

### Summary

The behavior of various types of ethers toward hydrogen over Raney nickel has been surveyed.

The results are summarized in Table I and in the section entitled discussion of results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

## The Synthesis of Condensed Polynuclear Hydrocarbons by the Cyclodehydration of Aromatic Alcohols. III. The Cyclization of Some Phenylated Alcohols and Related Olefins<sup>1</sup>

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For several years there has been great activity in the synthesis and study of polynuclear aromatic hydrocarbons, particularly those of biological significance or related to products occurring in nature. The volume of this work appears to be steadily mounting and has already reached formidable proportions.

A convenient method for the synthesis of such hydrocarbons, and one which has been frequently employed and extensively developed, is the cyclodehydration of aromatic alcohols, followed by dehydrogenation of the resultant hydroaromatic products.

In the eagerness to synthesize new and interesting compounds, but little time has been given to the study of the reaction itself or of its mechanism. We have therefore felt that studies in this direction might contribute information of value to many investigators in this field, and the data so far accumulated have justified that belief.

Of the results already published from our laboratories, those on the synthesis of ionene,<sup>2</sup> of phenanthrene,<sup>3</sup> and of the indanes,<sup>4</sup> indicate that in most cases the main course of the reaction is first the dehydration of the alcohol to an olefin, and then the rearrangement of the latter by cyclization. In only one case (Table A, XVII) was there evidence that the cyclization was effected by a direct condensation of the alcoholic hydroxyl with the ortho hydrogen of the aromatic nucleus.

(1) Presented at the St. Petersburg, Fla., Meeting of the American Chemical Society, Mar. 27, 1934, before the Division of Organic Chemistry. Based upon the Dissertation submitted by Richard O. Roblin, Jr., 1934, in partial fulfillment of the requirements for the Ph.D. degree in the Faculty of Pure Science, Columbia University, to which the reader is referred for further experimental details and literature citations.—M. T. B.

(2) Bogert, Davidson and Apfelbaum, *THIS JOURNAL*, **56**, 95 (1934).

(3) Bogert, *Science*, [N. S.] **77**, 289 (Mar. 17, 1933).

(4) Bogert and Davidson, *THIS JOURNAL*, **56**, 185 (1934).

The present contribution describes a detailed investigation of the cyclization of some simple phenylated alcohols and related olefins, most of which are readily obtainable in good yield by the familiar Grignard reaction. The ease with which these alcohols and olefins can be converted into the corresponding tetralins and naphthalenes, makes the process a very satisfactory one for the synthesis of such hydrocarbons.

In addition to confining our experiments to a limited group of closely related initial compounds, it seemed wise also to adopt some one standard cyclizing agent, in order that the results might be more truly comparable and more clearly interpretable. Of the many reagents which have been employed for such a purpose, sulfuric acid was found most satisfactory for use at room temperature, except for primary alcohols. Because of the oxidizing and sulfonating action of this acid at the high temperatures required to dehydrate such alcohols, phosphoric acid was substituted in those cases.

In Table A we have incorporated also the alcohols and olefins investigated in our earlier papers,<sup>2,4</sup> so as to make this summary more comprehensive and to give a better survey of the results to date.

Classified according to final products, the initial compounds tabulated below can be arranged as follows: (1) those giving mainly polymers = I, IV, VII, IX, X and XXVI; (2) those giving mainly indanes = II, III, VIII, XI, XII, XIII and XXV; (3) those giving both indanes and tetralins = VI and XVI; (4) those giving mainly tetralins = V, XIV, XV, XVII, XVIII, XIX, XXI, XXII, XXIII, XXIV, XXVII, XXVIII and XXIX.

An examination of these results will disclose the following interesting facts among others:

TABLE A  
ACTION OF SULFURIC (OR PHOSPHORIC) ACID UPON SOME PHENYLATED ALCOHOLS AND OLEFINS

a. Alcohols				
	Ph at 1	Initial compound	Final product	Reference
I	OH at 1	PhCH(OH)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Polymer	This paper
II	OH at 2	PhCH <sub>2</sub> CH(OH)CH(CH <sub>3</sub> )CH <sub>3</sub>	1,1-Dimethylindane	4
III	OH at 2	PhCH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH(CH <sub>3</sub> )CH <sub>3</sub>	1,1,2-Trimethylindane	4
IV	OH at 2	PhCH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>2</sub> CH <sub>3</sub> <sup>a</sup>	Polymer	4
V	OH at 2	PhCH <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1-Methyltetralin	This paper
VI	OH at 2	PhCH <sub>2</sub> CH(OH)CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	1,2-Dimethyltetralin 1-Methyl-1-ethylindane	This paper
VII	OH at 3	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	Polymer	4
VIII	OH at 3	PhC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1,1-Dimethylindane	4
IX	OH at 3	PhCH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	Polymer	4
X	OH at 3	PhCH <sub>2</sub> CH(CH <sub>3</sub> )CH(OH)CH <sub>3</sub>	Polymer	4
XI	OH at 3	PhCH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>3</sub>	1,1-Dimethylindane	4
XII	OH at 3	PhC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	1,1,3-Trimethylindane	4
XIII	OH at 3	PhC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>3</sub>	1,1,3,3-Tetramethylindane	4
XIV	OH at 3	PhCH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub>	1-Methyltetralin	This paper
XV	OH at 3	PhCH <sub>2</sub> CH <sub>2</sub> CH(OH)CH(CH <sub>3</sub> )CH <sub>3</sub>	1,1-Dimethyltetralin	2
XVI	OH at 3	PhCH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>2</sub> CH <sub>3</sub>	1,2-Dimethyltetralin 1-Methyl-1-ethylindane	This paper
XVII	OH at 4	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	Tetralin	4
XVIII	OH at 4	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	1-Methyltetralin	This paper
XIX	OH at 4	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>3</sub>	1,1-Dimethyltetralin	2
XX	OH at 4	PhCH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH(OH)CH <sub>3</sub>		This paper
XXI	OH at 5	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-Methyltetralin	This paper
XXII	OH at 5	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	1-Ethyltetralin	This paper
XXIII	OH at 5	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>3</sub>	1-Isopropyltetralin	This paper
XXIV	OH at 6	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	1-n-Propyltetralin	This paper

b. Olefins				
XXV	Δ at 2	PhCH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>3</sub>	1,1-Dimethylindane	4
XXVI	Δ at 3	PhCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	Polymer	4
XXVII	Δ at 3	PhCH <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>3</sub>	1,1-Dimethyltetralin	2
XXVIII	Δ at 4	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	1-Methyltetralin	This paper
XXIX	Δ at 5	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	1-Ethyltetralin	This paper

<sup>a</sup> PhCH<sub>2</sub>C(CH<sub>3</sub>)(OH)CH<sub>3</sub> also yields a polymer when dehydrated by sulfuric acid.

(a) One olefin (XXVIII) and four different alcohols (V, XIV, XVIII and XXI) all gave 1-methyltetralin.

The formation of the tetralin from the olefin (XXIX) apparently involves a preliminary shift in the position of the double bond, from Position 5 to Position 4, prior to cyclization, and illustrates the strong tendency in such cyclizations to form six- rather than seven-membered rings.

A similar shift in the location of the unsaturation must be assumed for the olefin constituting the intermediate product in the conversion of either the alcohol (V) or (XXIV) into a tetralin.

Such trans-location of double bonds has been observed frequently, under the influence of alkalis,<sup>5</sup> but not often under that of sulfuric acid. Norris and Joubert<sup>6</sup> found that the latter caused

the following rearrangement: (CH<sub>3</sub>)<sub>2</sub>CHCH=CH<sub>2</sub> → (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>3</sub>. In their study of the effect of sulfuric upon oleic acid, Michael, Constantin and Saytzeff<sup>7</sup> reported a change in the position of the double bond. Panagoulas,<sup>8</sup> although unable to confirm this shift, suggested that there might be involved a preliminary addition of the sulfuric acid to the unsaturation followed by its splitting off again in a different way; but both Brooks and Humphrey<sup>9</sup> and Linhart,<sup>10</sup> have proven that such sulfuric esters are entirely too stable to allow for such a mechanism. Whitmore<sup>11</sup> has advanced the interesting postulate

(7) (a) Michael, Constantin and Saytzeff, *J. prakt. Chem.*, [2] **35**, 369 (1887); (b) **37**, 269 (1888).

(8) Panagoulas, "Inaug. Dissertat.," University of Leipzig, 1930, p. 13.

(9) Brooks and Humphrey, *THIS JOURNAL*, **40**, 826 (1918).

(10) Linhart, *Am. J. Sci.*, **35**, 283 (1913).

(11) (a) Whitmore, *THIS JOURNAL*, **54**, 3277, footnote 13 (1932); (b) *Ind. Eng. Chem.*, **26**, 94 (1934).

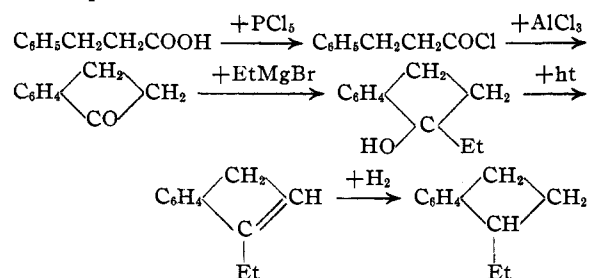
(5) Klages, *Ber.*, **37**, 2301 (1904); etc.

(6) Norris and Joubert, *THIS JOURNAL*, **49**, 873 (1927).

of the successive addition and removal of a proton. If the proton removed is not the same as the one added, the result will then be a change in the original position of the double bond.

The alcohol (XVIII) may yield the methyl-tetralin either by a direct cyclodehydration, or through a cyclization of an intermediate olefin. When the cyclization of this alcohol (XVIII) was interrupted before completion and the reaction mixture titrated with bromine, the presence of 30-40% of olefin was indicated. The inference is therefore that even in this case, where the structure of the alcohol seemed so favorable for a direct cyclodehydration, the cyclization proceeded chiefly through the olefin.

In the case of the 1-phenylpentanol-3 (XIV), there was the possibility of the formation of the isomeric 1-ethylindane instead of the methyl-tetralin, although Bogert and Davidson<sup>4</sup> found that the analogously constituted 1-phenylbutanol-3 (IX) yielded a polymer but no indane under similar conditions. As further proof that our product was actually 1-methyltetralin and not 1-ethylindane, the latter was synthesized by the steps



The 1-ethylindane so prepared was totally different from the product obtained by the cyclodehydration of (XIV).

The application which Whitmore<sup>11</sup> has made of his hypothesis of rearrangements to cyclizations of this type, requires the saturation of one of the doubly bound carbons by a proton from the benzene nucleus, followed by the mutual saturation of the two deficient carbon atoms. It is not clear how this hypothesis accounts for the non-formation of 1-ethylindane from the 1-phenylpentanol-3 (XIV), as noted above. In such cases, it is possible that the explanation may lie in the relative velocities of formation of five- and six-membered rings.

Thorpe and his co-workers<sup>12</sup> found that, in

(12) (a) Attwood, Stevenson and Thorpe, *J. Chem. Soc.*, **123**, 1755 (1923); (b) Speight, Stevenson and Thorpe, *ibid.*, **126**, 2185 (1924).

the analogous cyclization of phenylated carboxylic acids in the presence of sulfuric acid, six-membered rings could be formed at 0°, whereas the formation of five-membered ones required a temperature of 100° or above. So far as the experiments of Bogert and Davidson<sup>4</sup> went, the presence of a *gem*-dimethyl group in the side chain led in every instance to the formation of an indane.

The limit of this shifting of the unsaturation in the intermediate olefins to yield tetralins from phenylated pentanols appears to have been reached with 1-phenylpentanol-1 (I), which gave only a polymer and no tetralin.

(b) The two alcohols (XV) and (XIX), and the olefin (XXVII) into which they are converted by dehydration, all gave 1,1-dimethyltetralin,<sup>2</sup> corresponding to the conversion of the alcohols (V), (XIV), (XVIII) and (XXI), and the olefin (XXVIII), into 1-methyltetralin.

(c) The transition of (XXII), (XXIII), (XXIV) and (XXIX) into the ethyl and propyl tetralins, rather than into cycles of more than six carbons is a further illustration of the mobile character of the olefin unsaturation. From its structural analogy to the lower homologs (XI) and (XIX), which yielded, respectively, five- and six-membered cycles, the 1-phenyl-5-methylhexanol-5 (XXIII) might have been expected to form a seven- rather than the six-membered system actually obtained. It is noteworthy that the yield in this instance (35%) was much lower than usual in the cyclization of our other tertiary alcohols, and Darzens and Lévy<sup>13</sup> were unable to obtain any bicyclic compound whatever from a carboxylic derivative of similar type.

(d) 1-Phenyl-3-methylpentanol-2 (VI) and 1-phenyl-3-methylpentanol-3 (XVI) proved especially interesting, because in their dehydration by sulfuric acid the velocities of formation of the possible five- and six-membered cycles were more nearly balanced, with the result that both were obtained.

For the pentanol-2 (VI), the ratio of 1-methyl-1-ethylindane formed to 1,2-dimethyltetralin was approximately 3:1; for the pentanol-3 (XVI), this ratio was reversed, being about 1:4. These alcohols thus represent the intermediate, or transition, stage between the indane-producing compounds described by Bogert and Davidson,<sup>4</sup> and those of the present paper and of Bogert, Davidson and Apfelbaum,<sup>2</sup> which formed tetralins preferably.

(13) Darzens and Lévy, *Compt. rend.*, **191**, 1455 (1930).

In view of these results with alcohols (VI) and (XVI), it is our belief that the 1-phenyl-3-methylpentanol-4 (XX), when cyclized similarly, will yield a still larger proportion of the 1,2-dimethyltetralin, with little, or perhaps none, of the 1-methyl-1-ethylindane. Unfortunately, we have not yet succeeded in preparing this alcohol (XX).

Other, more complex, tertiary alcohols have been reported as giving more than one cyclic system,<sup>14,15</sup> but the isolation and identification of the resulting hydrocarbons were so difficult that their structures are still in some doubt.

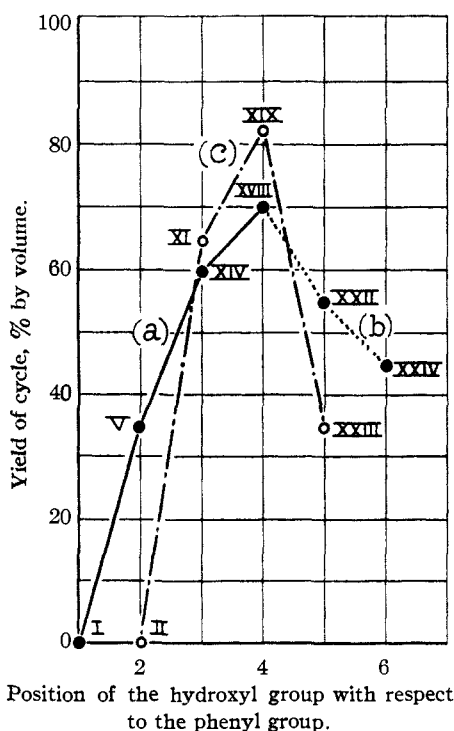


Fig. 1.—Yield of cycles as a function of the position of the hydroxyl group: Curves (a) and (b), phenylated secondary pentanols; curve (c), phenylated tertiary alcohols. Roman numerals refer to Table A.

In Fig. 1 we have plotted the yields of cyclization products as a function of the position of the hydroxyl group. Curve (a) concerns the group of secondary alcohols which gave 1-methyltetralin. In these experiments the initial concentration of sulfuric acid was identical (90%), and the yields therefore are more fairly comparable. It is to be noted that these yields increase as the OH approaches Position 4, the phenyl group being taken

as Position 1. Curve (b) represents two additional secondary alcohols, of similar structure, and shows that the yields decrease as the hydroxyl recedes from Position 4. The results depicted by Curve (c) are not strictly comparable, since the experimental conditions were different but, nevertheless, the curve shows the same trend.

Under the conditions of our experiments, it may be concluded that phenylated alcohols and olefins of the type studied, with an unbranched normal linear side chain of 5-7 carbon atoms, which carries an olefin, or potential olefin, unsaturation and a free ortho position on the benzene nucleus, can be cyclized to a tetralin by the action of sulfuric acid; except in those instances where the hydroxyl (I) or the double bond (styrenes) is carried by the same carbon as the phenyl group, when polymers result. The influence of the position of the unsaturation upon the yield of tetralin has just been discussed in connection with Fig. 1.

When the side chain bears a methyl group at 3 (Ph at 1), as in (VI) and (XVI), both indane and tetralin derivatives may be formed.

**Acknowledgments.**—In the prosecution of this research, we were aided by several good friends to whom our grateful thanks are due. Ethylene oxide was supplied by the Carbide & Carbon Chemicals Corporation, of New York, through the courtesy of Dr. George O. Curme, Jr.; ethyl acetoacetate, by the U. S. Industrial Chemical Co., Inc., New York, thanks to Dr. H. W. Haines. We are also under obligations to Professor Homer Adkins, of the University of Wisconsin, for giving us the benefit of his considerable experience in distillations with Widmer columns. Financial assistance, in connection with the large amount of analytical work necessary, was provided through the generosity of the Committee on the Cyrus M. Warren Fund of the American Academy of Arts and Sciences. The experimental work on the propyl-naphthalenes recorded beyond was carried out by Mr. N. Bakalar of these Laboratories, to whom we are greatly indebted.

### Experimental

The thermometers used in our experiments were calibrated against others which had been certified by the U. S. Bureau of Standards. Corrections for exposed stems were made for all boiling points and melting points recorded. Melting points were read while the temperature of the bath was being raised at the rate of 2° per minute. Density determinations were made with a pycnometer of about 1 cc. capacity and were accurate to  $\pm 0.0002$ .

(14) Fulton and Robinson, *J. Chem. Soc.*, 1463 (1933).

(15) Cook and Hewett, *ibid.*, 365 (1934).

Refractive indices were measured with a Pulfrich refractometer to  $\pm 0.00002$ , using the 5875 Å. line of the helium spectrum. For the purpose of calculating the molecular refractivity, this line may be used instead of the usual sodium D line without introducing an error greater than 0.01 in the value for (RL).



As will be seen in Table G, the observed molecular refractivities (RL) of all of our cyclization products, both indanes and tetralins, showed a considerable exaltation (EM) above the calculated values. Von Auwers<sup>16</sup> found this to be true for tetralin itself, and when the molecular refractivity recorded by him for that compound was used in calculating RL for its alkyl derivatives, results were obtained which checked well with the equation. Thus, the observed value for 1-methyltetralin from various

This removed most of the more volatile impurities. The residue was extracted with benzene, the benzene extracts washed, dried and fractioned under reduced pressure, to separate the alcohol from the dibenzyl formed as a by-product. Analysis indicated that the alcohol even then was not entirely pure, but further fractionation under diminished pressure failed to remove the last traces of impurities.

In the preparation both of this and of the antecedent alcohol (I), less than the theoretical quantity of aldehyde was used, so as to reduce the undesirable side reactions likely to occur in the presence of any (even local) excess of the latter.

**1-Phenylpentanol-3 (XIV).**—Hewitt and Kenyon<sup>21</sup> obtained this alcohol by reduction of 1-phenylpentanone-3.

TABLE B  
PREPARATION OF INTERMEDIATE ALCOHOLS AND OLEFINS

Table A	Alcohol	From
I	PhCH(OH)(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	PhCHO + CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> MgBr
V	PhCH <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	PhCH <sub>2</sub> MgCl + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO
VI	PhCH <sub>2</sub> CH(OH)CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	PhCH <sub>2</sub> CHO + CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )MgBr
XIV	Ph(CH <sub>2</sub> ) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub>	Ph(CH <sub>2</sub> ) <sub>2</sub> CHO + CH <sub>3</sub> CH <sub>2</sub> MgBr
XVI	Ph(CH <sub>2</sub> ) <sub>2</sub> C(CH <sub>3</sub> )(OH)CH <sub>2</sub> CH <sub>3</sub>	Ph(CH <sub>2</sub> ) <sub>2</sub> MgBr + CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>
XVII	Ph(CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	Ph(CH <sub>2</sub> ) <sub>2</sub> MgBr + 
XVII	Ph(CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	Ph(CH <sub>2</sub> ) <sub>2</sub> MgBr + HCHO
XVIII	Ph(CH <sub>2</sub> ) <sub>3</sub> CH(OH)CH <sub>3</sub>	Ph(CH <sub>2</sub> ) <sub>2</sub> MgBr + CH <sub>3</sub> COH
XXI	Ph(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OH	Ph(CH <sub>2</sub> ) <sub>3</sub> MgBr + 
XXI	Ph(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OH	Ph(CH <sub>2</sub> ) <sub>3</sub> MgBr + HCHO
XXII	Ph(CH <sub>2</sub> ) <sub>4</sub> CH(OH)CH <sub>3</sub>	Ph(CH <sub>2</sub> ) <sub>3</sub> MgBr + CH <sub>3</sub> CHO
XXIII	Ph(CH <sub>2</sub> ) <sub>4</sub> C(CH <sub>3</sub> )(OH)CH <sub>3</sub>	Ph(CH <sub>2</sub> ) <sub>3</sub> MgBr + CH <sub>3</sub> COCH <sub>3</sub>
XXIV	Ph(CH <sub>2</sub> ) <sub>3</sub> CH(OH)CH <sub>3</sub>	Ph(CH <sub>2</sub> ) <sub>2</sub> MgBr + CH <sub>3</sub> CHO
XXVIII	Ph(CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	Ph(CH <sub>2</sub> ) <sub>2</sub> MgBr + BrCH <sub>2</sub> CH=CH <sub>2</sub>
XXVIII	Ph(CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	Ph(CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH + H <sub>3</sub> PO <sub>4</sub>
XXIX	Ph(CH <sub>2</sub> ) <sub>4</sub> CH=CH <sub>2</sub>	Ph(CH <sub>2</sub> ) <sub>3</sub> MgBr + BrCH <sub>2</sub> CH=CH <sub>2</sub>

sources, as given in Table H, was 47.53–47.56, whereas that calculated as the sum of the atomic refractivities was 47.20. When, however, von Auwers' figure for tetralin (42.95) was used, the calculated value for 1-methyltetralin was 47.53, and the results were equally satisfactory for the other tetralin derivatives.

In the case of the indanes likewise (Table G), the molecular exaltation (EM) was even greater than for the analogous tetralins. The value of (EM) for indane, given by von Auwers' measurements on that compound,<sup>17</sup> was +0.51. Our figures for the 1-ethyl and 1-methyl-1-ethyl derivatives were, respectively, +0.56 and +0.54.

#### A. Preparation of Materials

##### Intermediate Alcohols and Olefins

The preparation and identification of the alcohols and olefins used in our experiments are summarized in Tables B, C and D. All of the alcohols so obtained were colorless transparent oily liquids.

In the preparation of 1-phenylpentanol-2 (V), the reaction mixture was distilled with steam until the amount of oil going over was less than 3% of the total distillate.

(16) Von Auwers, *Ber.*, **46**, 2990 (1913).

(17) Von Auwers, *Ann.*, **415**, 106 (1918).

TABLE C  
YIELD AND B. P. OF INTERMEDIATE ALCOHOLS AND OLEFINS

Table A	Yield, g. %	B. p., found °C.	B. p., found press., mm.	B. p. in literature °C.	Press., mm.	Ref.
I	81 62	137	21	120–5	20	20
V <sup>a</sup>	35 28	127	15			
VI	37 31	132	15			
XIV	62 50	130	15	143	19	21
XVI	107 60	138	20			
XVII	90 60	137	14	140	14	18
XVIII	123 75	134–135	16			
XXI	140 68	151	13	155	20	18
XXII	64 72	148	18			
XXIII	64 71	143	14			
XXIV	53 69	164	23			
XXVIII	32 55	206		203–204		19
XXIX	44 70	104	17	94–95	10	19

<sup>a</sup> Probably contained traces of impurities.

(18) Von Braun, *Ber.*, **44**, 2867 (1911).

(19) Von Braun, Deutsch and Schmatloch, *ibid.*, **45**, 1246 (1912).

(20) Fourneau, Montaigne and Puyal, *Anales soc. espan. fis quim.*, **18**, 323 (1920); *C. A.*, **16**, 240 (1922).

(21) Hewitt and Kenyon, *J. Chem. Soc.*, **127**, 1096 (1925).

TABLE D  
 IDENTIFICATION OF ALCOHOLS AND OLEFINS

Table A	Analyses, %						$d_4^{25}$	$n_D^{25}$	Calcd.	RL	Obs.
	C	Calcd.	H	C	Found	H					
V <sup>a</sup>	80.42		9.83	81.03		9.83	0.9579	1.51017	50.93		51.26
VI	80.83		10.18	80.60		10.18	.9576	1.50714	55.54		55.38
XVI	80.83		10.18	80.52		10.23	.9582	1.50981	55.54		55.58
XVIII	80.42		9.83	80.24		9.77	.9643	1.51110	50.93		51.00
XXII	80.83		10.18	80.45		10.05	.9567	1.50787	55.54		55.49
XXIII	81.19		10.49	81.06		10.68	.9429	1.50362	60.16		60.31
XXIV	81.19		10.49	81.14		10.09	.9482	1.50575	60.16		60.19

<sup>a</sup> Probably contained traces of impurities.

**1-Phenyl-3-methylpentanol-3 (XVI).**—Phenylethylmagnesium bromide when condensed with methyl ethyl ketone, separated from the dry ether solution as a solid which hydrolyzed so rapidly on exposure to the air that it was impractical to remove it by filtration, and its ether suspension therefore was decomposed by a mixture of ice and cold acetic acid, to avoid dehydration, and the resulting tertiary alcohol was then purified in the usual way.

By the two processes used for the production of **1-phenylbutanol-4 (XVII)**, the yield was approximately the same (60–61%). That in which ethylene oxide was used,<sup>22</sup> however, proved the more satisfactory.

**1-Phenyl-3-methylpentanol-4 (XX).**—Attempts were made to synthesize this alcohol by the following two methods: (a)  $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{MgBr} + \text{CH}_3\text{CHO}$ , and (b)  $\text{PhCH}_2\text{CH}_2\text{C}(\text{Ac})(\text{COOR})\text{Na} + \text{MeI}$ , etc.  $\xrightarrow{+\text{redn.}}$   $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{COCH}_3 \xrightarrow{+\text{redn.}}$   $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_3$ . Both methods have failed so far to yield the alcohol sought.

**Phenylurethans.**—For the full identification of the alcohols, the phenylurethans were prepared as follows.

A mixture of 0.01 mole of the alcohol with 0.01 mole of phenyl isocyanate was heated (90°) for three hours. The resulting solid, or viscous liquid, was dissolved in 30 cc. of boiling petroleum ether (b. p. 40–50°) and the solution filtered. As the filtrate cooled, the urethan separated in rossets of colorless needles, which were recrystallized to constant melting point from the same solvent; yield, 70–80%. Better results were obtained with the tertiary alcohols (XVI) and (XXIII) by allowing

 TABLE E  
 PHENYLURETHANS

(Table A) alc.	M. p., °C.	Analyses, %			
		C	Calcd.	H	Found
V	80	76.28		7.44	76.19 7.46
VI	103	76.72		7.80	76.77 7.87
XIV	74 <sup>a</sup>				
XVI	94	76.72		7.80	77.01 7.60
XVIII	57	76.28		7.44	76.31 7.31
XXII	65	76.72		7.80	76.70 7.89
XXIII	64.5	77.12		8.13	77.51 8.15

<sup>a</sup> M. p. of phthalate. This agrees with the melting point found by Hewitt and Kenyon<sup>21</sup> for the phthalate of their product.

(22) Dreger, "Organic Syntheses," Coll. Vol. I, 1932, p. 299.

the mixture of alcohol and isocyanate to stand for five or six days in a tightly stoppered bottle, at the end of which time it set to a solid mass of urethan. The phenylheptanol (XXIV) would not form a solid urethan even after standing for several months.

Melting points and analyses of these phenylurethans are given in Table E.

## B. Cyclization

A study of the conditions best suited to the cyclization of secondary alcohols by sulfuric acid showed that they required a more concentrated acid than the corresponding tertiary alcohols. Bogert and Davidson<sup>4</sup> found that an 85% acid gave the best results with the tertiary alcohols they examined; but that with the secondary, a stronger acid was needed, or the 85% acid had to be used in larger amount, at a higher temperature and heated for a longer time. Our experience was similar, for when we used upon a secondary alcohol an 85% acid under conditions suitable for the dehydration of a tertiary alcohol, the product was a mixture of olefin and cycle, as proven by a bromine titration.

The following procedure therefore was adopted for the cyclization of our alcohols and olefins, except in the case of the primary alcohol (XXI). With careful control of time and temperature, the yields could be duplicated to within approximately 1%.

One volume (20 cc.) of the alcohol (or olefin) was added very slowly (forty to fifty minutes), with efficient stirring, to 1.5 volumes of 90% (by titration) sulfuric acid in a 100-cc. beaker immersed in an ice-bath, maintaining the temperature of the mixture at 9–10°. The ice-bath was then removed and the stirring continued for two hours longer. The temperature rose slowly to 30–35°, after which it fell to that of the room (25–30°). The reaction mixture was diluted with 250 cc. of a mixture of ice water, part of which was used to rinse the beaker and stirrer. The whole was then distilled directly, the apparatus being so arranged that the aqueous part of the distillate was returned automatically to the distilling flask. This steam distillation carried over the cyclized product leaving be-

hind any polymer or sulfonic acid. When the quantity of oil going over amounted to less than 0.5% of the total distillate, the distillation was interrupted. If high purity was essential, as in the determination of the physical constants of the products, this steam distillation was repeated, for a trace of polymer was occasionally carried over in the first distillation. The volatile hydrocarbon was separated, dried over calcium chloride and distilled at atmospheric pressure. The results are summarized in Table F.

TABLE F  
PRODUCTS OF CYCLIZATION

Initial compound (see Table A)	Product	B. p., °C.	Yield, % by volume
I	Polymer	163-5 at 2 mm.	100
V <sup>a</sup>	1-Me-tetralin	218-220	35
VI	1-Me-1-Et-indane	218	50
VI	1,2-Di-Me-tetralin	235	
XIV	1-Me-tetralin	218-219	60
XVI	1-Me-1-Et-indane	218	87
XVI	1,2-Di-Me-tetralin	235	
XVIII	1-Me-tetralin	218-219	70
XXI	1-Me-tetralin	218-219	
XXII	1-Et-tetralin	237-238	55
XXIII	1- <i>i</i> -Pr-tetralin	247	35
XXIV	1- <i>n</i> -Pr-tetralin	253	45
XXVIII	1-Me-tetralin	218-219	75
XXIX	1-Et-tetralin	237-238	65
1-Indanone	1-Et-indane	212	80

<sup>a</sup> Slightly impure.

In addition to the losses inevitably associated with separation and purification, the yields of cyclized products

The cyclization of 1-phenyl-3-methylpentanol-3 (XVI) resulted in the formation of a mixture (A) of 1-methyl-1-ethylindane and 1,2-dimethyltetralin, in the proportion of 20.5% of the former to 79.5% of the latter. These were separated by fractional distillation at 6 mm. pressure, using a Widmer column and a barostat.

The above cyclization process, repeated with 85% in place of 90% sulfuric acid, gave a ratio of 27.5 of the indane to 72.5 of the tetralin.

Similarly, cyclization of 1-phenyl-3-methylpentanol-2 (VI) gave a 50% (by volume) yield of a mixture of 1-methyl-1-ethylindane (76.3%) and 1,2-dimethyltetralin (23.7%). This mixture had  $d_4^{25}$  0.9326 and  $n_{D}^{25}$  1.52127.

When 1-phenylpentanol-4 (XVIII) was dehydrated with 85% sulfuric acid, under the above standard conditions, there resulted a mixture of 1-methyltetralin and olefin. A titration of this mixture in carbon tetrachloride solution below 10° (at higher temperatures, some substitution occurred) with a 10% solution of bromine in the same solvent, disclosed the presence of 20-30% of olefin. Further treatment of the mixture with 90% sulfuric acid, however, changed it all to the tetralin.

If 90% sulfuric acid, instead of 85%, were used upon the original alcohol (XVIII) and the reaction mixture were distilled with steam immediately after removal of the ice-bath, the result again was a mixture of tetralin and olefin. A bromine titration of this indicated the presence of 30-40% of the olefin.

### C. Identification of the Cyclization Products

Analyses and physical constants for the cyclization products are presented in Table G.

TABLE G  
IDENTIFICATION OF CYCLIZATION PRODUCTS

Product	Source	Analyses, %				$d_4^{25}$	$n_{D}^{25}$	Calcd. <sup>RL</sup>	Obs.	EM
		Calcd. C	H	Found C	H					
Polymer	I	90.34	9.66	90.57	9.64					
1-Me-tetralin	XIV	90.34	9.66	90.34	9.68	0.9536	1.53316	47.20	47.56	+0.36
1-Me-tetralin	XVIII					.9547	1.53366	47.20	47.55	+ .35
1-Me-tetralin	XXVIII					.9546	1.53332	47.20	47.53	+ .33
1,2-Di-Me-tetralin	XVI	89.93	10.07	90.22	10.19	.9433	1.52652	51.82	52.15	+ .33
1-Et-tetralin	XXII	89.93	10.07	90.14	10.08	.9498	1.52999	51.82	52.08	+ .26
1-Et-tetralin	XXIX					.9511	1.52992	51.82	52.00	+ .18
1- <i>n</i> -Pr-tetralin	XXIV	89.58	10.42	89.66	10.62	.9415	1.52496	56.43	56.68	+ .25
1- <i>i</i> -Pr-tetralin	XXIII	89.58	10.42	89.37	10.14	.9450	1.52705	56.43	56.66	+ .23
1-Et-indane	1-Indanone	90.34	9.66	90.49	9.58	.9348	1.52286	47.20	47.76	+ .56
1-Me-1-Et-indane	XVI	89.93	10.07	90.08	10.07	.9232	1.51563	51.82	52.36	+ .54

were further cut down by the fact that there was invariably some polymerization of the intermediate olefins.

Inasmuch as primary alcohols usually form stable esters in contact with sulfuric acid, phosphoric acid was employed for the dehydration of such alcohols, as described in our previous communication.<sup>4</sup> The only primary alcohols used in the present series of experiments were the 1-phenylbutanol-4 (XVII) and the 1-phenylpentanol-5 (XXI).

The polymer obtained from 1-phenylpentanol-1 (I) was a thick viscous oil, of the same percentage composition as 1-methyltetralin, and was probably a dimer. Analogous to the formation of phenylated indanes,<sup>18</sup> it may have been a phenylated tetralin.

**Synthesis of 1-Ethylindane.**—Hydrocinnamyl chloride was condensed to 1-indanone by the action of aluminum chloride, as described by Amagat.<sup>23</sup> This was subjected to the action of ethylmagnesium bromide, followed by dehydration of the intermediate tertiary alcohol by distillation at 20 mm. pressure, as recommended by Von Braun.<sup>24</sup> The 1-ethylindene so obtained was dissolved in 95% alcohol and reduced by hydrogen under pressure, in the presence of the Adams platinum oxide catalyst.<sup>25</sup>

(23) Amagat, *Bull. soc. chim.*, [4] **41**, 942 (1927).

(24) Von Braun, *Ber.*, **50**, 1660 (1917).

(25) (a) Voorhees and Adams, *This Journal*, **44**, 1402 (1922); (b) Kern, Shriner and Adams, *ibid.*, **47**, 1147 (1925).

Distillation of the crude product gave an 80% yield of 1-ethylindane. It was necessary to treat this product with some 90% sulfuric acid, to remove, by polymerization, traces of the 1-ethylindene, which imparted a yellow color to the indane and could not be eliminated by repeated distillations. After the sulfuric treatment, steam distillation carried over the indane, leaving behind the polymerized indene.

#### Oxidation

**1-Methyltetralin.**—Attempts to prepare homogeneous crystalline nitro derivatives or sulfonic acids proved fruitless. Oxidized with potassium permanganate, phthalic acid resulted (m. p. of anhydride, 131°).

**1,2-Dimethyltetralin,** similarly oxidized with potassium permanganate, yielded phthalic acid (m. p. of anhydride, 131°), and no methylethylhomophthalic acid (HOOC<sub>6</sub>-H<sub>4</sub>CMeEtCOOH).

**1-Methyl-1-ethylindane,** oxidized with potassium permanganate, gave 1-methyl-1-ethylhomophthalic acid, as a colorless crystalline solid, melting at 115° with loss of water, and forming a liquid anhydride when distilled under reduced pressure.

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.86; H, 6.35. Found: C, 64.76; H, 6.55.

The formation of this acid is analogous to that of the 1,1-dimethylhomophthalic from 1,1-dimethylindane.<sup>4</sup> No phthalic acid could be isolated from the oxidation product, but a qualitative test<sup>26</sup> demonstrated its presence.

#### Dehydrogenation

This was carried out with all products of cyclization by fusion with sulfur. In the case of the tetralins, this yielded the corresponding naphthalene derivatives, which were easily identified through their picrates. The indanes, subjected to the same treatment, either gave a tarry mass or a volatile product which formed no picrate. The hydrogenated compounds themselves, such as 1-methyltetralin and 1-ethylindane, gave no insoluble picrates under the conditions used for the preparation of the naphthalene picrates.

The sulfur fusion<sup>27</sup> was conducted most satisfactorily as follows: 2 g. of the hydrocarbon and the calculated quantity of sulfur were placed in a 5-cc. distilling flask, the exit tube of which was bent up and carried a small reflux condenser. After three hours of heating, the evolution of hydrogen sulfide subsided considerably, so that the reflux could be turned down and the flask contents allowed to distil. In this way about 60–70% of the original tetralin was dehydrogenated to the corresponding naphthalene derivative.

This distillate (1.3–1.5 g.) of naphthalene derivative was dissolved in 10 cc. of 95% alcohol, the solution heated to boiling and mixed with a boiling solution of 3 g. of picric acid in 30 cc. of the same solvent. The picrate which separated (2–3 g.) as the solution cooled was recrystallized from 95% alcohol to constant melting point. Mixed melting points were always taken with authentic products and where the same product had been prepared from various initial materials, as, for example, in the case

(26) Breithut and Apfelbaum, *Ind. Eng. Chem.*, **17**, 534 (1925).

(27) (a) Vesterberg, *Ber.*, **36**, 4201 (1903); (b) Ruzicka and Rudolph, *Helv. Chim. Acta*, **10**, 918 (1927).

of the 1-methylnaphthalene obtained from 1-methyltetralin of four different origins. In no case was any appreciable depression observed. The melting points of these picrates are given in Table H.

TABLE H  
PICRATES OF NAPHTHALENE DERIVATIVES

Tetralin deriv.	Source	Naphthalene deriv.	M. p., °C.		Ref.
			Found	Lit.	
1-Methyl	V	1-Methyl	141–142	141–142	28
1-Methyl	XIV	1-Methyl	141–142		
1-Methyl	XVIII	1-Methyl	141–142		
1-Methyl	XXVIII	1-Methyl	141–142		
1,2-Dimethyl	XVI	1,2-Dimethyl	130–131	129.5–130.5	29
1-Ethyl	XXII	1-Ethyl	100	98	30
1-Ethyl	XXIX	1-Ethyl	100		
1- <i>n</i> -Propyl	XXIV	1- <i>n</i> -Propyl	91–2	92 <sup>a</sup>	31
1- <i>i</i> -Propyl	XXIII	1- <i>i</i> -Propyl	85–6	85–6	32

<sup>a</sup> Prepared in these Laboratories by Mr. N. Bakalar.

**1-*n*-Propylnaphthalene.**—When 1-*n*-propyltetralin was dehydrogenated by fusion with sulfur, the naphthalene derivative obtained yielded a picrate which melted at 91–92°.

Bargellini and Melacini<sup>31</sup> have reported a 1-propylnaphthalene picrate of m. p. 141–142°. These authors obtained their 1-propylnaphthalene by reduction of 1-naphthyl ethyl ketone, which latter was prepared, as described by Rousset,<sup>33</sup> from naphthalene, propionyl chloride and aluminum chloride. This Friedel-Crafts reaction resulted in the simultaneous production of both 1- and 2-naphthyl ethyl ketones, which were separated by virtue of the fact that the 1-naphthyl derivative formed an insoluble picrate. The "1-propylnaphthalene" used by Bargellini and Melacini formed a picrate, as noted, of m. p. 141–142°, and their "2-propylnaphthalene" a picrate which melted at 90–92°, in agreement with the melting point of the picrate of our propylnaphthalene.

Since it seemed highly improbable that a 2-propyl derivative could be formed by the action of sulfuric acid upon our 1-phenylheptanol-6 (XXIV), the work of the above investigators was repeated in these Laboratories by Mr. N. Bakalar.

Rousset's results were checked exactly, including the oxidation of the 1-naphthyl ethyl ketone to 1-naphthoic acid. Bargellini and Melacini reduced their naphthyl ethyl ketone by heating it with phosphorus and iodine for seven or eight days. By the Clemmensen method,<sup>34</sup> we succeeded in reducing our naphthyl ethyl ketone to the corresponding propylnaphthalene in six hours. This propylnaphthalene was driven over by steam and then distilled at atmospheric pressure, giving a 45% yield of a product boiling at 275–276°. Bargellini and Melacini gave the boiling point of their "1-propylnaphthalene" as 274–275°. The picrate prepared from our product melted at 92°. Mixed with the picrate of the 1-propylnaphthalene obtained by dehydrogenation of our 1-propyltetralin, the m. p. was 91–92°. Based upon these results, it is our

(28) Meyer and Fricke, *Ber.*, **47**, 2770 (1914).

(29) Carnelutti, *ibid.*, **13**, 1672 (1880).

(30) Herzenberg and V. Winterfeld, *ibid.*, **64**, 1044 (1931).

(31) Bargellini and Melacini, *Gazz. chim. ital.*, **38**, II, 570 (1908).

(32) Schroeter, Lichtenstadt and Irineu, *Ber.*, **51**, 1599 (1918).

(33) Rousset, *Bull. soc. chim.*, [3] **15**, 62 (1896).

(34) (a) Clemmensen, *Ber.*, **46**, 1837 (1913); (b) *ibid.*, **47**, 51 (1914); (c) *ibid.*, **47**, 681 (1914).



belief that, in some way or other, Bargellini and Melacini must have confused the two isomers, and that the literature should be corrected accordingly.

### Summary

1. A series of phenylated alcohols and olefins, closely related structurally, has been prepared, including a number of new ones.

2. These alcohols and olefins have been subjected to the action of sulfuric acid (85 or 90%) and the conditions studied under which they are cyclized.

3. Evidence is presented that generally these alcohols pass first into one or more olefins, which then cyclize or polymerize, rather than the cycles being formed directly by condensation of the alcoholic OH with an ortho-H of the benzene nucleus.

4. The unsaturation in these phenylated olefins is of such a character that it can apparently occupy different locations in the side

chain and still form the same cycle, although the yield varies accordingly. This shift in the location of the double bond is established by the structure of the cyclization products. Thus 1-methyltetralin is formed from 1-phenylpentanol when the OH group is in position 2, 3, 4 or 5.

5. Two alcohols have been found containing the Ph—C—C—C(C)—C—C—skeleton, each of which gives with sulfuric acid both a 5- and a 6-membered cycle.

6. Those cyclization reactions which lead to tetralins offer a convenient method for the preparation of naphthalene derivatives, for the tetralins are easily dehydrogenated by fusion with sulfur.

7. Evidence is submitted showing that the alpha- and beta-propylnaphthalenes, as recorded in the literature, have been confused.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## On the Mechanism of Reactions of Acetoacetic Ester, the Enolates and Structurally Related Compounds. I. C- and O-Alkylation

BY ARTHUR MICHAEL

According to Kekulé's<sup>1</sup> interpretation of intermolecular chemical change, molecules are attracted to one another by chemical affinity, forming at first a loosely-joined, double molecule. The coherence of the atoms in the approaching molecules becomes loosened, and this condition continues in the double molecule, until it separates into two, chemically different, molecules.<sup>2</sup>

Representing "the vibratory volumes"<sup>3</sup> of atoms by spheres, chemical union has been designated by their segmentation, increasing with the magnitude of the bound chemical energy holding atoms together, and polymolecular, chemical

union by contact between the spheres.<sup>4</sup> Two atoms, A and B, of an organic molecule may enter into polymolecular union with two, directly joined atoms, X and Y, of a reagent with no or slight energetic hindrance, only when tetragon-, pentagon- and hexagon-shaped, polymolecular complexes may be formed. Projections of the polymolecular part of such graphic structures upon plane surfaces lead to the following representations of chemical and polymolecular union.<sup>5</sup>

Sodium acetoacetic ester consists of  $\text{CH}_3\text{C}(\text{ONa})=\text{CHCOOEt}$ , with some  $\text{CH}_3\text{COCH}=\text{C}(\text{ONa})\text{OEt}$ <sup>6</sup> and isomeric polymolecules of types

(4) Michael, *THIS JOURNAL*, **40**, 705 (1918). Polymolecular union in structural formulas will be indicated by asterisks between the respective atoms and unsaturation by periods over their symbols.

(5) When all four atoms A, B, C and D in III are unsaturated, addition may proceed at A and D, with appearance of double linkage between B and C, or at A + B and C + D according to I. Since ring-formation appears to be "a periodic function of the length of the chain" [Michael, *J. prakt. Chem.*, **49**, 28 (1894); **60**, 337 (1899)] polymolecular union may be relatively favored at the terminal atoms in certain longer chains in substances; but it is probable that this would occur with greater chemical hindrance than in the formation of penta- and hexacyclic polymolecules. These views may be applied to all chemical reactions and elucidate many now unexplained.

(6) Michael, *ibid.*, **37**, 488 (1888). The formation of acetylmalonic ester (less than 10%) in the chlorocarbonic ester reaction is experimental evidence of the existence of the second, car-

(1) Kekulé, *Ann.*, **106**, 141 (1858); "Lehrb. org. Chem.," Vol. I, 1868, p. 142.

(2) These views received but little attention for many years. Armstrong [*J. Chem. Soc.*, **51**, 261 (1887)] supported them and Thiele [*Ann.*, **306**, 92 (1899)], without cognizance apparently, used partial valences in place of chemical affinity. This was criticized by Erlenmeyer, Jr. [*Ann.*, **316**, 49 (1901)], who applied Kekulé's views to explain the formation of cyclic compounds. Michael [*Ber.*, **34**, 4028 (1901); *THIS JOURNAL*, **32**, 991 (1910)], conceived the double or "polymolecule" as resulting from the affinities exerted between the free chemical energy of certain atoms in the respective molecules. He, therefore, concluded that they must have definite intermolecular atomic structures and that isomeric polymolecules may be formed in accordance with the "principle of partition" [*J. prakt. Chem.*, **60**, 341, 431 (1899); *Ber.*, **39**, 2138 (1906)].

(3) Traube, "Raum der Atome," 1899, p. 70.