both cases. Thus some of the alkyl halides used by early workers may actually have been mixtures of isomers. Thionyl chloride in pyridine gave replacement without rearrangement.

At 80°, *n*-butyl chloride gave mixtures of *n*-butylbenzene, *sec*-butylbenzene and isobutylbenzene (Table II) as might be expected on the basis of the results from *sec*-butyl chloride. However, the ratio of isobutylbenzene to *sec*-butylbenzene was always much lower than in the mixtures produced from *sec*-butyl chloride. It is not clear why this was true, since the isobutylbenzene must arise from rearrangement of *sec*-butylbenzene in both

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[18] J. E. Copenhaver and A. M. Whaley, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 142.

[19] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., New York, N. Y., 1956, p. 274.

[20] R. M. Roberts and S. G. Brandenberger, THIS JOURNAL, **79**, 5484 (1957).

TABLE II

ALKYLATION OF BENZENE (2.5 MOLES) WITH *n*-BUTYL CHLORIDE (0.5 MOLE) AND ALUMINUM CHLORIDE (0.045 MOLE)

Temp., °C.	Time,[a] hr.	Products								
		Yield (%) from								
		Cut II	Cut III	Cut IV	$n^{24.5}_{\mathrm{D}}$[b]	*n*-BuPh	*s*-BuPh		*i*-BuPh	Anal.[c]
0	2.5	39	31	6	1.4879	36[d]	64[d]			IR
						34[d]	66[d]			VC
0	2.5	29	32	5	1.4882	32	68			IR
						34	66			VC
80	2.5	52	18	3	1.4875	22[d]	62[d]		16[d]	IR
						23[d]		77[d,c]		VC
80	2.5	48	23	1	1.4876	23	63		14	IR
						24		76[e]		VC
80	4.0	48	19	4	1.4875	23	60		17	IR
						24		76[e]		VC
80[f]	2.5	43	18	1	1.4877	19	54		27	IR
						20		80[e]		VC

[a] See Experimental section. [b] Cut II. [c] Analysis by IR (infrared), VC (vapor phase chromatography). Cuts II, III and IV were combined for analysis. In some experiments these three cuts were analyzed separately by VC; good agreement with the combined samples' analyses was obtained. [d] The *n*-butyl chloride used contained 17% *sec*-butyl chloride. These values are corrected to correspond to the products which would have originated from *n*-butyl chloride only. [e] *sec*-Butylbenzene and isobutylbenzene were not separated by the instrument. [f] 0.090 mole of catalyst used in this expt.

TABLE III

ALKYLATION OF BENZENE (2.5 MOLES) WITH ISOBUTYL CHLORIDE (0.5 MOLE) AND ALUMINUM CHLORIDE (0.045 MOLE)

Temp., °C.	Time,[a] hr.	Products		
		Yield, %[b]	$n^{24.5}_{\mathrm{D}}$	Identity[c]
−18	2.5	66	1.4902	100% *t*-butylbenzene
0	6	66	1.4906	100% *t*-butylbenzene
80	2.5	47	1.4906	100% *t*-butylbenzene

[a] See Experimental section. [b] Product from cuts I and II, mainly cut I; other cuts were negligible; see Experimental section. [c] Infrared analysis.

TABLE IV

ALKYLATION OF BENZENE (2 MOLES) WITH *n*-PROPYL CHLORIDE (1 MOLE) AND ALUMINUM CHLORIDE (0.08 MOLE)

Temp., °C.	Time,[a] hr.	Yield, %[b]	Products		
			n-PrPh	*i*-PrPh	Anal.[c]
−18	5	30	34	66	IR
			35	65	VC
−18	5	32	35	65	IR
			34	66	VC
− 6	5	49	33	67	IR
			34	66	VC
− 6	5	55	35[d]	65[d]	IR
			35[d]	65[d]	VC
35	5	59	33	67	IR
			32	68	VC
35	5	60	33[d]	67[d]	IR
			34[d]	66[d]	VC
80	2	56	31	69	IR
			30	70	VC
80	2	53	32	68	IR
			31	69	VC

[a] See Experimental section. [b] Products from cuts I and II; see Experimental section. [c] Analysis by IR = infrared, VC = vapor phase chromatography; see Experimental section. [d] The *n*-propyl chloride used contained 11.4% isopropyl chloride. These values are corrected to correspond to the products which would have originated from *n*-propyl chloride only.

cases. The principal way in which the experiments differed was in the presence of *n*-butylbenzene (and, possibly di- and poly-*n*-butylbenzenes) in the mixtures from *n*-butyl chloride. However, we cannot at this time give any definite explanation of how this causes inhibition of the rearrangement of *sec*-butylbenzene to isobutylbenzene.

The reports that isobutyl chloride yields only *t*-butylbenzene[8,10,11] were found to be entirely correct, at temperatures from −18 to 80° (Table III). There was no evidence of even traces of other isomers from the infrared spectrograms.

The results from reactions of *n*-propyl chloride (Table IV) at 35° were not unusual. The proportion of isopropylbenzene and *n*-propylbenzene was 67/33, about as close to the 60/40 ratio reported by Ipatieff, Pines and Schmerling[16] as would be expected in view of the limitations of the method used by these workers, which involved quantitative separation of derivatives. However, the finding that the proportion of the two isomers was almost the same at −6° (66/34), whereas Ipatieff, Pines and Schmerling found the *n*-propyl isomer to predominate at this temperature, was quite unexpected.[21] In view of this result we went on to determine the ratio of products at still lower and higher temperatures and, as may be seen in Table IV, *there was only a 4% difference in the composition of the mixture of isomers produced at −18 and at 80°!*

Mechanisms of the Reactions.—The production of isobutylbenzene from *sec*-butyl chloride undoubtedly involves the initial formation of *sec*-butylbenzene, followed by its rearrangement to isobutylbenzene by a mechanism which has been discussed in previous papers.[1,2]

The production of *sec*-butylbenzene from *n*-butyl chloride, of *t*-butylbenzene from isobutyl chloride, and of isopropylbenzene from *n*-propyl chloride deserves further discussion. All of these chlorides are *primary* alkyl chlorides. The excellent and extensive recent work of Brown and his collabora-

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(21) Although the amounts and conditions we used were patterned after the published account, a personal communication from Professor H. Pines has disclosed that the mode and time of addition of the *n*-propyl chloride were not quite identical. In the earlier work, half of the benzene was used to dilute the *n*-propyl chloride before it was added to the other half of the benzene and the catalyst; their addition required the full 5 hr., whereas our addition was complete in 2.5 hr. and the mixture was then stirred an additional 2.5 hr. It seems unlikely that these slight differences would have any large effect on the product composition.

tors[22,23] has called attention to the fact that the Friedel–Crafts reactions of a number of primary derivatives exhibit characteristics of a bimolecular displacement mechanism, rather than a carbonium ion mechanism. However, one should not lose sight of the fact that there are still some features of reactions of primary derivatives (as well as those of secondary, which have been adequately recognized) which are not compatible with a simple displacement process. The present work shows that the *major* result of alkylation with *n*-propyl and *n*-butyl chlorides even at low temperature is rearranged product. The fact that the exclusive product from isobutyl chloride is the *t*-butyl derivative, which has now been confirmed, has received little comment in discussions of alkylation mechanisms. The rearrangements accompanying Friedel–Crafts alkylations with these primary halides may involve σ- or π-complexes in a mechanism analogous to that proposed by Streitwieser, Schaeffer and Andreades[4b] for alkylations with alcohols and boron trifluoride. However, it is also possible that the alkyl halides are isomerized prior to alkylation. Further experimental data will be required before a choice can be made between these alternatives.

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AUSTIN 12, TEX.

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[22] (a) H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953); (b) H. C. Brown and H. Jungk, *ibid.*, **78**, 2182 (1956); (c) H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956).

[23] K. L. Nelson and H. C. Brown, Chapter 56 in B. T. Brooks, S. S. Kurtz, Jr., C. E. Boord and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1955, Vol. 3, p. 465.

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Investigations on Lignins and Lignification. XXII.[1] The Conversion of D-Glucose into Lignin in Norway Spruce

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The formation of lignin in plants follows the scheme: carbohydrate → shikimic acid → *p*-hydroxyphenylpyruvic acid → lignin building stones → lignin. The carbohydrate has been identified as glucose.

From the viewpoint of plant physiology, the chemistry of wood is but a special case of the utilization by plants of the carbon absorbed from the atmosphere as carbon dioxide. But for the wood chemist, this raw material represents a difficult and intriguing substance: difficult because the components of which wood is comprised are very complex; intriguing because about one-half of the substance of wood has proven extremely difficult to exploit chemically on a scale even nearly comparable with that of the manufacture of paper.

When softwoods are subjected to the pulping process for paper manufacture, approximately one-half of the wood is dissolved. Of the dissolved material, about one-half again consists of the aromatic polymer, lignin. It is the lignin which gives wood its rigidity, and it is precisely the lignin of wood which has resisted exploitation, but may, at some future time, provide the basic raw material for new chemical industries.

The mechanism of the biogenesis of lignin in living plants remained obscure until the role of shikimic acid in the lignification process was brought to light in 1955.[2] Shikimic acid (I) was originally found to function as an intermediate in the biogenesis, from glucose, of the aromatic ester, methyl *p*-methoxycinnamate, by the mold *Lentinus lepideus*, which is a species of wood-rotting fungi which has the capacity, when growing in its natural habitat, of removing the cellulose from sound wood, *i.e.*, of producing "brown rot." In addition, this fungus also possesses among its metabolic activities the ability to convert carbohydrates into methyl *p*-methoxycinnamate.[3a,b] As the result of certain metabolic studies carried out in this Laboratory,[4] the biogenesis of methyl *p*-methoxycinnamate by *L. lepideus* may be formulated as: cellulose → glucose → sedoheptulose → shikimic acid → *p*-hydroxyphenylpyruvic acid → methyl *p*-methoxycinnamate.

The structural similarity of methyl *p*-methoxycinnamate (II) to the postulated building stones of lignin,[5] namely *p*-coumaryl alcohol (III), coniferyl alcohol (IV) and sinapyl alcohol (V), indicated a possible relationship between the biosynthesis of the ester II and the biogenesis of lignin. The intervention of shikimic acid in lignification was clearly demonstrated[6] by the feeding of specifically labeled shikimic acid (containing C^{14} in positions 2 and 6 of its cyclohexene ring) to growing sugar cane plants, and the subsequent recovery of a radioactive lignin yielding on oxidation vanillin (VI) which retained the isotopic activity of the C^{14} in the corresponding positions

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[1] For papers XIX and XX see S. N. Acerbo, W. J. Schubert, H. Shimazono and F. F. Nord, THIS JOURNAL, **80**, 1990, 1992 (1958); for paper XXI see H. Shimazono, *Arch. Biochem. and Biophys.*, **83**, 206 (1959). This investigation was supported in part by grants of the National Science Foundation, the U. S. Atomic Energy Commission and the U. S. Public Health Service. Parts of this paper are taken from a portion of a dissertation to be submitted by S. N. A. to the Graduate Faculty of Fordham University, 1960. In addition, S. N. A. wishes to thank Drs. H. Shimazono and H. Stockmann of this Department for many enlightening discussions.

[2] G. Eberhardt and F. F. Nord, *Arch. Biochem. and Biophys.*, **55**, 578 (1955).

[3] (a) F. F. Nord and J. C. Vitucci, *Arch. Biochem.*, **14**, 243 (1947); (b) **15**, 465 (1947).

[4] G. Eberhardt, THIS JOURNAL, **78**, 2832 (1956).

[5] P. Klason, *Svensk Kemisk Tidskr.*, **9**, 133 (1897).

[6] G. Eberhardt and W. J. Schubert, THIS JOURNAL, **78**, 2835 (1956).