sirability of further study of the rather difficultly prepared 2,2′,6-trisubstituted diphenyls and their tendency to racemize. If the assumptions outlined are sound, it might be anticipated that trisubstituted compounds of all gradations of stability to racemization could readily be found. In fact, if the sum of the distances from the carbons to each of the three substituting groups and of the carbon to hydrogen is appreciably greater than twice the perpendicular distance between the α,α'-carbon atoms (2×2.90 Å.), no racemization should occur. If the sum is only slightly greater, the substances should racemize and if less, no resolution should be possible. Following out this plan of reasoning, it should even be possible to resolve merely a disubstituted α,α'-diphenyl provided the two groups were sufficiently large.

Slightly different methods of calculating interferences which are also based on x-ray data may be used, but the relative values are nearly the same. As a consequence the simplest method which involved the least amount of calculation was selected for discussion in this paper.

The authors wish to express here their appreciation to Dr. George L. Clark of the Chemistry Department of the University of Illinois for his assistance and advice in using the x-ray data.

Summary

A discussion is given of the expected isomerism of certain diphenyl compounds from a consideration of distances between the ring carbons and the centers of the substituting groups as deduced from x-ray data.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

SOME DERIVATIVES OF DIPHENYL ETHER

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Raiford and Colbert[1] brominated 4-nitrodiphenyl ether and obtained a dibromo derivative that melted at 79°,[2] but the halogen atoms were not oriented. In the work now reported this structure was determined by two syntheses. When 4-nitrochlorobenzene was heated with the potassium salt of 2,4-dibromophenol,[3] as explained below, the ether melt-

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[1] Raiford and Colbert, THIS JOURNAL, **48**, 2652 (1926).

[2] This melting point is not recorded in the published report but is given in the typed thesis on file in the University Library.

[3] The material available was not pure. It contained 62.26% of bromine instead of 63.49% calculated. It was converted into the benzoyl ester which, after several crystallizations, melted at 96° [*Ber.*, **40**, 747 (1907)] and analysis for bromine indicated a pure product. The phenol obtained by hydrolysis melted at 35°. Körner [*Ann.*, **137**, 205 (1866)] reported 40°. while Peratoner [*Gazz. chim. ital.*, **16**, 402 (1886)] found 35–36°.

ing at 79° was obtained. In a second synthesis 4-nitrochlorobenzene was heated with the potassium salt of 2-bromophenol and the resulting ether, m. p. 82°, which must have halogen in position 2′, was subjected to the action of bromine. The dibromo ether melting at 79° was obtained in this case also, which shows that the product in question is 4-nitro-2′,4′-dibromodiphenyl ether. Attempts to obtain this product by bromination of the 4-nitro-4′-bromo derivative under the same conditions were not successful, which indicates that in the preparation of the dibromo compound by direct bromination of *p*-nitrodiphenyl ether the halogen atom that entered first must have taken position 2′.

Similar observations were made with a dinitro derivative of phenyl ether. The 2,4-dinitro-2′-bromo compound, obtained by the interaction of 2,4-dinitrochlorobenzene with the potassium salt of *o*-bromophenol, was converted by standing with excess of bromine and a crystal of the iodine into a dibromo derivative. The position of the second bromine atom in this product was indicated by synthesis of the compound directly from 2,4-dibromophenol. The isomeric 2,4-dinitro-4′-bromodiphenyl ether did not react with bromine under the conditions of the previous experiments. When the mixture was heated in a sealed tube at 180° for seven hours, it gave a product that melted at 140–141°, and which appeared upon analysis to be a dinitrotribromo derivative, but which was not identical with 2,4-dinitro-2′,4′,6′-tribromodiphenyl ether, m. p. 130.5°, previously reported by Raiford and Colbert.[1] It is still under consideration.

A second point of interest in this work was the behavior of some of these ethers when nitrated. 4-Nitro-4′-bromodiphenyl ether lost bromine and gave the 2,4,2′,4′-tetranitro derivative[4] first prepared by Willgerodt. When the 2′,4′-dibromo compound was nitrated, two products were isolated, but not always from the same reaction mixture.[5] One was Willgerodt's tetranitro ether, while the other gave analytical data indicating a trinitro compound in which the bromine of the starting material had been retained. It melted at 139° and was not identical with 2,4,6-trinitro-2′,4′-dibromodiphenyl ether, m. p. 163–164°, which was synthesized from picryl chloride and 2,4-dibromophenol for this comparison.

The structures of the mono and dibromo derivatives of diphenyl ether first obtained by Hoffmeister[6] and by Mailhe and Murat[7] by direct bromination of the ether have recently been determined by LeFèvre, Saunders and Turner.[8] Nevertheless, the difficulties met in this Laboratory in trying to replace the nitro radical of 4-nitro-2′,4′-dibromodiphenyl ether

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[4] Willgerodt, *Ber.*, **13**, 887 (1880).

[5] The experiment was repeated several times but not with constant results.

[6] Hoffmeister, *Ann.*, **159**, 210 (1871).

[7] Mailhe and Murat, *Bull. soc. chim.*, **11**, 328 (1912).

[8] LeFèvre, Saunders and Turner, *J. Chem. Soc.*, 1168 (1927).

with halogen by diazotizing the corresponding amino compound and subjecting the product to the Sandmeyer reaction made it necessary to study this change with simpler derivatives. Therefore, mono and dibromo derivatives of diphenyl ether were prepared in this way.

Treatment of the diazonium salt[9] of 4-aminodiphenyl ether with cuprous bromide solution gave a 42% yield of the monobromo derivative that boiled at 295–298° at room pressure and at 143–144° at 7 mm.[10] The 4,4′-dibromo ether was obtained in a similar way. When 4-acetylaminodiphenyl ether, m. p. 128–129°,[11] in glacial acetic acid solution was treated with the theoretical quantity of bromine it gave a monobromo compound. Hydrolysis of this acetyl derivative with hydrochloric acid gave a 93% yield of the amine hydrochloride. This was diazotized and the product converted into the perbromide by a slight modification of the method of Bülow and Schmachtenberg.[12] Decomposition of this product by refluxing it with glacial acetic acid for thirty minutes gave a 73% yield of a dibromo derivative identical with that obtained by direct bromination of diphenyl ether.

The behavior just noted is in marked contrast to that observed when 4-amino-2′,4′-dibromodiphenyl ether was used. In this case the diazonium salt did not give a clear solution, and treatment of the suspension with cuprous bromide gave a quantity of material too small to purify and identify. Treatment of another portion with a potassium bromide solution of bromine gave a low yield of yellow solid that appeared to be perbromide. Boiling this with acetic acid gave a very small amount of dark oil which could not be identified.

When 4-amino-2′,4′-dichlorodiphenyl ether, prepared from 4-nitrochlorobenzene and 2,4-dichlorophenol by the general method, was diazotized, a clear solution of the diazonium salt was obtained. Treatment of this with cuprous chloride gave but 17% of the required trichloro ether, which indicates the extent to which activity is decreased by the presence of the second halogen atom.

Experimental Part

The diphenyl ethers studied here were prepared, in general, as follows. When only one nitro radical was present in the halogenated benzene used, this was mixed with a water solution containing one-fourth more than

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[9] This did not give a clear solution but a pale yellow suspension.

[10] Suter [This Journal, 51, 2585 (1929)] recorded 160–165° at 14 mm. for *p*-bromodiphenyl ether prepared by direct bromination.

[11] Mailhe [*Compt. rend.*, **154**, 1241 (1921)] reported 99°, but Haeussermann and Teichmann [*Ber.*, **29**, 1447 (1896)] had previously recorded 127°. Neither author analyzed his product, but the discrepancy may be explained by the possibility that Mailhe had the diacetyl derivative, for Sudborough [*J. Chem. Soc.*, **79**, 536 (1901)] found that the monoacetyl compound has the higher melting point of the two.

[12] Bülow and Schmachtenberg, *Ber.*, **41**, 2607 (1908).

TABLE IA

DERIVATIVES OF DIPHENYL ETHER

	Compound	Solvent	Crystal form	Yield, %
1	4-Acetylamino-4-bromo	EtOH	Colorless plates	Nearly quant.
2	4-Nitro-2′-bromo	EtOH + AcOH[a]	Nearly colorless needles	44
3	4-Nitro-2′,4′-dibromo	EtOH	Pale brown needles	83
4	4-Amino-2′,4′-dibromo	......	Oil	77
5	4-Acetylamino-2′,4′-dibromo	Dil. AcOH	Nearly colorless needles	Nearly quantitative
6	2,4-Dinitro-2′-bromo	EtOH + AcOH	Pale yellow needles	82
7	2,4-Dinitro-2′,4′-dibromo	EtOH	Yellow flakes	Nearly quant.
8	4-Nitro-2′,4′-dichloro	EtOH + AcOH	Cream-colored needles	79
9	4-Amino-2′,4′-dichloro	EtOH	Brown diamond-shaped crystals	60
10	4-Acetylamino-2′,4′-dichloro	EtOH	Colorless needles	Nearly quantitative
11	4,2′,4′-Trichloro	EtOH	Colorless needles	17
12	2,4-Dinitro-2′,4′-dichloro	EtOH + AcOH	Pale yellow plates	78
13	2,4,6-Trinitro-2′,4′-dibromo	EtOH + AcOH	Short yellow needles	85
14	?-Trinitro-2′,4′-dibromo	AcOH + toluene	Yellow flakes	Nearly quant.

[a] Approximately 2 volumes of alcohol and 1 volume of glacial acetic acid.

TABLE IB

DERIVATIVES OF DIPHENYL ETHER

	Formula	M. p., °C.	Subs., g.	Analyses					
				0.1 *N* acid, cc.	Nitrogen, % Calcd.	Nitrogen, % Found	0.1 *N* $AgNO_3$, cc., or wt. of Ag hal., g.	Halogen, % Calcd.	Halogen, % Found
1	$C_{14}H_{12}O_2NBr$	157	0.2977	...	..	..	0.1815	26.12	26.11
2	$C_{12}H_8O_3NBr$	82	.4111	13.65	4.76	4.59	.....	...	...
			.2939	...	..	..	10.18	27.21	27.27
3	$C_{12}H_7O_3NBr_2$	79	.2238	5.89	3.75	3.80	.....	...	...
			.3317	...	..	..	17.93	42.89	42.48
4	$C_{12}H_9ONBr_2$	Oil, 225–230° (10 mm.)	.2356	...	..	..	0.2580	46.61	46.60
5	$C_{14}H_{11}O_2NBr_2$	158	.2023	...	..	..	0.1971	41.55	41.47
6	$C_{12}H_7O_5N_2Br$	88–89	.5180	30.52	8.25	8.25	.....	...	...
			.3472	...	..	..	10.61	23.59	23.99
7	$C_{12}H_6O_5N_2Br_2$	131	.2304	11.22	6.69	6.83	.....	...	...
			.2019	...	..	..	9.87	38.27	38.24
8	$C_{12}H_7O_3NCl_2$	71	.2524	...	..	..	0.2545	25.08	24.96
9	$C_{12}H_9ONCl_2$	62	.2512	...	..	..	.2843	27.95	27.98
10	$C_{14}H_{11}O_2NCl_2$	144	.2783	...	..	..	.2707	23.97	24.07
11	$C_{12}H_7OCl_3$	51	.2056	...	..	..	.3216	38.93	38.72
12	$C_{12}H_6O_5N_2Cl_2$	118	.2472	15.02	8.51	8.51	.....	...	...
			.2684	...	..	..	16.56	21.58	21.52
13	$C_{12}H_5O_7N_3Br_2$	163–164	.3116	20.0	9.07	9.04	.....	...	...
			.3019	...	..	..	13.25	34.55	35.00
14	$C_{12}H_5O_7N_3Br_2$	139	.2294	15.66	9.07	9.56	.....	...	...
			.2823	...	..	..	12.36	34.55	34.40

the theoretical amount of the potassium salt of the required phenol, the mixture evaporated to dryness and then heated on an oil-bath for three hours at 150–170°. Unchanged nitrobenzene derivative was then removed by distillation with steam, and the non-volatile residue (ether) purified in a suitable manner. When two or more nitro radicals were present in the starting material, the "wet method" described by Raiford and Colbert[13] gave best results. With the exceptions noted above, other derivatives were prepared by standard methods that will not be described here. The yields, general properties and analytical data for these substances are given in the tables.

Summary

1. When 4-nitrodiphenyl ether is brominated as here described, the halogen atoms enter positions 2′ and 4′ only, although excess of bromine may be present. Position 2′ is probably attacked first.

2. Nitration of 4-nitro-2′,4′-dibromodiphenyl ether gave two products: the 2,4,2′,4′-tetranitro compound, and a trinitro derivative in which all bromine is retained.

3. Increase in the number of substituents seems to interfere with diazotization of an aminophenyl ether.

4. Several new derivatives of diphenyl ether have been synthesized and their structures established.

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A STUDY OF THE PENTOSE AND URONIC ACID CONTENT OF ORANGE ALBEDO, AND AN ARABINO-GALACTURONIC ACID DERIVED FROM ORANGE PECTIN

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I. Introduction

This work was undertaken to determine the relative amounts of combined pentose and uronic acid in orange pectin, as it occurs in the albedo of commercial ripe oranges, and subsequently to see if the relation of these substances is similar to that in apple pectin.

Apple tissue has been found previously to contain no free pentose and the pectin to contain no combined pentose.[1] The furfural obtained on distillation with hydrochloric acid was quantitatively attributed to the galacturonic acid part of the pectin, arabinose being an intermediate stage in the decomposition.

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[13] Ref. 1, p. 2659.

[1] Ronald B. McKinnis, THIS JOURNAL, **50**, 1911 (1928).