

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

## THE VARIATIONS IN THE BEHAVIOR OF PHENYLETHENES AND ETHANES DURING CATALYTIC HYDROGENATION

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A study of the effect of carbon containing substituents upon the ease of hydrogenation over nickel<sup>1</sup> has been continued by hydrogenating the series of compounds, phenylethylene (styrene), 1,2-diphenylethylene (stilbene), 1,1,2-triphenylethylene, 1,1,2,2-tetraphenylethylene, and 1,1-diphenyl-2-phenoxyethylene. These five compounds offer the opportunity of determining the effect of the phenyl group upon the hydrogenation of alkene linkages. The ethylenes are thereby converted into the corresponding ethane derivatives, which in turn offer the possibility of noting the effect of the presence of phenyl (and cyclohexyl) groups upon the hydrogenation of other phenyl groups. Pentaphenylethane and triphenylacetophenone were added to the group because it became apparent that a third effect of structure was manifesting itself, *i. e.*, the weakening of carbon to carbon linkages.

**Phenyl Groups and the Hydrogenation of Ethenes.**—There is presented in the first half of Table I a summary of certain data obtained in the hydrogenation of various phenyl substituted ethylenes. It is impractical to make an *exact* comparison of the effect of phenyl groups upon the hydrogenation of ethene linkages because there appears to be no set of conditions under which these five ethenes will undergo hydrogenation at a measurable rate. The pressure of hydrogen as well as the temperature has a marked effect upon the rate of these hydrogenations of ethene linkages. For example, 1,2-diphenylethylene at 20° required fifteen minutes at 93 atm., thirty-five minutes at 30 atm. and eighty minutes at 2.7 atm.

Phenylethylene was so readily hydrogenated over nickel that it was completely converted into ethylbenzene at 20° and 2.5 atm. pressure. The substitution of a second phenyl group in ethylene lowered the reactivity of the double bond but slightly toward hydrogenation. The substitution of a third phenyl group increased by ten-fold the time required at 20° for its hydrogenation as compared with diphenylethylene. Tetraphenylethylene was sufficiently resistant to hydrogenation so that the reaction did not occur at a measurable rate at 20° over nickel, and required over two hours at 100° under 125 atm. pressure. 1,1-Diphenyl-2-phenoxyethylene was hydrogenated much more rapidly than was triphenylethylene but much less rapidly than was diphenylethylene.

The ethene linkage in four of the phenylethylenes was also hydrogenated

<sup>1</sup> Adkins, Zartman and Cramer, *THIS JOURNAL*, **53**, 1425 (1931).

TABLE I

Hydrogen acceptor	Milli- moles	HYDROGENATION OF PHENYL ETHENES AND ETHANES						Product(s) <sup>a</sup>
		Time, min.	Temp., °C.	Press., atm.	Catalyst, g.	Solvent, ml.		
				Ethylene Linkages				
Phenylethylene (styrene)	200	75	20	2.5 ± 0.5	2 (Ni)	None	Ethylbenzene	
Phenylethylene	200	25	20	34 ± 6	2 (Ni)	None	Ethylbenzene	
Phenylethylene	200	7	125	125 ± 11	1 (Cu-Cr)	None	Ethylbenzene	
1,2-Diphenylethylene (stilbene)	100	80	20	2.7 ± 0.3	2 (Ni)	75 <sup>b</sup>	1,2-Diphenylethane	
1,2-Diphenylethylene	100	35	20	30 ± 3	2 (Ni)	75 <sup>b</sup>	1,2-Diphenylethane	
1,2-Diphenylethylene	100	15	20	93 ± 6	2 (Ni)	75 <sup>b</sup>	1,2-Diphenylethane	
1,2-Diphenylethylene	100	4	150	130 ± 6	1 (Cu-Cr)	75 <sup>b</sup>	1,2-Diphenylethane	
1,1,2-Triphenylethylene	100	150	20	95 ± 5	2 (Ni)	75 <sup>b</sup>	1,1,2-Triphenylethane	
1,1,2-Triphenylethylene	100	5	150	135 ± 3	1 (Cu-Cr)	75 <sup>b</sup>	1,1,2-Triphenylethane	
1,1,2,2-Tetraphenylethylene	36	130	100	125 ± 3	2 (Ni)	75 <sup>b</sup>	1,1,2,2-Tetraphenylethane	
1,1,2,2-Tetraphenylethylene	36	15	150	133 ± 4	1 (Cu-Cr)	75 <sup>b</sup>	1,1,2,2-Tetraphenylethane	
1,1-Diphenyl-2-phenoxyethylene	100	80	100	110 ± 10	2 (Ni)	75 <sup>b</sup>	1,1-Diphenyl-2-phenoxyethane	
				Phenyl Groups				
Phenylethylene <sup>d</sup>	200	100 <sup>c</sup>	125	113 ± 10	2 (Ni)	None	Cyclohexylethane	
1,2-Diphenylethylene <sup>d</sup>	100	185 <sup>c</sup>	120	103 ± 16	2 (Ni)	75 <sup>b</sup>	1,2-Dicyclohexylethane	
1,2-Diphenylethane	55	35 <sup>c</sup>	175	120 ± 7	2 (Ni)	50 <sup>b</sup>	1,2-Dicyclohexylethane	
1,1-Diphenylethane	55	105 <sup>c</sup>	175	125 ± 3	2 (Ni)	75 <sup>b</sup>	1,1-Dicyclohexylethane	
1,1,2-Triphenylethylene <sup>d</sup>	100	225 <sup>c</sup>	160	110 ± 16	2 (Ni)	75 <sup>b</sup>	1,1,2-Tricyclohexylethane	
1,1,2,2-Tetraphenylethylene <sup>d</sup>	50	130 <sup>c</sup>	175	113 ± 20	4 (Ni)	75 <sup>b</sup>	1,1,2,2-Tetracyclohexylethane	
1,1,1,2-Tetraphenylethane	40	125 <sup>c</sup> 240	175	116 ± 16	2 (Ni)	75 <sup>b</sup>	1,1,1,2-Tetracyclohexylethane	
1,1-Diphenyl-2-phenoxyethylene <sup>d</sup>	100	300 <sup>c</sup> 330	160	107 ± 11	2 (Ni)	75 <sup>b</sup>	Cyclohexyl-2,2-dicyclohexylethyl ether	
Pentaphenylethane	37	270 <sup>c</sup> 390	125	115 ± 17	4 (Ni)	75 <sup>b</sup>	Pentacyclohexylethane (6%) Tricyclohexylmethane (77%) Dicyclohexylmethane (58%)	
Pentaphenylethane	37	150 <sup>c</sup> 200	160	115 ± 15	2 (Ni)	75 <sup>b</sup>	Pentacyclohexylethane (20%) Tricyclohexylmethane (42%) Dicyclohexylmethane (45%)	

<sup>a</sup> All yields were practically quantitative except from pentaphenylethane. <sup>b</sup> Methylcyclohexane. <sup>c</sup> Time for hydrogenation of "middle 80%," *i. e.*, disregarding the time for the first and last 10%. The greater significance of these figures as compared with the time for complete hydrogenation has been previously discussed.<sup>4</sup> <sup>d</sup> The alkene linkage is so rapidly hydrogenated in this compound, under the conditions of the hydrogenation, that it was accomplished long before the temperature for the hydrogenation of the phenyl groups was reached.

over a copper-chromium oxide catalyst at 150°. This catalyst is not active for hydrogenation at temperatures as low as nickel. However, it is very active from 125–150° so that the hydrogenation of all four of the phenylethylenes went to completion within a few minutes at 150°.

The activity of the copper-chromium oxide catalyst in hydrogenating alkene linkages as first noted by Connor<sup>2</sup> and further illustrated above seems significant in connection with Lazier's hypothesis that oxides do not catalyze the hydrogenation of carbon to carbon double bonds.<sup>3</sup>

**Effect of Phenyl Groups upon the Hydrogenation of Phenyl Groups.**—A precise comparison of the rate of hydrogenation of the six phenylethanes under consideration would be very difficult of attainment. The difference in ease of hydrogenation makes it questionable whether all of them could be hydrogenated at a measurable rate at the same temperature. Even if this were possible there appears to be no ratio of catalyst to hydrogen acceptor which would enable a fair comparison to be made. This is true because there is such a large difference in the amount of hydrogen absorbed per mole of the various phenylethanes. The hydrogenation of ethylbenzene requires 3 moles of hydrogen while pentaphenylethane requires 15 moles of hydrogen. This would necessitate a choice being made between keeping the ratio of catalyst constant with respect, (1) to weight of hydrogen acceptor, or (2) to moles of hydrogen acceptor, or (3) to moles of hydrogen to be absorbed. One of these choices would be as open to criticism as another. A further complication enters in that the effect of any slow deactivation of the catalyst by heat or by the presence of accidental impurities is greatly magnified in the slower hydrogenations. Thus the slow hydrogenations become many times slower, while the more rapid hydrogenations are little, if any, affected by deactivation of the catalyst.

Thus it is impossible to draw any conclusions of a quantitative nature from the data in Table I on the hydrogenation of various phenylethanes to cyclohexylethanes. However, the following rather important conclusion appears to be justified. Although there is somewhat of a decrease in the rate of hydrogenation of phenyl groups as the number of these groups in the molecule increases, it will be seen that this decrease in rate is small when the great increase in molecular weight, number of unsaturated linkages, and complexity of the molecule is taken into consideration. This conclusion is also in accord with the finding that triphenylbenzene was hydrogenated without difficulty to tricyclohexylcyclohexane.<sup>1</sup> It thus appears that increase in the *number* of phenyl groups in a molecule does not inhibit or greatly slow down its rate of hydrogenation.

**Effect of Phenyl Groups upon the Cleavage of Carbon to Carbon Bonds.**—The hydrogenation over nickel of the ethanes containing four

<sup>2</sup> Adkins and Connor, *THIS JOURNAL*, **53**, 1091 (1931).

<sup>3</sup> Vaughn and Lazier, *ibid.*, **53**, 3719 (1931).

or less phenyl groups in the molecule proceeded smoothly and quantitatively to the corresponding cyclohexylethanes at temperatures from 120 to 175°. A very different result was obtained when pentaphenylethane was subjected to hydrogenation over nickel. In the case of this compound, even at 125°, the molecule was rapidly cleaved so that the major products were di- and tricyclohexylmethanes. A 20% yield of pentacyclohexylethane was obtained by a more rapid hydrogenation at 160°.

The further study (data in Table II) of the cleavage of carbon to carbon linkages by hydrogenation was carried out chiefly by using a copper-chromium oxide catalyst rather than nickel. This was advantageous, because while copper-chromium oxide catalyzes the cleavage it does not induce the hydrogenation of phenyl groups, so that the cleavage of the phenylethanes may be distinguished from a possible cleavage of cyclohexylethanes. Thus pentaphenylethane over the copper catalyst at 200° gave di- and triphenylmethane rather than the cyclohexylmethanes obtained with nickel. With this catalyst at 200° tetraphenylethane was also cleaved to diphenylmethane, and even triphenylethane showed a detectable amount of cleavage. However, diphenylethane appears to be quite resistant to cleavage. An oxygen substituted phenylethane (triphenylacetophenone) was also cleaved. The oxygen to carbon linkage in diphenylphenoxyethylene was also cleaved, the products being phenol and diphenylethane.

TABLE II  
CLEAVAGE WITH COPPER-CHROMIUM OXIDE CATALYST<sup>a</sup>

Hydrogen acceptor	Milli-moles	Time, hrs.	Catalyst, g.	Solvent, ml. <sup>b</sup>	Product(s)
Triphenylacetophenone ( $\beta$ -benzopinacol)	55	10	2	50	81% Triphenylmethane
Triphenylacetophenone	50	8	2	100	22% Toluene 65% Triphenylmethane 12% Tetraphenylethylene
1,1,2,2-Tetraphenylethylene	24	6.5	2	50	90% Diphenylmethane
1,1-Diphenyl-2-phenoxyethylene	100	7.5	2	75	75% Phenol 67% 1,1-Diphenylethane
1,1,1,2-Tetraphenylethane	9	12	1	25	70% Toluene 85% Triphenylmethane
Pentaphenylethane	20	12	1	25	60% Diphenylmethane 80% Triphenylmethane
1,1,2-Triphenylethylene	10	12	1	25	5% Diphenylmethane 70% 1,1,2-Triphenylethylene
1,1,2,2-Tetracyclohexylethane	10	12	2	25	No reaction
1,1,1,2-Tetracyclohexylethane	13	12	2	25	No reaction
Pentacyclohexylethane	7	12	1	25	No reaction <sup>c</sup>

<sup>a</sup> 200° and 130 atm. pressure of hydrogen. <sup>b</sup> Methylcyclohexane is the solvent referred to except in the second experiment where ether was used. <sup>c</sup> There was also no cleavage in nine hours at 200°, 0.5 g. nickel catalyst with 2.7 millimoles of the ethane.

In contrast with the above is the finding that the cyclohexylethanes, even pentacyclohexylethane, resisted cleavage even after twelve hours at 200° in the presence of an active nickel or copper-chromium oxide catalyst.

TABLE III  
 ANALYSES AND PHYSICAL CONSTANTS

Compound	Molecular formula or physical constants	M. p. or b. p. °C. obs.	Mm.	Analyses, %					
				Carbon			Hydrogen		
				Calcd.	Found		Calcd.	Found	
Ethylcyclohexane	B. p. <sup>d</sup> 128-130°	B 128-130	738						
1,2-Diphenylethane	M. p. <sup>a</sup> 51-52°	M 52-53							
1,2-Dicyclohexylethane	B. p. <sup>a</sup> 270-271°; <sup>b</sup> 274-275°; <sup>c</sup> 147-148.5° (12 mm.)	B 266-268	748						
1,1,2-Triphenylethane	M. p. <sup>e</sup> 54-55°; <sup>f</sup> 53.5-54.5°; <sup>h</sup> 54°	M 54-55 B 209-211	12						
1,1,2-Tricyclohexylethane <sup>1</sup>	C <sub>20</sub> H <sub>36</sub>	B 191-192	8	86.86	86.80	86.94	13.14	13.37	13.28
1,1,2,2-Tetraphenylethane	M. p. <sup>f</sup> 209°	M 208-209							
1,1,2,2-Tetracyclohexylethane	C <sub>26</sub> H <sub>42</sub>	M 158-159		87.06	87.04	87.06	12.94	12.98	13.15
1,1,1,2-Tetracyclohexylethane <sup>f</sup>	C <sub>26</sub> H <sub>46</sub>	M 112-114		87.06	87.07	86.96	12.94	12.66	12.46
1,1-Diphenylethane	B. p. <sup>a</sup> 270-272°; <sup>e</sup> 143° (15 mm.); <sup>h</sup> 268-270°	B 130-133	10						
1,1-Diphenyl-2-phenoxyethane	C <sub>20</sub> H <sub>18</sub> O	M 64-65 B 214-217	8	87.54	87.24	87.54	6.62	6.79	6.82
Cyclohexyl 2,2-dicyclohexylethyl ether <sup>k</sup>	C <sub>20</sub> H <sub>36</sub> O	B 200.5-201	10	82.11	82.09	82.09	12.42	12.32	12.56
1,1-Dicyclohexylethane	B. p. <sup>a</sup> 256-257°; <sup>e</sup> 112° (7 mm.)	B 264-265	740						
Tetraphenylethylene	M. p. <sup>f</sup> 221°	M 221-222							
Pentacyclohexylethane <sup>f</sup>	C <sub>28</sub> H <sub>46</sub>	M 191-192		87.18	86.97	86.72	12.82	12.90	12.96
1,1-Diphenyl-2-phenoxyethylene	C <sub>20</sub> H <sub>16</sub> O	M 58-59 B 235	23	88.19	88.05	87.82	5.93	6.00	5.88

<sup>a</sup> Sabatier and Murat, *Compt. rend.*, **154**, 1771 (1923). <sup>b</sup> Ipatiev, *Ber.*, **40**, 1281 (1907). <sup>c</sup> Adams and Marshall, *This Journal*, **50**, 1970 (1928). <sup>d</sup> Sabatier and Senderens, *Compt. rend.*, **132**, 1255 (1901). <sup>e</sup> Boeseken and Bastet, *Rec. trav. chim.*, **32**, 184 (1913). <sup>f</sup> Biltz, *Ann.*, **296**, 221 (1897). <sup>g</sup> Lévy and Lagrave, *Bull. soc. chim.*, **43**, 437 (1928). <sup>h</sup> Klages and Heilmann, *Ber.*, **37**, 1455 (1904). <sup>i</sup>  $d_{25}^{25}$  0.9301;  $n_D^{25}$  1.5030;  $MR'_D$ , calcd. 87.86; found, 87.81. <sup>j</sup>  $d_{25}^{25}$  0.9636;  $n_D^{25}$  1.5217;  $MR'_D$ , calcd. 113.38; found, 113.39. The compound solidified after several weeks. <sup>k</sup>  $d_{25}^{25}$  0.9495;  $n_D^{25}$  1.4947;  $MR'_D$ , calcd. 89.54; found, 89.69. <sup>l</sup> The di- and tricyclohexylmethanes had the properties previously noted.<sup>1</sup>

It thus appears that the successive substitution of phenyl groups in ethane lowers the binding power of the carbon to carbon linkage of ethane so that with five phenyl substituents the linkage may be broken at 125° with nickel as a catalyst. With a copper-chromium oxide catalyst the linkage may be broken at 200° when there are only three phenyl substituents. Cyclohexyl groups showed no labilizing effect upon carbon to carbon linkages.

### Experimental Part

The preparation of the copper-chromium oxide<sup>2</sup> and the nickel<sup>4</sup> ("sodium bicarbonate type A") catalysts have been described previously. Processes described in the literature were used for the preparation of phenylethylene (styrene) (b. p. 44–46° (40 mm.));<sup>5</sup> 1,2-diphenylethylene (m. p. 121–123°);<sup>6</sup> 1,1,2-triphenylethylene (m. p. 67–68°);<sup>7</sup> triphenylacetophenone (m. p. 168–170°);<sup>8</sup> 1,1,1,2-tetraphenylethane (m. p. 142–143°)<sup>9</sup> pentaphenylethane (softened at 161–162°)<sup>9</sup> and tetraphenylethylene (m. p. 220–222°);<sup>10</sup> except that in the case of the last compound dehydration was accomplished with sulfuric acid rather than with acetyl chloride. The monophenyl ether of unsymmetrical diphenylethyleneglycol ((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(OH)CH<sub>2</sub>OC<sub>6</sub>H<sub>5</sub>) was prepared as by Stoermer,<sup>11</sup> and converted into 1,1-diphenyl-2-phenoxyethylene in a 98% yield by refluxing it for twenty hours with 500 ml. of methanol containing 10 ml. of concentrated sulfuric acid. The resulting oil was taken up with carbon tetrachloride, distilled under reduced pressure, and crystallized from 95% alcohol or acetic acid and water. The data on the physical constants and analysis of this and other important compounds encountered in this investigation are given in Table III.

The experimental methods and apparatus were essentially the same as those previously described.<sup>12</sup> The products were separated by fractionation through Widmer columns of suitable size. The solvents used for the recrystallizations of three of the new compounds are as follows: 1,1,1,2-tetracyclohexylethane from ethyl acetate, 1,1,2,2-tetracyclohexylethane from benzene or methylcyclohexane, and pentacyclohexylethane from ethyl acetate.

### Summary

An increase in the number of phenyl groups in the phenylethenes increases the temperature and (or) pressure required for hydrogenation to the corresponding phenyl and cyclohexylethanes, and decreases the rate of hydrogenation under comparable conditions. However, the increase in difficulty of hydrogenation with increase in molecular weight is not large since tetraphenylethylene could be converted into the ethane at 100° and pentaphenylethane into pentacyclohexylethane at 125° at reasonably rapid rates.

<sup>4</sup> Adkins and Covert, *J. Phys. Chem.*, **35**, 1684 (1931).

<sup>5</sup> "Organic Syntheses," John Wiley and Sons, New York, 1928, Vol. VIII, p. 84.

<sup>6</sup> Hell, *Ber.*, **37**, 453 (1904).

<sup>7</sup> Hell and Wiegandt, *ibid.*, **37**, 1429 (1904).

<sup>8</sup> Paal, *ibid.*, **17**, 911 (1884).

<sup>9</sup> Gomberg and Cone, *ibid.*, **39**, 1461 (1906).

<sup>10</sup> Lévy and Lagrave, *Bull. soc. chim.*, **43**, 437 (1928).

<sup>11</sup> Stoermer, *Ber.*, **39**, 2288 (1906).

<sup>12</sup> Adkins and Cramer, *THIS JOURNAL*, **52**, 4349 (1930).

The successive substitution of phenyl groups in ethane materially lowers the stability of the linkage of the ethane carbon atoms so that when three phenyl groups are in the molecule the ethane may be cleaved at 200° over a copper–chromium oxide catalyst. Pentaphenylethane may be cleaved over nickel at temperatures as low as 125°. The labilizing effect (if any) of cyclohexyl groups on the ethane carbon atoms is so small that pentacyclohexylethane was perfectly stable at 200° over nickel or copper–chromium oxide catalysts.

Four cyclohexylethanes and three ethers have been prepared and described for the first time. Further evidence of the activity of the copper–chromium oxide catalyst for the hydrogenation of alkene linkages has been presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY]

## THE PREPARATION AND PROPERTIES OF A DOUBLE SERIES OF ALIPHATIC MERCAPTANS<sup>1,2,3</sup>

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Though aliphatic mercaptans have been known for nearly a century, our knowledge concerning any of them except a few of the lower ones is not extensive. The purpose of the present investigation was to prepare the normal and alpha secondary mercaptans up to nonyl in high purity for accurate determinations of their physical properties and to provide materials for studies of their reactions, some of which have been published. It seemed desirable to have these series complete for the comparisons of properties within the series and with the corresponding series of alcohols.

The literature on the mercaptans through butyl is too extensive to quote. *n*-Amyl mercaptan was prepared by Pexters,<sup>6</sup> *n*-hexyl by Pelouze and

<sup>1</sup> This paper contains some results obtained in an investigation on "The Reactions of Certain Selected Organic Sulfur Compounds" listed as Project No. 28 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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<sup>6</sup> Pexters, *Bull. sci. acad. roy. Belg.*, 801 (1906).