[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE POLYMETHYLBENZENES. II. THE MELTING POINTS OF THE TETRAMETHYLBENZENES, AND OF PENTA- AND HEXAMETHYLBENZENE, AND THE FREEZING POINT DIAGRAM OF MIXTURES OF DURENE AND ISODURENE

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The easiest method for preparing the polymethylbenzenes is by the direct methylation of commercial xylene[1] but at present the only pure polymethylbenzenes which can be isolated from the reaction mixture are durene, pentamethylbenzene and hexamethylbenzene. This is because alkylation, using the Friedel-Crafts reaction, yields all possible isomers, and while it is possible to separate by distillation the different steps in the alkylation, it is not possible to separate the isomers of the same step by this method. Durene (1,2,4,5-tetramethylbenzene) can, however, be made in this way because it has a relatively high melting point (80°) and can be frozen out of a mixture of its isomers containing relatively large proportions of it.

The yield of tetramethylbenzenes obtained by methylating xylene usually amounts to about 35% based on the xylene used, and contains about 40–45% of durene. When this is frozen out, the filtrate contains all of the isodurene (1,2,3,5-) and prehnitene (1,2,3,4-), and this mixture is saturated, of course, with durene at the temperature of crystallization. This filtrate is at present useless as a source for isodurene and prehnitene because there is no known method by means of which the three tetramethylbenzenes can be separated from one another. The problem of this separation is now under investigation in this Laboratory, and the work reported in this paper deals with the preparation and (or) purification of each of the three tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene, and a determination of their melting points and the freezing-point diagram for the system durene–isodurene, together with some thermodynamic considerations based upon these experimental data.

Preparation and Purification of Materials

1. **Durene. Preparation[1] and Purification.**—Eight hundred grams of crude durene was recrystallized four times by dissolving it in an equal weight of hot 95% ethyl alcohol, then cooling to 0°, filtering and washing with a little cold alcohol. After four recrystallizations, the durene weighed 500 g. This was then recrystallized once from 300 g. of thiophene-free benzene, yielding 430 g. The melting point of the durene (determined in the ordinary way, using a capillary tube and not correcting) rose slowly after each recrystallization until the fourth and fifth recrystallizations, which gave products having practically the same melting points (79.3–79.9° for the fourth, and

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[1] Smith and Dobrovolny, THIS JOURNAL, 48, 1413 (1926).

79.3–79.7° for the fifth). The sample to be used for accurate determinations was then placed in a vacuum desiccator over phosphorus pentoxide for two or three days.

2. **Pentamethylbenzene. Preparation[1] and Purification.**—Five hundred and fifty grams of crude pentamethylbenzene, m. p. 49–51°, was recrystallized four times from its own weight of 95% ethyl alcohol, followed by one recrystallization from 60% of its weight of thiophene-free benzene. The melting point rose progressively and was 51.5–53.0° for the fourth recrystallization and 52.2–53.1° for the fifth. The yield was only 127 g., as pentamethylbenzene is very soluble in benzene. The final sample was placed in a vacum desiccator over phosphorus pentoxide for a few days.

3. **Hexamethylbenzene. Preparation[1] and Purification.**—Three hundred and fifteen grams of hexamethylbenzene, m. p. 157–161°, was recrystallized from 400 g. of chloroform. The first and second crops were combined, as they showed practically the same melting point; yield, 270 g.; m. p. 162–164°. This product was then recrystallized three times by dissolving it in twice its weight of boiling chloroform, adding its own weight of hot 95% ethyl alcohol and cooling; yield at this point, 200 g. This product was then recrystallized once from its own weight of thiophene-free benzene; yield, 147 g.; m. p. 164.3–164.8°. The final sample was placed in a vacuum desiccator over phosphorus pentoxide for a few days.

4. **Isodurene, 1,2,3,5-Tetramethylbenzene.**—This compound has been previously made from bromomesitylene. methyl iodide and sodium,[2] but the yields are very poor. In addition to this method of synthesis, Jacobsen[3] reports a synthesis from mesitylene, methyl chloride and aluminum chloride, while Claus and Foecking[4] report a synthesis from mesitylene, methyl iodide and aluminum chloride; in view of the effect of aluminum chloride on aromatic hydrocarbons, it is very doubtful if these last two syntheses yielded pure isodurene.[5]

The method of preparation used in this work is new and it gives a good yield of product which is easily purified, as the crude product contains no isomeric substances. The synthesis starts with pure mesitylene and involves the reactions

$$C_6H_3(CH_3)_3\text{-}(1,3.5) + Br_2 \longrightarrow C_6H_2Br(CH_3)_3 + HBr$$

$$C_6H_2Br(CH_3)_3 + Mg \longrightarrow C_6H_2(CH_3)_3MgBr$$

$$C_6H_2(CH_3)_3MgBr + (CH_3)_2SO_4 \longrightarrow C_6H_2(CH_3)_4\text{-}(1,2.3,5) + (CH_3)(MgBr)SO_4\ (?)$$

Bromination of Mesitylene.—Six hundred and thirty-six grams (5.3 moles) of pure mesitylene (b. p. 58.3–58.5° at 15 mm.) is dissolved in 600–700 g. of carbon tetrachloride and the solution placed in a 3-liter flask provided with a reflux condenser, motor-driven stirrer and a dropping funnel. The flask is placed in a cooling bath, the stirrer is started and the mesitylene is brominated by running into it a solution of 900 g. of bromine in 900 g. of carbon tetrachloride (about 5% excess of bromine). The bromination requires about three hours but the rate at which the bromine is added is limited only by the efficiency of the condenser, as the reaction itself is quite rapid. Direct sunlight should not be allowed to strike the flask, as this increases side-chain bromination, although it is not possible to prevent some of this even in very dim daylight. After the bromination is completed, the reaction mixture is allowed to stand for an hour or so at room temperature. It will then have a light yellow or orange color. It is washed with water and then with alkali, after which the solvent is removed by distillation through a good

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[2] Jannasch, *Ber.*, **8**, 356 (1875): Bielefeldt, *Ann.*, **198**, 380 (1879); Jannasch and Weiler, *Ber.*, **27**, 3442 (1894).

[3] Jacobsen, *ibid.*, **14**, 2629 (1881).

[4] Claus and Foecking, *ibid.*, **20**, 3097 (1887).

[5] See also Hofmann, *ibid.*, **17**, 1915 (1884); Armstrong and Miller, *ibid.*, **16**, 2259 (1883); Orndorff and Young, *Am. Chem. J.*, **15**, 267 (1893).

column. The oil remaining in the distilling flask is dark and fumes when heated, and to remove side-chain halogen compounds it is boiled for an hour or two with a solution of 50 g. of sodium in a liter of 95% ethyl alcohol and then allowed to stand overnight. Unless this treatment with sodium ethylate is carried out, it is impossible to get a product which will not evolve hydrogen bromide on standing or on distillation.

The alkaline solution is diluted with much water, bringing the oily layer to the top by adding ether. The ethereal solution is washed thoroughly with water, separated, dried over calcium chloride and the ether then distilled off. The remaining oil is fractionated *in vacuo* using a good column. If enough sodium ethylate has been used in the purification, the product will not give any trace of precipitate with alcoholic silver nitrate on standing for twenty-four hours; if it is to be used in a Grignard reaction, it should meet this silver nitrate test. It is a colorless oil. b. p. 105–107° at 16–17 mm., 102.5–103.5° at 14 mm.. m. p. −1 to +1°; yield, 800–900 g. (76 to 85%).

Grignard Reaction.—The apparatus consists of a 3-liter flask with 3 openings carrying a motor-driven stirrer. a dropping funnel and a reflux condenser, and provided with suitable calcium chloride guard tubes. In the flask are placed 48 g. of fine magnesium turnings,[6] 100 g. of bromomesitylene and 150 g. of ether, and the reaction is then started using the catalyst recommended by Gilman.[7] After the reaction has started, the stirrer is turned on and a solution of 298 g. of bromomesitylene in 600 g. of ether (total bromomesitylene, 398 g. = 2 moles) is added through the dropping funnel at such a rate that a brisk refluxing continues. After all of the halogen compound has been added, the reaction mixture is refluxed on the steam-bath until practically all of the magnesium is dissolved. The flask is then cooled and a solution of 600 g. of dimethyl sulfate (freshly distilled *in vacuo*) in 400 g. of ether is run in through the dropping funnel with *vigorous* stirring until the amount of precipitated solid renders stirring useless. The reaction is quite vigorous and as the solid magnesium compounds separate out there is violent bumping. After adding all of the dimethyl sulfate (two to three hours), the reaction mixture is allowed to stand overnight and is then decomposed by adding excess dilute hydrochloric acid. The layers are separated and the ether layer is washed with water two or three times until the magnesium salts are removed. after which the excess dimethyl sulfate is destroyed by adding strong sodium ethylate *carefully* and boiling for an hour. The alcohol is then washed out with water, the ether solution dried over calcium chloride and the ether boiled off. The orange oil remaining is heated on the steam-bath for three to four hours with 25–30 g. of sodium shavings, after which it is filtered and then fractionated *in vacuo* using an efficient column.

The products of two such runs, when combined and fractionated, gave the following: I, b. p. up to 85° at 18 mm.. 120 g.; II. b. p. 85–87° at 18 mm., 323 g.; III, b. p. above 87° at 18 mm. 10 g. (residue in the distilling flask). Fraction II is isodurene, with an almost constant boiling point of 86.5° at 18 mm. and a freezing point of −24.2 ±0.1°. The yield is slightly over 60%. Fraction I consists of regenerated mesitylene, which may be brominated and used again. If the yield of isodurene is based upon the mesitylene used up in the reaction instead of the mesitylene taken, it runs about 80%.

Although the isodurene made in this way is quite pure, for purposes of determining physical constants it was refractionated through a long (4-foot) jacketed column,[8] separating the middle half, which was then refractionated, again separating the middle

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[6] Gilman and Meyers, THIS JOURNAL, **45**, 159 (1923); Gilman and Zoellner, *ibid.*, **50**, 427 (1928).

[7] Gilman. *Rec. trav. chim.*, **47**, 19 (1928): **46**, 463 (1927). The authors are greatly indebted to Dr Gilman for private suggestions as to this procedure, and we take this opportunity of making acknowledgment.

[8] Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

half. This gave one quarter of the original material having a constant boiling point of 84.6–84.7° at 17 mm.

5. **Prehnitene, 1,2,3,4-Tetramethylbenzene.**—This was prepared from pentamethylbenzene through the Jacobsen reaction, according to the directions given in the paper by Smith and Lux. Purification: 492 g. of crude prehnitene was washed twice with concd. aqueous sodium hydroxide, then once with water, dried over calcium chloride and fractionated through a 4-foot jacketed Peters column. The prehnitene fraction which resulted weighed 393 g. and had a constant boiling point of 97–98° at 24–25 mm. This was refractionated and the middle half collected (b. p. 97.2–97.6° at 24.5 to 24.8 mm., freezing point −6.9°, weight 186 g.). This product was again fractionated, collecting a middle portion of 132 g., b. p. 96.9 to 97.9° at 24 mm., freezing point −6.8°. As the recorded melting point of prehnitene is higher than this figure,[9] it was decided to attempt a further purification by converting prehnitene into the monobromo compound, purifying this by crystallization, and then regenerating the prehnitene through the Grignard reaction. One hundred and forty-five grams of prehnitene b. p. 98.9–99.0° at 26 mm., was brominated in chloroform, using the same procedure and proportions of materials as were given previously for the bromination of mesitylene. The product was washed with sodium ethylate and purified also according to the procedure used in the case of bromomesitylene. The yield of bromoprehnitene was 180 g. or 77%; b. p. 166–167° at 50 mm.; m. p. +24°. This material, recrystallized twice from its own weight of petroleum ether gave 110 g., m. p. 26.2–26.4°. Although the recorded m. p. of bromoprehnitene is +30°,[10] no further purification was attempted because the crystallization is accompanied by relatively large losses; 80 g. of this material was converted into the Grignard reagent using the procedure already outlined in the case of bromomesitylene. The Grignard reaction with bromoprehnitene does not run as smoothly, however, as it does with bromomesitylene, for after decomposing with acid the yield of prehnitene was only 28 g. (61%). This was boiled with sodium ethylate for two hours: the alcohol then was washed out, the oil heated with metallic sodium for two hours and then allowed to stand overnight, after which it was filtered and distilled. There resulted 23 g. of colorless, highly refractive oil, b. p. 66.5–66.8° at 4 mm., freezing point −6.9°. It is doubtful whether any effective purification is obtained as a result of this long process, for the freezing point of −6.9° is practically the same as that of the product obtained by three fractional distillations of the crude prehnitene from the Jacobsen reaction (−6.8°). In order, however, to be certain of the purity of the prehnitene, it was purified by converting it into the picrate[11] as follows: 69 g. of picric acid (0.3 mole) and 42 g. of prehnitene (slightly more than 0.3 mole: b. p. of the sample used, 100.0–100.5° at 27.5 mm., freezing point −7.7°) were mixed together in a beaker and heated on the steam-bath until most of the solid had dissolved. Then 200 cc. of hot 95% ethyl alcohol was added, everything brought into solution and the mixture cooled to 0°. The picrate crystallizes beautifully in the form of bright yellow stout needles, and after one recrystallization from its own weight of ethyl alcohol melts at 89.5 to 90.5°. The melting point depends somewhat upon the rate at which the bath is heated and also upon the length of time that the picrate is exposed to the air, for it slowly loses prehnitene, and as this happens the color fades and the melting point rises until, after standing for about a week, it reaches the melting point and color of picric acid. This undoubtedly explains the higher melting points given for the picrate by Töhl (92–95°) and by Schultz and Würth (92–96°). The yield of recrystallized picrate was 52 g., or about 50%, though the

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[9] Jacobsen, *Ber.*, **19**, 1213 (1896), gives −4°; Töhl, *ibid.*, **21**, 905 (1888), gives −5°.

[10] Töhl and Eberhard, *ibid.*, **25**, 1526 (1892).

[11] Töhl, *ibid.*, **21**, 905 (1888); Schultz and Würth, *Chem. Centr.*, **76**, [1] 1443 (1905).

yield may be improved by using less alcohol in the preparation, as the second crop of crystals is as pure as the first. The picrate was decomposed by dropping it into an excess of concd. sodium hydroxide and steam distilling, when it gave practically the quantitative yield of prehnitene. The prehnitene is washed with alkali and then with water, dried and distilled. From 52 g. of pure picrate there resulted 17 g. of prehnitene and this, on distillation, gave 12 g. boiling at 75.0–75.5° (corr.) at 6.5 mm., and freezing at −6.4° (corr.).

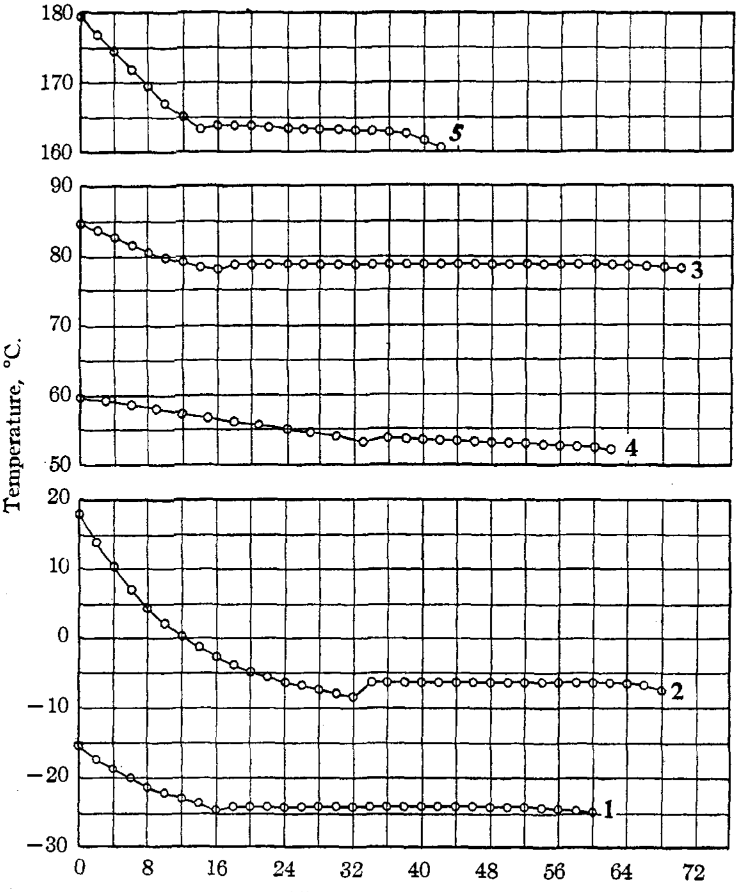

Fig. 1.—Cooling curves, freezing points of the polymethylbenzenes. 1, Isodurene (1,2,3,5-); 2, prehnitene (1,2,3,4-); 3, durene (1,2,4,5-); 4, pentamethylbenzene; 5, hexamethylbenzene.

Determination of Freezing Points.—The apparatus consisted essentially of the ordinary Beckmann Type for determining freezing points. The liquids used in the bath were water up to 100° and cottonseed oil for temperatures above 100°. For temperatures below that of the room, water and ice were used, while for temperatures below zero various freezing mixtures of ice and salt, ice and calcium chloride, or ice and hydrochloric acid were used. In a few cases carbon dioxide snow was used as the cooling agent, the temperature being limited by using as a bath a liquid freezing a few degrees below the freezing point of the sample. This procedure, however, is rather troublesome and does not have much advantage over a direct cooling bath of a freezing mixture, for with a little practice these freezing mixtures can be adjusted to almost any desired temperature and if a large enough bath is used, the temperature can be maintained for an hour without much difficulty. The thermometers used were all certified and in all cases the temperatures were corrected to total immersion. In taking the freezing points, the cooling curves were plotted, temperature against time, keeping the bath well below the temperature of the sample; in all cases the substances had been purified sufficiently so that at the freezing point there was a "plateau" in the curve and the temperature remained constant until all of the sample solidified. The results are given in Table I, together with the estimated accuracy, based chiefly on the length of the "plateau" in the freezing point curves, which are shown in Fig. 1.

TABLE I

CORRECTED FREEZING POINTS OF PURE POLYMETHYLBENZENES

Durene	79.28 ± 0.05°	Pentamethylbenzene	54.0 ± 0.1°
Isodurene	−24.0 ± 0.1°	Hexamethylbenzene	164.8 ± 0.1°
Prehnitene	− 6.40 ± 0.05°		

In much the same way the freezing point diagram for the system durene–isodurene was determined. The procedure in making up the sample was to start with a weighed amount of one of the pure constituents and add to it weighed amounts of the other, determining the freezing point of the mixture between each addition. There was always some supercooling,

TABLE II

FREEZING POINT DATA, SOLUTIONS OF ISODURENE IN DURENE

Mole fract. of durene	F. p., $t°$, °C.	Mole fract. of durene	F. p., $t°$, °C.	Mole fract. of durene	F. p., $t°$, °C.
100	79.28	62.68	57.41	25.23	18.75
94.04	76.27	55.76	52.21	21.35	10.19
88.76	73.47	49.90	47.47	17.26	2.50
84.00	70.86	45.40	43.35	16.00	− 3.17
79.40	68.30	41.70	39.69	14.00	−11.00
75.33	65.79	33.53	30.97	12.00	−16.35
68.70	61.55	28.85	23.53	10.00	−21.46

TABLE III

FREEZING Point DATA, SOLUTIONS OF DURENE IN ISODURENE

Isodurene, mol. fr.	100.00	99.00	98.02	97.00	96.02	95.07	94.12	93.00	92.00
F. p., $t°$	−24.02	−24.51	−24.94	−25.45	−26.00	−26.46	−26.95	−27.55	−28.10

but no attempt was made to correct for the amount of material separating out and the freezing point of the mixture was taken as the highest point to which the thermometer rose after crystals once appeared. The data are given in Tables II and III, and are shown graphically in Fig. 2.

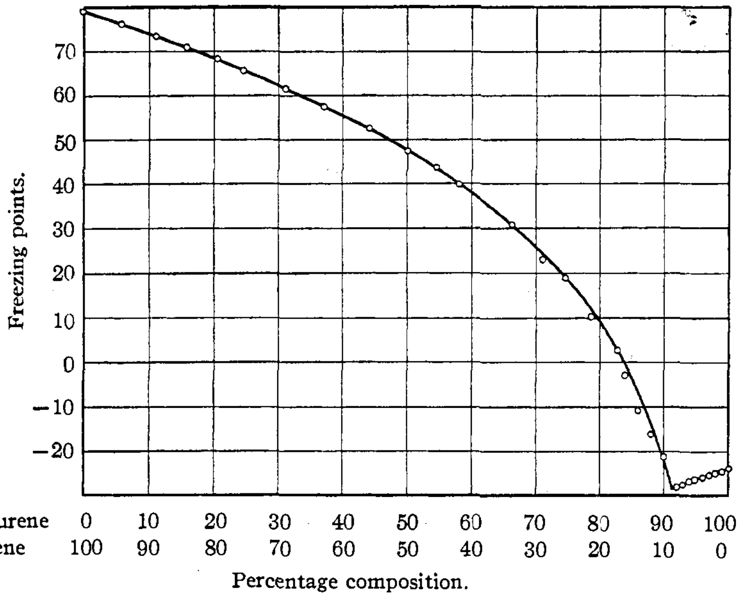

Fig. 2.—Freezing point diagram for the system durene–isodurene.

Discussion of the Results

A. Durene.—Assuming that durene and isodurene form an ideal liquid solution, at least over a certain range of concentrations, we obtain for the equilibrium constant, K_x (expressed in terms of mole fractions), the expression $K_x = x$ for the reaction

$$\text{Durene (solid)} \rightleftharpoons \text{Solution of Durene}$$

where x is the mole fraction of durene in the solution. Hence we may write

$$\frac{d \log_e x}{dT} = \frac{L_f}{RT^2} \text{ or } \frac{d \log_e x}{d(1/T)} = -\frac{L_f}{R}$$

where L_f is the molar latent heat of fusion of durene. Making the substitution, $u = 1000\ (1/T - 1/T_0)$, where T_0 is freezing point of pure durene, and changing to ordinary logarithms, we obtain

$$L_f \text{ (in calories)} = -4574 \frac{d \log_{10} x}{d\,u}$$

Over the range from 100% to about 66% of durene, it is found that the following equation represents satisfactorily the experimental data

$$-\log_{10} x = bu + cu^2$$

By the method of least squares, we find $b = 1.098$ and $c = 0.0993$. Hence

$$L_f = 4574\ (b + 2cu) = 5022 - 9.08 \times 10^5(1/T - 1/T_0)$$

For the temperature $T_0 = 352.38$, we find $L_f = 5022$ cal.

B. Isodurene.—The data for the freezing points cover the range from 100 to 92% isodurene with a maximum depression of the freezing point of only four degrees. An analysis of the results leads to the conclusion that liquid isodurene has a higher heat capacity than solid isodurene, but the accuracy of the measurements is not sufficient to enable us to make a more exact statement. The molar latent heat of fusion of isodurene turns out to be about 2550 calories.

Summary and Conclusions

1. The freezing points of all of the polymethylbenzenes containing four or more methyl groups have been determined, using carefully purified materials.
2. A new method for making isodurene in quantity is given.
3. The freezing point diagram for the system durene–isodurene has been studied, and from these data the latent heats of fusion have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA]

1,6-ADDITION OF HYDROGEN TO UNSATURATED 1,4-DIKETONES

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It is well known that conjugated systems of two or more multiple unions ending in oxygen are reduced with remarkable ease as compared with simple isolated ethylenic or carbonyl double linkages.[1] Typical examples are to be found in the conjugated systems of 1,2-diketones such as benzil, unsaturated 1,4-dicarbonyl and dinitro compounds such as fumaric and *o*-phthalic acids, unsaturated 1,4-diketones and ketonic acids, quinones, vat dyes and *o*-dinitrobenzenes; and doubly unsaturated 1,6-dicarbonyl and dinitro compounds such as muconic and *p*-phthalic acids and *p*-dinitrobenzene. The reductions of these compounds are generally interpreted as 1,4-, 1,6- or 1,8-addition of hydrogen to the terminal oxygen atoms to give dienols which, if the reductions are irreversible, immediately rearrange into stable forms or undergo some other secondary reaction such as the loss of water. Dibenzoylethylene (1), for example, is assumed to undergo the following changes in the course of reduction to dibenzoylethane (III).

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[1] Thiele, *Ann.*, **306**, 87 (1899): **308**, 333 (1899).