The alcohol was distilled off, the residue taken up in 100 cc. of water and the solution extracted with ether, removing about 0.5 g. of unchanged ester. The aqueous layer, carefully acidified with 4 *N* sulfuric acid, gave a white gummy precipitate which was taken up in ether and dried over anhydrous sodium sulfate. From this solution there was obtained a slightly yellow oil which solidified on cooling. Recrystallized from 30% alcohol (after decolorizing with Norite) there was obtained a colorless solid, m. p. 96–97°.[10]

*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 75.0; H, 8.3. Found: C, 74.7; H, 8.3.

**2,4,5-Trimethylhydrocinnamic Amide.**—One gram of the acid was treated with phosphorus pentachloride and, without isolating the chloride, the reaction mixture was poured into iced ammonia; colorless needles, m. p. 152–154° when crystallized from 35% alcohol.

*Anal.* Calcd. for $C_{12}H_{17}ON$: C, 75.5; H, 8.91. Found: C, 75.3; H, 9.05.

### Synthesis of 2,4,5-Trimethylhydrocinnamic Acid

I. **Dural malonic ester** $(CH_3)_3C_6H_2CH{=}C(COOC_2H_5)_2$ was prepared in 42% yield from 3.5 g. of durylic aldehyde, and 3.8 g. of malonic ester by heating them together on the steam-bath for eleven hours, adding initially two drops of piperidine and then one drop each hour. The reaction product was purified in the usual way, yielding 3 g. of ester, b. p. 182–186 at 11 mm. It was not analyzed.

II. **Dural Malonic Acid** $(CH_3)_3C_6H_2CH{=}C(COOH)_2$.—The ester was hydrolyzed by boiling it with an excess of aqueous 15% sodium hydroxide for three and one-half hours, adding water occasionally to keep the salt in solution. The cooled solution was extracted with ether, then acidified with 4 *N* sulfuric acid, and kept in the ice box overnight. The solid was recrystallized twice from 85% alcohol, giving 1.6 g. of fine colorless crystals of m. p. 183–185° with dec.

*Anal.* Calcd. for $C_{13}H_{14}O_4$: C, 66.7; H, 5.98. Found: C, 66.5; H, 5.95.

III. **2,4,5-Trimethylcinnamic Acid.**—Dural malonic acid (1.2 g.) was heated to 190–200° until the evolution of carbon dioxide ceased. Recrystallized from dilute alcohol, there resulted 0.7 g. of colorless plates, m. p. 154–155°.

*Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.9; H, 7.36. Found: C, 76.1; H, 7.23.

IV. **2,4,5-Trimethylhydrocinnamic Acid.**—The unsaturated acid (170 mg.) was dissolved in 20 cc. of 95% alcohol and reduced by the method of Adams and Voorhees;[11] 25 mg. of platinum oxide was used as the catalyst, and the reduction required forty-five minutes. The catalyst was filtered off, the alcohol removed *in vacuo*, and the residue, a colorless oil, solidified on cooling. A single crystallization from 40% alcohol yielded 0.15 g. of the hydrocinnamic acid, melting point, and mixed melting point with the acid obtained from the reaction of ethyl diazoacetate on durene, 96–97°.

## Summary

1. Ethyl diazoacetate has been added to durene. The only homogeneous product obtained was 2,4,5-trimethylhydrocinnamic acid, the reaction resulting in the introduction of an acetic ester residue into one of the methyl groups.

2. A synthesis of 2,4,5-trimethylhydrocinnamic acid from durylic aldehyde is described.

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(10) Willgerodt, *J. prakt. Chem.*, [2] **81**, 390 (1910), gives the m. p. as 92°.

(11) "Organic Syntheses," J. Wiley & Sons, Inc., New York, 1928, Vol. VIII, p. 10.

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

# Studies on the Polymethylbenzenes. X. Reaction with Aromatic Diazonium Compounds[1]

BY LEE IRVIN SMITH AND JOSEPH H. PADEN

Meyer and Schoeller[2] were the first to couple diazotized amines with hydrocarbons, obtaining crystalline azo compounds by coupling diazotized *p*-nitraniline and 2,4-di-nitroaniline with butadiene and some of its derivatives. The reaction failed, however, when applied to such hydrocarbons as mesitylene and anthracene, although the solutions showed colors which indicated some formation of azo compounds. In 1920 Misslin[3] succeeded in diazotizing picramide, and with this diazonium compound available, Meyer and Tochterman[4] succeeded in coupling it with mesitylene, obtaining a beautifully crystalline azo compound. With toluene and *m*-xylene no product could be isolated, although the solutions showed colors indicating the formation of some azo compounds, while with benzene there was not even the development of any color.

These experiments of Meyer indicated that the coupling of diazonium compounds with aromatic hydrocarbons was promoted by negative groups in the diazotized amine and by methyl groups in

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(1) Abstracted from a thesis by Joseph H. Paden, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science, July, 1933.

(2) Meyer and Schoeller, *Ber.*, **47**, 1711 (1914); *ibid.*, **52**, 1468 (1919).

(3) Misslin, *Helv. Chim. Acta*, **3**, 626 (1920).

(4) Meyer and Tochterman, *Ber.*, **54**, 2283 (1921).

the hydrocarbon. We have undertaken a study of the reaction of various diazotized amines with polymethylbenzenes containing four or more methyl groups, with a view to obtaining more information about this reaction, and in the hope of obtaining in quantity polymethyl azo compounds which could be split by reduction, thus making available the mono amino derivatives of these hydrocarbons.

Because of the solubility relationships, it was necessary for us to operate in concd. sulfuric acid or some combination of this with glacial acetic acid, and the best results were obtained by dissolving the diazotized amine in sulfuric acid and running into this a solution of the hydrocarbon in a mixture of sulfuric and acetic acids. In general, however, the coupling proved to be very difficult, and of the amines used (sulfanilic acid, 2,6-dibromoaniline-4-sulfonic acid, 2,4,6-tribromoaniline and picramide) only picramide showed any tendency to react. Good yields of azo compounds were obtained when diazotized picramide was coupled with isodurene (60% yield) or with pentamethylbenzene (85% yield) while no coupling took place with durene or monobromodurene.

The structure of the new azo compounds was proved by reduction, each one yielding the nuclear mono amino derivative of the corresponding polymethyl benzene. However, these two azo compounds are not suitable as intermediates in any large scale preparation of the amino hydrocarbons because of the difficulty involved in diazotizing large amounts of picramide, and because picramide cannot be recovered when an azo compound containing the trinitrophenyl group is reduced. Any reducing agent tried, which would split the azo linkage, also destroyed completely the nitrated part of the molecule.

The failure of durene and bromodurene to couple was surprising, and it indicates that the reaction is influenced greatly by factors other than the presence of negative groups in the amine and positive groups in the hydrocarbons, especially in view of the fact that diazotized aminopentamethylbenzene reacts with pentamethylbenzene, even though it gives, not an azo compound, but a hydrocarbon. This reaction was also unique, for pentamethylbenzene gave no reaction whatever with diazotized pseudocumidine, mesidine, or aminoisodurene. We were inclined, at first, to regard the hydrocarbon as decamethyldiphenyl, for the analysis agreed well with the formula $C_{22}H_{30}$, even though the formation of diphenyls from such a reaction has heretofore been observed only in alkaline solution.[5] However, a synthesis of decamethyldiphenyl by the method used by Adams[6] gave a substance differing by nearly 30° in melting point. In view of the analysis, the substance cannot be an octamethylanthracene or its dihydro derivative. The coupling, therefore, must have involved one of the methyl groups of pentamethylbenzene and the hydrocarbon must be one of the three possible nonamethyldiphenylmethanes that could be formed when diazotized aminopentamethylbenzene and pentamethylbenzene couple through a methyl group. We have the syntheses of these three hydrocarbons under way, and shall report upon them in a later paper.

## Experimental Part

Picramide was prepared by the method of Holleman[7] which we found to be superior to the method of Witt and Witte.[8]

For the diazotization of picramide, a slight modification of the method of Blangey[9] was used. This method is far superior to the method of Misslin[3] which requires very large volumes of solvents—320 cc. for 0.01 mole of picramide.

The question of finding a suitable solvent in which to carry out the coupling reaction presented many difficulties. Since nitrosyl sulfuric acid in concd. sulfuric acid is necessary for the diazotization, it is evident that a strongly acid medium must be used. We tried adding the diazonium solution to a solution of the polymethylbenzene in various solvents: alcohol, a mixture of equal parts of acetic acid and acetone, acetic acid containing just enough sulfuric acid to permit cooling to the desired temperature, but none of them were satisfactory. The acetic acid–acetone mixture was very good as a solvent, but only 15% yield of picrylazopentamethylbenzene was obtained, and no coupling at all occurred with mesitylene. With the acetic acid–sulfuric acid mixture, a 45% yield of picrylazopentamethylbenzene was obtained by the usual procedure but by reversing the procedure and running the hydrocarbon solution into the diazonium solution, yields as high as 85% were obtained. The best procedure was as follows.

Picramide (4.6 g., 0.02 mole) was diazotized with 1.4 g. of sodium nitrite in 50 cc. of concd. sulfuric acid and the solution then diluted with 50 cc. of concd. sulfuric acid (both at 0°). Pentamethylbenzene (2.5 g., 0.017 mole) in acetic acid (30 cc.), was slowly added (one hour), keeping the temperature below 2° and stirring continuously during the addition and for thirty minutes thereafter. The reaction mixture was poured onto 300 g. of ice, the purple solid filtered, washed, dried by suction, dissolved in

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(5) Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924); Gomberg and Pernert, *ibid.*, **48**, 1380 (1926).

(6) Adams and Knauf, *ibid.*, **55**, 4704 (1933).

(7) Holleman, *Rec. trav. chim.*, **49**, 112 (1910).

(8) Witt and Witte, *Ber.*, **41**, 3091 (1908).

(9) Blangey, *Helv. Chim. Acta*, **8**, 780 (1925).

100 cc. of ethyl acetate and precipitated by adding alcohol. Two such treatments gave 5.5 g. (84%) of a dark brown azo compound, m. p. 176° dec.

*Anal.* Calcd. for $C_{17}H_{17}O_6N_5$: C, 52.71; H, 4.39; N, 18.06. Found: C, 52.83; H, 4.43; N, 18.47.

When wet with solvents, the azo compound is purple, but when dry, it is dark brown. It can be recrystallized from acetic acid, and it reacts with acetic anhydride to give a bright red solid, m. p. 230°, which has not been investigated.

**Reduction.**—One gram of the azo compound in 20 cc. of acetic acid was reduced by warming with 5 g. of stannous chloride in 10 cc. of concd. hydrochloric acid. On cooling, the stannic chloride of the amine separated. This was filtered, suspended in excess alkali and the amine removed by extraction with ether. Recrystallized from dilute alcohol, there resulted 0.2 g. (65%) of a slightly yellow powder, m. p. 151–152°. Hofmann[10] gives the m. p. as 151–152°; Willstätter and Kubli[11] give it as 151°.

With acetic anhydride, the amine gives an acetyl derivative crystallizing in colorless needles, m. p. 212–213°. Hofmann[10] gives the melting point of this acetyl derivative as 213°.

A similar procedure, diazotizing 4.6 g. (0.02 mole) picramide and coupling it with isodurene, gave 4.5 g. (60%) of picrylazoisodurene, a brown, crystalline solid, m. p. 164° (dec.).

*Anal.* Calcd. for $C_{16}H_{15}O_6N_5$: C, 51.48; H, 4.02. Found: C, 51.73; H, 4.22.

Reduction of 3.5 g. of the azo compound by the method used for the pentamethyl compound gave 0.8 g. of isoduridine, an oil, which gave a white acetyl derivative, m. p. 214–215°. Hofmann[12] gives the m. p. of the base as 14°, Limpach[13] gives the m. p. as 23–24°; while for the acetyl compound, Noelting and Baumann[14] give the m. p. as 210–211°, Limpach[13] giving 215°.

Similar experiments, using 0.02 molar quantities of picramide and durene or bromodurene, led to no coupling of any kind, 70–80% of the durene or bromodurene being recovered unchanged, nor, with the exception of picramide, could any of the amines used be made to couple with mesitylene, durene or pentamethylbenzene.

**Reaction between Diazotized Aminopentamethylbenzene and Pentamethylbenzene.**—The amine (0.5 g.) was dissolved in a mixture of 25 cc. of acetic acid and 15 cc. of sulfuric acid, and diazotized at 0° with a solution of 0.3 g. of sodium nitrite in 20 cc. of sulfuric acid. Urea (0.5 g.) was added to remove any free nitrous acid, and then 0.5 g. of the hydrocarbon in 20 cc. of acetic acid was slowly added. After stirring for one to two hours, the reaction mixture was poured onto ice, the white solid filtered, extracted with alkali and recrystallized three times from acetic acid; yield 0.1 g., m. p. 212–213.5°.

*Anal.* Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.3. Found: C, 89.40; H, 10.4.

The substance is not decamethyldiphenyl, however, for a specimen prepared from bromopentamethylbenzene by the method of Adams and Knauf[8] melted at 239–241°.

Similar reactions were carried out using pentamethylbenzene and diazotized pseudocumidine, mesidine and aminoisodurene, but in every case about 80% of the hydrocarbon was recovered unchanged and no coupling product of any kind could be isolated.

## Summary

1. Diazotized picramide has been coupled with pentamethylbenzene and with isodurene, giving the corresponding azo compounds, and the latter have been reduced, yielding the mono amino derivatives of the hydrocarbons.

2. All attempts to couple diazotized amines (other than picramide) with polymethylbenzenes resulted in failure; while durene and bromodurene do not couple even with picramide.

3. Diazotized aminopentamethylbenzene couples with pentamethylbenzene to give a white hydrocarbon, $C_{22}H_{30}$, which is not decamethyldiphenyl.

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[10] Hofmann, *Ber.*, **18**, 1822 (1885).

[11] Willstätter and Kubli, *ibid.*, **42**, 4162 (1909).

[12] Hofmann, *ibid.*, **17**, 1913 (1884).

[13] Limpach, *ibid.*, **21**, 646 (1888).

[14] Noelting and Baumann, *ibid.*, **18**, 1149 (1885).