containing 30 ml. of benzene and 25 ml. of concentrated hydrochloric acid which stopped the reaction by converting all the free amine to the anilinium ion. The separatory funnel was shaken, allowed to stand and the aqueous layer was removed. The benzene layer was washed twice with water. Excess 0.1 *N* bromate–bromide solution was added to the aqueous layer and after the solution had been allowed to stand for 12 minutes an excess of potassium iodide was added. The iodine liberated was titrated with standard sodium thiosulfate. The excess bromate–bromide solution was never allowed to exceed 3 ml. of 0.1 *N* solution. Under these conditions it was shown by Chapman[5] that none of the other substances present, particularly ethanol, was oxidized or brominated.

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AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Oxidative Condensation of *p*-Cymene, Isopropylbenzene and Chloroisopropylbenzene[1]

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Oxidative condensation took place when air was passed through *p*-cymene at its reflux temperature. The principal identified products were 2,3-dimethyl-2,3-di-*p*-tolylbutane (di-*p*-cymene), *p*-acetyltoluene and dimethyl-*p*-tolylcarbinol. A 32% yield of di-*p*-cymene was obtained when aluminum turnings were used as a contacting material and the reaction was carried out in the presence of potassium carbonate. Oxidative condensation occurred also when isopropylbenzene was treated with air; 2,3-dimethyl-2,3-diphenylbutane was one of the principal products of reaction. A mixture of *o*-, *m*- and *p*-chloroisopropylbenzene yielded on oxidation a solid corresponding to di-chloroisopropylbenzene.

A crystalline substance, later identified as 2,3-dimethyl-2,3-di-*p*-tolylbutane ("di-*p*-cymene") was observed in the residue after distilling a large amount of *p*-cymene at atmospheric pressure. The distillation required several shutdowns before completion, allowing air each time to come in contact with the hot liquid. It was assumed that the formation of di-*p*-cymene resulted from oxidative condensation owing to the contact between the hot *p*-cymene and the air. This assumption was proved to be correct since it was found possible to prepare a large amount of the di-*p*-cymene by passing air through *p*-cymene at its reflux temperature. The study of oxidative condensation was extended to include isopropylbenzene and chloroisopropylbenzene.

To obtain comparative data the experiments were run for 18 hours during which not more than 20% of the alkylbenzene used underwent reaction.

***p*-Cymene. Effect of Potassium Carbonate and Contacting Materials.**—It was found that when air was passed through *p*-cymene at near reflux temperature oxidation occurred. The principal identified products were di-*p*-cymene, *p*-acetyltoluene and dimethyl-*p*-tolylcarbinol. Smaller amounts of 2-methyl-2,4-di-*p*-tolylpentane (VIII), *p*-isopropylbenzoic acid, *p*-isopropenyltoluene, methanol, water, methane, ethane and carbon dioxide were formed.

When glass rings were placed in the reaction flask to give a more intimate contact between the air and the *p*-cymene, the extent of reaction was increased.

The addition of potassium carbonate decreased the amount of higher boiling material and increased the amount of carbinol in the product without materially affecting the amount of the other compounds formed. It seems that the potassium carbonate reacted with the acids produced thus preventing the dehydration of the carbinol to isopropenyltoluene, which under these conditions condenses to higher boiling compounds. This conclusion was further supported by an experiment in which a small amount of benzoic acid was added to the *p*-cymene; the product contained less carbinol and more high boiling material than when potassium carbonate was added.

The addition of a small amount of 2,3-dimethyl-6-*t*-butylphenol to the *p*-cymene decreased the extent of reaction.

It was found that by substituting aluminum turnings for glass rings as the contact material, the yield of dimeric material was increased. The addition of potassium carbonate further enhanced the yield of dimeric compounds and at the same time increased the yield of carbinol and reduced the amount of high boiling material formed. The experimental results are summarized in Table I.

Other contacting materials such as turnings made from magnesium, iron, copper, zinc, nickel, silver and aluminum bronze were also evaluated. Di-*p*-cymene was formed in the presence of all of these to an extent equal to or higher than when glass rings were used, but to a lower extent than when aluminum turnings was the contacting material. There was a marked increase in the production of compounds boiling above the dimer when contacting materials other than aluminum turnings were used; this was especially true in the case of cadmium and silver.

Effect of Temperature.—The temperature at which the oxidation was carried out greatly affected the composition of the reaction product. At 140°, in the presence of glass rings, 79% of the reacted product was ketone–carbinol fraction and only 3.2% was dimeric compound. At 171°, however, the oxygenated compounds amounted only to 48% while the amount of the dimeric compound increased to 22.9%. The peroxide number of the product was higher at the lower temperature, but the extent of reaction was about the same at the two temperatures. A similar effect of temperature was noticed when aluminum turnings were used as a contact material.

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[1] U. S. Patent 2,614,130 (October 14, 1952).

[2] The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University.

[3] Deceased November 29, 1952.

TABLE I

OXIDATIVE CONDENSATION OF *p*-CYMENE: EFFECT OF CONTACT MATERIAL, TEMPERATURE AND ADDITIVES

The experiments were made with 600 g. of *p*-cymene. The rate of the air passed was 12 liters per hour and the duration was 18 hours.

Expt. no.	1	2	3	4	5	6	7	8
Contact material,[a] kind	glass rings				aluminum turnings			glass rings
Temp., °C.	140	171	171	171	140	171	171	171
Additive kind	. . .	. . .	K_2CO_3	benzoic acid	. . .	. . .	K_2CO_3	inhbitor[k]
Additive grams	. . .	. . .	20	12	. . .	. . .	20	3.1
Wt. % of product boiling above *p*-cymene[b,c]	17.4	15.4	15.2	13.7	13.1	13.1	17.0	8.1
Peroxide number	485	21.6	70	40	10	3.5	4.0	10
Comp. of product boiling above *p*-cymene, wt. %								
Acid[d]	2.0	. . .	3.3	1.3[j]	. . .	. . .	3.3	. . .
Ketone[e]	79.0	26.4	18.2	23.8	56.7	23.8	17.6	27.3
Carbinol[f]		21.6	42.2	23.3		4.0	17.4	24.4
Di-*p*-cymene[g]	3.2	22.9	17.9	13.7	12.1	26.9	32.5	7.5
Higher boiling liquid[h]	10.7	16.4	16.0	25.2	10.7	18.2	22.7	27.5
Residue[i]	5.1	12.7	2.2	12.7	20.5	27.1	6.5	13.3

[a] In each experiment 400 cc. of contact material was used. The turnings and glass rings were $^2/_8$–$^3/_8$ inches long. [b] Weight of product after washing and drying was used for this calculation. [c] There was some isopropenyltoluene in the product but the amount was not determined. [d] Cumic acid in all cases analyzed. [e] *p*-Acetyltoluene. [f] Dimethyl-*p*-tolylcarbinol. [g] 2,3-Dimethyl-2,3-di-*p*-tolylbutane, melting at 156°, as compared with 157° reported previously.[l,m] [h] Liquid boiling above ketone–carbinol range (about 240–385°). [i] Liquid boiling over 385°. [j] In excess of what was added. [k] 2,4-Dimethyl-6-*t*-butylphenol. [l] E. Boedtker, *J. Pharm. Chim.*, [8] **9**, 417 (1929). [m] E. Boedtker and R. Kerlor, *Compt. rend.*, **188**, 1681 (1929).

In many experiments, the gaseous products from the reaction were analyzed, and it was found that from 5 to 20% of the oxygen reacted. The gaseous product contained 2 to 5% methane, about 0.1 to 1.3% ethane and a similar amount of carbon dioxide.

Effect of Acids and Acid Acting Materials.—The effect of acidic materials upon the oxidation of *p*-cymene was investigated at the conditions described in Experiment 2, Table I, using glass rings as a contacting medium. No reaction took place when 85% phosphoric acid (169 g.), amylacidpyrophosphate (15 g.) or superfiltrol (35 g.) was present. The inhibiting effect of the acids might have been due to a chain breaking reaction involving reactions such as the decomposition of hydroperoxides to phenols.[4,5] The use of oxygen instead of air did not affect the results.

Isopropylbenzene.—The oxidation of isopropylbenzene (cumene) shown in Table II, was made at its reflux temperature using either glass rings or aluminum turnings as contact materials. As in the case of *p*-cymene, it was found that aluminum turnings increase two to threefold the yield of 2,3-dimethyl-2,3-diphenylbutane (dicumene) at the expense of acetophenone and dimethylphenylcarbinol. The highest yield of dicumene was 27% based on isopropylbenzene reacted. Unlike *p*-cymene, isopropylbenzene, owing to the absence of a methyl group on the ring, formed little or no organic acids and probably for that reason the amount of higher boiling products present was relatively small and, for the same reason, potassium carbonate had very little effect upon the reaction. The peroxide number of the product obtained from the oxidation of isopropylbenzene was higher than that obtained from *p*-cymene; this was probably due to the lower temperature of reaction owing to the lower reflux temperature of isopropylbenzene.

Chloroisopropylbenzene.—The condensative oxidation is not limited to aromatic hydrocarbons only. Small amounts of dichlorocumene were obtained when a mixture of *o*-, *m*- and *p*-chlorocumene reacted with air under conditions used in experiments 3 and 7, Table I. The yield of compounds corresponding to dichlorocumene in the respective experiments was 1 and 7%. Since the starting material consisted of a mixture of chlorocumenes, no attempt was made to identify the solid dichlorocumene which melted at 166–167°. The

TABLE II

OXIDATION CONDENSATION OF ISOPROPYLBENZENE

The experiments were made using 600 g. of isopropylbenzene and 400 cc. of contact material. Air was passed in at a rate of 12 liters per hour for 18 hours.

Expt. no.	1	2	3	4
Temp., °C.	148	149	148	149
Contact material, kind	glass rings		aluminum turnings	
Potassium carbonate, g.	. . .	20	. . .	20
Peroxide number	303	460	6.4	100
Wt. % of liquid product boiling above cumene	10.4	13.7	10.2	10.8
Comp. of product boiling above cumene:				
Acid	3.0	0	0	0
Ketone	35.3	33.6	34.8	40.1
Carbinol	47.3	50.5	26.1	27.8
Dicumene[a]	9.1	10.8	26.9	22.4
Higher boiling[b]	4.8	3.8	7.3	7.5
Residue[c]	3.2	1.3	4.9	2.2

[a] 2,3-Dimethyl-2,3-diphenylbutane, m.p. 115–116° and corresponding to that reported in the literature (*d*). No depression in mixed melting point with dicumene prepared by the method of Kharasch, *et al.*[e] [b] Liquid boiling above ketone–carbinol range. [c] Liquid boiling over 340°. [d] A. Klages, *Ber.*, **35**, 2638 (1902). [e] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

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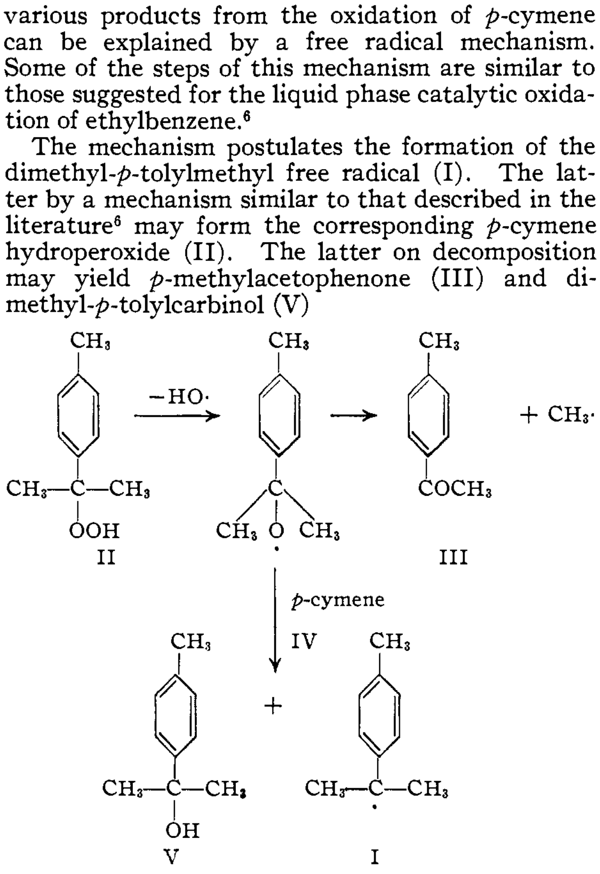
(4) E. G. E. Hawkins, *J. Chem. Soc.*, 2076 (1949).

(5) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

product of the reaction also contained chloroacetophenone and chlorophenyldimethylcarbinol.

Mechanism of Reaction.—The formation of the various products from the oxidation of *p*-cymene can be explained by a free radical mechanism. Some of the steps of this mechanism are similar to those suggested for the liquid phase catalytic oxidation of ethylbenzene.[6]

The mechanism postulates the formation of the dimethyl-*p*-tolylmethyl free radical (I). The latter by a mechanism similar to that described in the literature[6] may form the corresponding *p*-cymene hydroperoxide (II). The latter on decomposition may yield *p*-methylacetophenone (III) and dimethyl-*p*-tolylcarbinol (V)



The methyl free radical on reaction with *p*-cymene will form methane and I. The interaction of two methyl free radicals will yield ethane. The solid "dimer" 2,3-dimethyl-2,3-di-*p*-tolylbutane was most probably produced by the condensation of two *p*-cymyl free radicals (I).

The methanol probably was formed by the following series of reactions.

$$H_3C\cdot + O_2 \longrightarrow H_3COO\cdot$$

$$H_3COO\cdot + R_1\cdot \longrightarrow H_3COOR_1$$

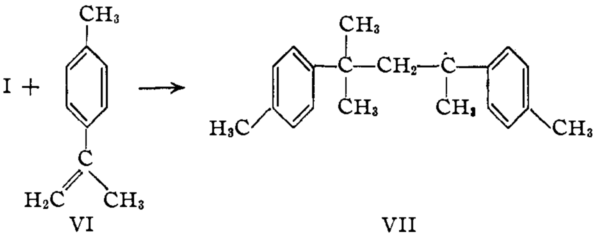
$$[R_1\cdot = \text{I or any other free radical}]$$

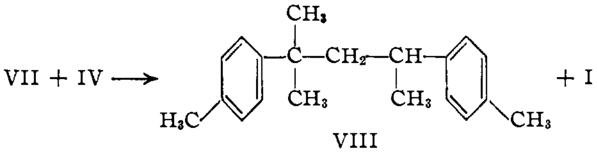
$$H_3COOR_1 \longrightarrow H_3CO\cdot + R_1O\cdot$$

$$H_3CO\cdot + \text{IV} \longrightarrow CH_3OH + \text{I}$$

$$R_1O\cdot + \text{IV} \longrightarrow R_1OH + \text{I}$$

The 2-methyl-2,4-di-*p*-tolylpentane present in the liquid "dimeric" fraction might have been formed by the addition of I to *p*-isopropenyltoluene, as

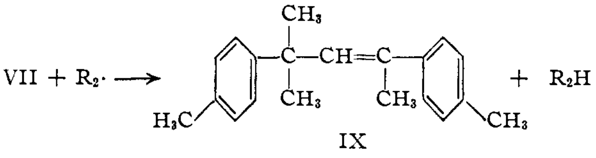




The presence of *p*-isopropenyltoluene may be due either to the dehydration of the dimethyl-*p*-tolylcarbinol by means of the organic acids formed or by hydrogen disproportionation involving the interreaction of compound I with another free radical

$$\text{I} + R\cdot \longrightarrow \text{VI} + RH$$

The liquid dimeric fraction also contained some unsaturated aromatic hydrocarbons which could have been formed by the reaction of VII with a free radical, according to the equation



It is not ruled out that unsaturates such as IX could have been due to the polymerization of VI through a carbonium ion mechanism since the reaction medium in some cases contained organic acids. The organic acids were formed through the oxidation of the methyl group attached to the aromatic ring in *p*-cymene.

The oxygenated higher boiling compounds, although not identified, were probably formed through the interreaction of the dicymyl free radical VII with oxygen to form as a primary product a peroxy free radical. The latter by a mechanism proposed above could have been converted to the dicymyl alcohol.

Experimental Part

Apparatus and Procedure.—The experiments were made in one-liter round bottom flask provided with a thermocouple well and a capillary air inlet extending to the bottom of the flask. The flask containing the reactants was attached to a distillation column of about 6 to 8 plates efficiency and was heated to reflux temperature. Air was passed in, usually at 12 liters per hour for a period of 18 hours. The aqueous product was removed as it was formed through the distillation column in order to maintain a constant reflux temperature. The exit gas was passed through a Dry Ice–acetone cooled trap and the noncondensable gas was sampled and analyzed in some cases. The peroxide number and the acid content of the liquid product was determined. When potassium carbonate was not used as an additive, the product was washed free of organic acids with 10% aqueous sodium hydroxide before washing with water and drying with anhydrous potassium carbonate; most of the peroxide present was removed by the alkali wash. The liquid product was distilled in the presence of a small amount of potassium carbonate to prevent dehydration of the carbinols. The unreacted aromatic hydrocarbon was distilled off at atmospheric pressure and the remainder was fractionated at reduced pressure. The fraction boiling within the ketone–carbinol range was analyzed by infrared spectroscopy. The residue was cooled and filtered to determine the amount of crystalline "dimer" present. The crystalline product obtained from *p*-cymene was 2,3-dimethyl-2,3-di-*p*-tolylbutane and that from cumene was 2,3-dimethyl-2,3-diphenylbutane.

Investigation of the liquid boiling above the ketone–carbinol range, designated as higher boiling liquid in the table and obtained from the reaction of *p*-cymene, revealed that over half of it was composed of isomeric di-*p*-cymenes. The infrared spectrum of the liquid dicymene fraction, after

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[6] W. S. Emerson, J. W. Heyd, V. E. Lucas, W. B. Cook, W. I. Lyness and J. K. Stevenson, THIS JOURNAL, **70**, 3764 (1948).

the removal of oxygenated compounds by refluxing with sodium and after selective hydrogenation to saturate the small amounts of olefinic double bonds present, showed that it contained only *para* disubstituted aromatic hydrocarbons. Comparison of the above infrared spectrum with that of pure 2,3-dimethyl-2,3-di-*p*-tolylbutene and pure 2-methyl-2,4-di-*p*-tolylpentane showed that the former was present in moderate concentration and that the latter was present in rather high concentration. The remainder of the fraction consisted of isomeric hydrocarbons.

Materials. *p*-Cymene.—Eastman Kodak Co. practical grade *p*-cymene was shaken with fresh portions of 96% sulfuric acid until there was very little color change. It was then washed with water and steam distilled from 3% sodium hydroxide and redistilled on an efficient column; $n^{20}\mathrm{D}$ 1.4902. The infrared spectrogram was identical with that of *p*-cymene reported by the American Petroleum Institute (API) Project 44.

Isopropylbenzene obtained from the Atlantic Refining Company was purified in the same manner as described for *p*-cymene. It distilled at 151°, $n^{20}\mathrm{D}$ 1.4912. The infrared spectrum was identical with that given in API Project 44.

Chloroisopropylbenzene was prepared by treating chlorobenzene, 830 g., with isopropyl alcohol, 300 g., in the presence of 2,800 ml. of 80% sulfuric acid, according to the method of Meyer and Bernhauer.[7] The chloroisopropylbenzene fractions boiled at 185–189°, $n^{20}\mathrm{D}$ 1.5147–1.5157. An inspection of the infrared spectrogram indicated that it was a mixture of the *ortho, meta* and *para* isomers.

Preparation of 2-Methyl-2,4-di-*p*-tolylpentane. a.—**4-Methyl-4-*p*-tolyl-2-pentanone** was prepared by treating toluene with mesityl oxide in the presence of aluminum chloride, according to the method described previously.[8]

b. **4-Methyl-2,4-di-*p*-tolyl-2-pentol** was prepared by condensing the above ketone with *p*-tolylmagnesium bromide.[8]

C. **2-Methyl-2,4-di-*p*-tolylpentane** was prepared by a two-step reaction in which the above alcohol was dehydrated, by refluxing with oxalic acid in toluene, to the corresponding olefin, b.p. 127–128° (0.3 mm.), $n^{20}\mathrm{D}$ 1.5605. The olefin was selectively hydrogenated under 100 atmospheres of hydrogen pressure at 80° in the presence of copper–chromite catalyst[9] to 2-methyl-2,4-di-*p*-tolylpentane, b.p. 132° (0.4 mm.), $n^{20}\mathrm{D}$ 1.5420.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.15; H, 9.78.

Dimethyl-*p*-tolylcarbinol and ***p*-Methyl-α-methylstyrene** were prepared according to the procedure described previously.[8]

Oxidative Condensation of *p*-Cymene.—The combined liquid fractions, designated as "higher boiling liquid" in Table I, were redistilled. The fraction distilling within the "dicymene" range was again redistilled over sodium in order to remove any oxygenated product present. The distillate boiling at 132–145° at 2 mm., $n^{20}\mathrm{D}$ 1.5454, which showed unsaturation by the potassium permanganate test,[10] was selectively hydrogenated under pressure at 80° in the presence of copper–chromite catalyst.[9] About 25% of the "dimeric" fraction was olefinic according to the hydrogen absorbed. The selectively hydrogenated product had a boiling range of 140–150° at 2 mm., $n^{20}\mathrm{D}$ 1.5435.

A fraction of the selectively hydrogenated material b.p. 141–144° at 2 mm., $n^{20}\mathrm{D}$ 1.5438 and representing 75% of the total product was analyzed.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.76; H, 9.87.

The ultraviolet spectral analysis showed that the liquid "dimeric" *p*-cymene had the same absorption bands as the solid 2,3-dimethyl-2,3-di-*p*-tolylbutane but with a lower absorption coefficient.

The liquid "dimeric" *p*-cymene fraction was shown by infrared analysis to be essentially all *para*-di-substituted aromatics. The bands at 1795 and 1910 cm.$^{-1}$ are clear-cut evidence for a *para*-di-substituted aromatic structure.[11] The intensities of these bands indicate that the compounds present are essentially all *para*-di-substituted aromatics. This analysis is further borne out by the intense *para* band in the 820 cm^{-1} region, and by the absence of meta and *ortho* bands near 780 and 760 cm.$^{-1}$.[12]

2,3-Di-*p*-tolylbutane is probably present in the liquid "dimeric" *p*-cymene fraction, and to the extent of 10% (950 and 1150 cm.$^{-1}$ bands). Compound VIII is probably the major constituent since all of its major bands appear.[13] Other *para*-di-substituted isomers would account for the remainder.

Oxidation of chloroisopropylbenzene was made according to conditions described in experiments 3 and 7, Table I. In each case 180 g. of the chloroisopropylbenzene was used. A dichlorocumene isolated from the product melted at 166–167° after crystallization from absolute alcohol.

Anal. Calcd. for $C_{12}H_{20}Cl_2$: C, 70.36; H, 6.56; Cl, 23.08. Found: C, 70.23; H, 6.66; Cl, 23.17.

Acknowledgment.—The authors wish to thank Dr. D. R. Long and Mr. E. Baclawski of UOP for the infrared spectral analyses.

RIVERSIDE, ILLINOIS

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[7] H. Meyer and K. Bernhauer, *Monatsh.*, **53-54**, 721 (1929).

[8] V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2123 (1948).

[9] V. N. Ipatieff, B. Kvetinskas, E. E. Meisinger and H. Pines, *ibid.*, **75**, 3323 (1953).

[10] V. N. Ipatieff, W. W. Thompson and H. Pines, *ibid.*, **70**, 1658 (1948).

[11] C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

[12] J. Bomstein, *ibid.*, **25**, 512 (1953).

[13] The reference compound VIII had bands at 705, 760 and 785 cm.$^{-1}$ which were due to small amounts of the corresponding *meta* and *ortho* isomers, but their bands did not appear in the spectrum of the liquid "dimeric" *p*-cymene fraction.