poured upon it. The solid was pressed on a porous plate and washed with a little ether; m. p., 116–118°, with preliminary softening at 114°. The physical properties of this compound are very similar to those of diphenylmethyl urethan,[12] prepared similarly.

Anal. Subs., 0.1267: N, 4.69 cc. (over 40% KOH; 24°, 746.7 mm.). Calcd. for $C_{28}H_{23}O_2N$: N, 4.06. Found: 4.10.

Diphenyl-*p*-tolylmethyl Isocyanate, $CH_3C_6H_4C(C_6H_5)_2NCO$.—The ether solution was shown to contain the isocyanate, by allowing it to react with aniline. Neither the urethan, nor the amine, $CH_3C_6H_4C(C_6H_5)_2NH_2$, which are other possible solutes due to rearrangement, exhibited any change with aniline. The isocyanate should, however, form the disubstituted urea, $CH_3C_6H_4C(C_6H_5)_2NHCONHC_6H_5$. Such was found to be the case. A high-melting solid remained when the solvents were evaporated. It was recrystallized from ether.

Phenyl Diphenyl-*p*-tolylmethyl Urea.—This compound melted at 213–215°. It is insoluble in ligroin and water; only slightly soluble in ether, cold alcohol, or cold benzene; it is very soluble in ethyl acetate.

Summary

Diphenyl-*p*-tolyl-acethydroxamic acid and certain of its derivatives have been prepared. They undergo the Lossen rearrangement with great readiness, and thus afford affirmative evidence for the hypothesis of Jones and Hurd.

The preparation of the pure alkali metal salts of the esters of this acid was not possible. It is a striking fact that the same circumstance has been encountered with every other series of hydroxamic acid derivatives to which the hypothesis applies.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. V. THE BROMINATION OF 2-AMINO-PARA-CYMENE AND CERTAIN NEW AZO DYES

SECOND PAPER[1]

BY ALVIN S. WHEELER AND HAYWOOD M. TAYLOR

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The first work on the bromination of 2-amino-*p*-cymene was reported by Wheeler and Smithey.[2] In that work it was found that the bromination was most successfully carried out by treating a carbon tetrachloride solution of aceto-amidocymene with bromine. The free base was obtained as a colorless oil, soon turning yellow and then red, similar to the behavior of aniline. Its hydrochloride, hydrobromide and certain diazo deriva-

[12] Ref. 1, p. 2434.

[1] This paper is an abstract of a thesis submitted by Haywood M. Taylor in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of North Carolina in June, 1924.

[2] Wheeler and Smithey, THIS JOURNAL, **43**, 2611 (1921).

tives were described. In the orientation of the bromine atom the compound was oxidized in neutral permanganate solution and an acid obtained which was regarded as a toluic acid. It did not melt at 186–187° which is the melting point of 2-amino-5-bromo-*p*-toluic acid. The other two isomers, with bromine in Positions 3 and 6 are unknown. Since the acid melted at 151° it might be one of these unknown acids. Therefore we located the bromine provisionally at Position 3. In this paper we describe the same method of attack as well as another. The possibility of the bromine entering any of the three side chains was easily ruled out by the properties of the compound which correspond to aryl amines with halogen in the nucleus. Positions 3, 5 and 6 are open for the entrance of halogens, and the question easily narrows itself to which of these three is occupied. The oxidation of bromo-aceto-amidocymene by neutral permanganate was repeated and the monobasic acid obtained proved to be a cuminic acid, melting at 166–167° and agreeing in properties with the 2-amino-5-bromo-4-*iso*propylbenzoic acid of Fileti and Crosa.[3] The 2-amino-3-bromocuminic acid melts at 173—174° and the third isomer with bromine in Position 6 is unknown. The cuminic acid that we obtained was converted by diazotization into a dibromocuminic acid. This melted at 149° and agreed in its properties with the 2,5-dibromo-4-*iso*propylbenzoic acid of Fileti and his co-workers.[4] The 2,3-dibromocuminic acid melts at 128–129° and the 2,6-isomer is unknown. According to the conclusions of Remsen[5] the *iso*propyl group should not be oxidized if the bromine atom is *ortho* to it. Since the *iso*propyl group is actually protected in the oxidation with permanganate, the bromine must be at Position 3 or 5, and can not be at 6. While the formation of 2,5-dibromocuminic acid leads to the conclusion that the bromine is at Position 5, we thought it best to follow another line of attack and convert our compound if possible into a terephthalic acid. By the Sandmeyer reaction we diazotized our amino-bromocymene to 2,5-dibromocymene and oxidized this with nitric acid to 2,5-dibromoterephthalic acid, melting at 315°. This acid is described by Claus and Wimmel[6] who obtained it by oxidizing 2,5-dibromocymene; by Schultz[7] who oxidized 2,5-dibromo-*p*-toluic acid; by Fileti and Crosa[8] and by Claus.[9] The conversion of our compound into a cuminic acid with a bromine in Position 5 and also into a terephthalic acid with a bromine in the same position gives full proof that the bromine is not in

[3] Fileti and Crosa, *Gazz. chim. ital.*, [1] **21**, 33 (1891).

[4] Ref. 3. Fileti and Basso, *Gazz. chim. ital.*, [1] **21**, 59 (1891). Fileti and Boniscontro, *ibid.*, [2] **21**, 394 (1891).

[5] See footnote in THIS JOURNAL, **44**, 2606 (1922) for references.

[6] Claus and Wimmel, *Ber.*, **13**, 903 (1880).

[7] Schultz, *Ber.*, **18**, 1762 (1885).

[8] Fileti and Crosa, *Gazz. chim. ital.*, **18**, 309 (1888).

[9] Claus, *J. prakt. chem.*, [2] **37**, 22 (1888).

Position 3 but must be in Position 5. As stated above, Wheeler and Smithey located the bromine in Position 3 on account of the acid (m. p., 151°) which they thought to be a toluic acid and which was not known. We also obtained this acid in setting free our cuminic acid from its hydrochloride (m. p., 190°). It melted at 151° and its melting point did not rise after two recrystallizations. Believing, however, that it should be the 5-bromocuminic acid of Fileti and Crosa which melts at 166–167°, we repeated their work. Thymol was converted by phosphorus pentabromide into monobromocymene; this was oxidized by nitric acid to a bromocuminic acid; the latter gave on nitration 2-nitro-5-bromocuminic acid which on reduction with ferrous sulfate in ammonium hydroxide gave the 2-amino-5-bromocuminic acid which we found melted at 166–167°, as given by Fileti and Crosa. Having confirmed their work, we reëxamined our cuminic acid, subjected it to six more recrystallizations from dil. alcohol and carried the melting point up to 166–167°. Thus the difficulty of Wheeler and Smithey is explained.

Our investigation was started with *p*-cymene obtained from spruce turpentine. This was converted into 2-nitrocymene by the method of Andrews[10] as modified by the Eastman Kodak Company. The nitrocymene was reduced by tin and hydrochloric acid to aminocymene which was acetylated with equal parts of glacial acetic acid and acetic anhydride. The acetyl derivative was brominated by the method of Wheeler and Smithey.[2] The free base was prepared as well as its hydrochloride and hydrobromide, all agreeing in their properties with the products described by these authors.

A series of new azo dyes was prepared by coupling the aminobromocymene with a group of phenols, the reaction proceeding smoothly in the majority of cases. Dyes were obtained with the following phenols: phenol, resorcinol, thymol, 1-naphthol, 2-naphthol, 1-naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid, 2-naphthol-7-sulfonic acid, 2-naphthol-3,6-disulfonic acid, 2-naphthol-6-sulfonic acid and 1,8-dihydroxy-naphthalene-3,6-disulfonic acid. Satisfactory conditions were not found for coupling with salicylic acid, *o*- and *p*-nitrophenol, 2,4-dinitrophenol-*p*-cresol and carvacrol. The dyes containing the sulfo group, being soluble in water, were applied to textiles in an acid bath. The others were applied by the development method. The colors produced on silk and wool were varied, comprising yellow, gold, orange, pink, bright reds and wine reds. The acid dyes produce brilliant shades and give a very high degree of exhaustion. The influence of the bromine was determined by coupling R-acid with aminocymene and also with aminobromocymene. The first produces a rich, deep red on wool, the second also a deep red but more brilliant. Tests for fastness were made. On wool the tests included

[10] Andrews, *J. Ind. Eng. Chem.*, **10**, 453 (1918).

light, water, washing, crocking, weather, stoving, acids, alkali, perspiration, lime and street dust. Those on silk included light, water, washing and crocking. The acid dyes show remarkable fastness to light. Various chemical tests were also made.

TABLE I

NEW AZO DYES DERIVED FROM 2-AMINO-5-BROMO-*p*-CYMENE

These dyes were prepared by diazotizing the aminobromocymene at 0°, adding the phenol dissolved in alkali, precipitating the dye by acidifying the solution with hydrochloric acid and crystallizing the product from a suitable solvent.

	Coupler	Solvent	Color of crystals	M. p. °C. corr.
1	Phenol	Hot acetic acid	Argus brown	212
2	Resorcinol	Hot ligroin	Claret brown	202
3	Thymol	Hot ligroin	Van Dyke brown	249
4	1-Naphthol	Hot ligroin	Bronze	228
5	2-Naphthol	Hot acetone	Rose red	168–169
6	1-Naphthol-2-sulfonic acid	Hot alcohol	Garnet red	238
7	1-Naphthol-4-sulfonic acid	Hot alcohol	Spectrum red	285
8	2-Naphthol-7-sulfonic acid	Hot acetic acid	Scarlet red	Not under 325
9	2-Naphthol-6-sulfonic acid	Hot alcohol	Scarlet	Decomp. above 300
10	1,8 - Dihydroxynaphthalene-3,6-disulfonic acid	Hot alcohol	Purplish-red	269

	Formula	Analysis Wt. Subs.	AgBr	% Cl Calcd.	Found	Dyeing color Wool	Silk
1	$C_{26}H_{28}ON_4Br_2$	0.2074	0.1364	27.97	27.99	Empire yellow	Maize yellow
2	$C_{16}H_{17}O_2N_2Br_2$	.1308	.0734	22.92	23.34	Primuline yellow	Golden yellow
3	$C_{30}H_{36}ON_4Br_2$	.0894	.0543	25.47	25.85	Light cadmium	Buff yellow
4	$C_{30}H_{30}ON_4Br_2$	.1718	.1052	25.72	25.49	Old rose	Reddish-gold
5	$C_{20}H_{19}ON_2Br$	.2038	.1018	20.88	21.25	Flesh ocher	Orient pink
6	$C_{20}H_{19}O_4N_2BrS$	.1470	.0605	17.28	17.54	Reddish-orange	Eosin pink
7	$C_{20}H_{19}O_4N_2BrS$	.1332	.0544	17.28	17.38	Spectrum red	Spectrum red
8	$C_{20}H_{19}O_4N_2BrS$	.2187		17.28	17.36	Scarlet red	Scarlet red
9	$C_{20}H_{19}O_4N_2BrS$	.1492	.0892 .0588	17.28	16.76	Scarlet	Scarlet
10	$C_{20}H_{18}O_8N_2BrS_2$	.1350		14.31	14.56	Bordeaux	Amaranth purple

Other *p*-cymene studies are in progress in this Laboratory, including nitration studies as well as further work with halogens.

Experimental Part

The following four compounds, although previously described by Wheeler and Smithey[2] were analyzed again as a check upon their purity.

2-Aceto-amido-5-bromo-*p*-cymene, $C_6H_2CH_3.NHCOCH_3.C_3H_7.Br$: needles from alcohol; m p., 122.5°. Calcd. for $C_{12}H_{16}ONBr$: Br, 29.62. Found: 29.45.

2-Amino-5-bromo-*p*-cymene hydrochloride: hexagonal plates; m. p., 205° with decomposition. Calcd. for $C_{10}H_{14}NBr.HCl$: Cl, 13.43. Found: 13.75.

2-Amino-5-bromo-*p*-cymene hydrobromide: octagonal plates from alcohol; m. p., 200° with decomposition. Calcd. for $C_{10}H_{14}NBr.HBr$: Br, 25.88. Found: 26.13.

2-Amino-5-bromo-*p*-cymene, $C_6H_2CH_3NH_2C_3H_7Br$: a colorless oil, soon turning yellow, then red; b. p., 169–170° (20 mm.). Calcd. for $C_{10}H_{14}NBr$: Br, 35.04. Found: 35.10.

Orientation of the Bromine Atom

2-Aceto-amido-5-bromo-*p*-cuminic Acid, $C_6H_2COOH.NHCOCH_3.C_3H_7.Br$.—Two g. of aceto-amidobromocymene and 4 g. of magnesium sulfate were dissolved in 240 cc. of water, the solution was warmed to 80°, and 6 g. of powdered potassium permanganate added. Heating was continued for one and a half hours. The precipitated manganese dioxide was filtered off, the excess of permanagante destroyed by alcohol and the colorless filtrate acidified with sulfuric acid. An abundant mass of crystals was precipitated, which when recrystallized from alcohol gave colorless needles; m. p., 217° (corr.).

Anal. Subs., 0.1258: AgBr, 0.0796. Calcd. for $C_{12}H_{14}O_3NBr$ (mol. wt., 300): Br, 26.66. Found: 26.92. Calcd. for a toluic acid: 29.41; for a cuminic acid: 26.66.

This compound was first described by Wheeler and Smithey[2] who regarded it as a toluic acid, this conclusion being based on a determination of its acidity in alcoholic solution.

2-Amino-5-bromo-*p*-cuminic Acid Hydrochloride, $C_{10}H_{12}O_2NBr.HCl$.—The acetyl derivative was boiled for a half hour with concd. hydrochloric acid. On cooling the salt crystallized in leaves. It was recrystallized from a mixture of alcohol and hydrochloric acid; m. p., 191–192° (corr.) with decomposition.

Anal. Subs., 0.1000, 0.2000: AgCl, 0.0480, 0.0983. Calcd. for $C_{10}H_{13}O_2NClBr$: Cl, 12.04. Found: 11.88, 12.16. Calcd. for a toluic acid: 13.33; for a cuminic acid: 12.04.

The salt was first described by Wheeler and Smithey and was regarded as a toluic acid salt.

2-Amino-5-bromo-*p*-cuminic Acid, $C_6H_2COOH.NH_2C_3H_7.Br$.—The free acid was obtained by treating the hydrochloride with sodium hydroxide and then acidifying with acetic acid. The crude product melted at 148°. On recrystallizing from dil. alcohol the melting point was raised to 151° and a second recrystallization did not change it. Since this agreed also with the value given by Wheeler and Smithey it was regarded as pure. Believing later that it might be the 5-bromocuminic acid of Fileti and Crosa melting at 166–167°, we prepared the acid according to the method of these authors (see introduction) and found that the melting point given, 166–167°, was correct. We then turned our attention to our acid and found that when it had been recrystallized five more times from dil. alcohol its melting point, 151°, was raised to 166–167°.

Anal. Subs., 0.1552: AgBr, 0.1140. Calcd. for $C_{10}H_{12}O_2NBr$ (mol. wt., 258): Br, 31.00. Found: 31.26. Calcd. for a toluic acid: 34.78; for a cuminic acid: 31.00.

2,5-Dibromocuminic Acid, $C_6H_2COOH.Br_2C_3H_7$.—The amino acid just described was diazotized in the presence of cuprous bromide. The dibromocuminic acid melted at 149° when recrystallized from dil. alcohol. It was first described by Claus.[11]

Anal. Subs., 0.1453, 0.1050: AgBr, 0.1713, 0.1233. Calcd. for $C_{10}H_{10}O_2Br_2$ (mol. wt., 322): Br, 49.68. Found: 50.17, 49.97. Calcd. for a toluic acid: 54.42; for a cuminic acid: 49.68.

2,5-Dibromo-*p*-cymene, $C_6H_2CH_3C_3H_7Br_2$.—The amino-bromocymene was diazotized in the presence of cuprous bromide. On steam distillation a colorless oil was obtained; b. p., 272°. This was oxidized to 2,5-dibromo-terephthalic acid by heating one part with 20 parts of nitric acid, d. 1.12, in a sealed tube for eight hours at 180°. The

[11] Claus, *Ber.*, **13**, 903 (1880).

crystalline acid melted at 314–315°. It was converted into its diethyl ester; m. p., 124.5°.

Anal. Calcd. for $C_8H_4O_4Br_2$: Br, 49.38. Found: 49.59.

The names given to the colors were determined by comparison with the charts of Ridgway.[12]

The following names for the dyes are based on analogy and not on any special experimental work.

1. 2,4(5-bromo-carvacryl-disazo)-phenol
2. 4(5-bromo-carvacrylazo)-resorcinol
3. 2,6(5-bromo-carvacryl-disazo)-thymol
4. 2,4(5-bromo-carvacryl-disazo)-1-naphthol
5. 1(5-bromo-carvacrylazo)-2-naphthol
6. 4(5-bromo-carvacrylazo)-1-naphthol-2-sulfonic acid
7. 2(5-bromo-carvacrylazo)-1-naphthol-4-sulfonic acid
8. 1(5-bromo-carvacrylazo)-2-naphthol-7-sulfonic acid
9. 1(5-bromo-carvacrylazo)-2-naphthol-6-sulfonic acid
10. 2(5-bromo-carvacrylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid

The behavior of the dyes with concd. sulfuric acid is given in Table II.

TABLE II

BEHAVIOR OF DYES WITH CONCENTRATED SULFURIC ACID

Acid	1	2	3	4	5	6	7	8	9	10
Cold	Rose-red	Red-violet	Cherry-red	Dark blue	Cherry-red	Crimson	Red-violet	Cherry-red	Light cherry	Red-violet
Hot	Red-brown	Dark red	Red-brown	Dark straw	Dull brown	Dark brown	Dark straw	Dull brown	Dark brown	Dark brown
Dil.	Pale straw	Colorless	Light amber	Colorless	Orange	Light orange	Orange	Orange	Orange	Pink

All of the sulfonic acid dyes are decolorized by zinc dust in ammonia or in acetic acid. Stannous chloride gives with No. 6 a red precipitate; decolorizes Nos. 7 and 8; gives with No. 9 an orange precipitate and with No. 10 a pink solution.

The dyes are fast to light, water, alkali, washing, weather, perspiration, crocking, acids, sulfuring. Exception must be made for the sulfonic acid dyes, which are not fast to water, alkali and washing.

Summary

1. The bromination of 2-amino-*p*-cymene (acetyl derivative) places a bromine atom in Position 5 as proved by the conversion of the compound into 2,5-dibromo-terephthalic acid.

2. A series of new azo dyes was prepared by coupling the bromocymidine with phenols: phenol, resorcinol, thymol, 1-naphthol, 2-naphthol, 1-naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid, 2-naphthol-7-sulfonic acid, 2-naphthol-6-sulfonic acid and 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

3. The dyes form a series of beautiful colors which are very fast on

[12] Color Standards and Color Nomenclature, Robert Ridgway, Washington, D. C., 1912.

wool and silk in all tests for fastness with the exception of those containing the sulfo group which are not fast in the water, alkali and washing tests.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLI. THE SYNTHESIS OF HYDANTOINS CONTAINING PHENOLIC GROUPS IN THE GLYOXALINE NUCLEUS[1]

BY ROBERT D. COGHILL[2,3] AND TREAT B. JOHNSON

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Introduction

There is no doubt that a really efficient, non-toxic, internal antiseptic is one of the great needs of the medical profession today. Discussion of this topic with a prominent medical man recently brought forth from him the following statement: "There is nothing in the medical line so desperately needed today as a non-toxic, effective germicide or antiseptic for internal use. There is not a field of disease more interesting than that involving infections located in the intestinal and urinary tracts and there is certainly none over which medical practitioners have so little control." This is apparently a quite general and accepted opinion among leading medical men today. It is, therefore, quite apparent to anyone conscious of the ravages of specific diseases that this field of internal antisepsis[4] offers many problems of immediate interest to the organic chemist.

In considering the problem of developing new possible antiseptic principles applicable for internal sterilization, we have been influenced and guided by the requirements of a practical antiseptic agent so lucidly set forth by Assmann[5] and have, therefore, undertaken as a preliminary phase of this field of research, an investigation of some phenolic derivatives of hydantoin. As no phenolic derivatives of this cycle have hitherto been

[1] A contribution to the research on antiseptics now being carried on in the Sterling Chemistry Laboratory in coöperation with the National Research Council Sub-Committee on "Internal Antisepsis."—T. B. Johnson, Chairman.

[2] Holder of the du Pont Fellowship in Chemistry, **1923–24.** Papers XLI and XLII are constructed from a dissertation presented by Robert D. Coghill in June, **1924,** to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[3] An abstract of this paper was presented before the Division of Medicinal Products at the Spring Meeting of the American Chemical Society, held in Washington, D. C., April, **1924.**

[4] Harris, *J. Am. Med. Assoc.*, **59,** 1344 (1912).

[5] Assmann, *Z. Tiermed.*, **15,** 122, 264, 352 (1911). Ref. 4.