626. *Electrophilic Substitution. Part XII.* The Nitration of Diphenylmethane, Fluorene, Diphenyl Ether, Dibenzofuran, Diphenylamine, and Carbazole; Relative Reactivities and Partial Rate Factors.*

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The nitrations mentioned in the title, carried out in acetic anhydride, have been studied quantitatively. The proportions of isomers and relative overall reactivites have been determined and partial rate factors calculated. Dibenzofuran is less reactive than diphenyl ether, and carbazole than diphenylamine.

THE purpose of this series of papers is to test the molecular-orbital theory of chemical reactivity, in particular the simplified version put forward[1] by one of us some years ago. Previous investigations have dealt with the nitration of alternant aromatic hydrocarbons[2] and heterocycles;[3] here we report preliminary work on the effect of $-E$ substituents and of ring-closure to non-alternant systems. In these cases the simple molecular-orbital

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* Part XI, *J.*, 1957, 2521.

[1] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3345, 3350, 3353, 3355, 3357.
[2] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[3] Dewar and Maitlis, *J.*, 1957, 2521.

treatment[1] is not so applicable, and more elaborate theoretical methods must be used; the results of such a treatment will be reported in a later paper.

The compounds studied were diphenylmethane, fluorene, diphenyl ether, dibenzofuran, diphenylamine, and carbazole. They were first nitrated individually in acetic anhydride, and the proportions of isomers in the product were estimated spectrophotometrically by the method previously described.[4] The conditions were chosen to lead almost exclusively to mononitro-compounds and the estimations of isomers in most cases were accurate within ±1%. The individual compounds are discussed below. Our results are summarised in Table 1.

Diphenylmethane.—It has been reported [5] that nitration of diphenylmethane with cold fuming nitric acid yields 2 : 4′- and 4 : 4′-dinitrodiphenylmethane. By using an excess of hydrocarbon with nitric acid–acetic anhydride we were able to obtain mainly a mixture of mononitro-derivatives. Since the spectra of these are similar, and since a little benzophenone was also formed, the error in estimating the proportions of isomers was larger (±10%) than usual.

Fluorene.—Nitration of fluorene in acetic acid with an excess of fuming nitric acid gives 2 : 5- and 2 : 7-dinitrofluorene,[6] suggesting that the 2- and the 4-position have comparable reactivites; Weissberger [7] has indeed isolated 4-nitrofluorene in preparation of 2-nitrofluorene. We found both isomers in the nitration product and some indication that the 3-isomer was also present; however, the amount of the latter (2%) was not much greater than our estimated experimental error (±1%).

Diphenyl Ether.—Suter [8] reported that nitration of diphenyl ether gives the *p*- and the *o*-nitro-derivative in the ratio 1·2 : 1; this agrees with our value (1 : 1).

Dibenzofuran.—The isomer distribution has already been reported.[9]

Diphenylamine.—Ryan and Ryan,[10] who studied the nitration of diphenylamine in a variety of solvents, reported that nitration in acetic acid took place only in presence of an excess of nitric acid and gave a green solution, presumably implying that the diphenylaminium ion-radical was formed to some extent.[11] The products isolated were 2 : 2′- and 2 : 4′-dinitrodiphenylamine together with some *N*-nitrosodiphenylamine. We have been able to obtain a mixture of 2- and 4-nitrodiphenylamine as the main nitration product by using an excess of diphenylamine in acetic anhydride; *N*-acetyldiphenylamine was also formed, together with *N*-acetyl-2- and -4-nitrodiphenylamine. Since *N*-acetyldiphenylamine was not significantly attacked under our conditions we assumed that the by-products arose from acetylation of *N*-nitrodiphenylamines; the proportions of isomers given in Table 1, therefore, refer to the combined yields of nitro-compounds and their acetyl derivatives.

Carbazole.—Nitration of carbazole in acetic acid has been reported [12] to give mainly 3-nitrocarbazole, together with about 5% of the 1-isomer; we found that the product contained much more than 5% of the 1-isomer, and there were indications that a little 2-nitrocarbazole had also been formed (cf. fluorene).

The relative overall reactivities of the compounds were then determined by the competitive method. Each mixture of mononitro-compounds was analysed spectrophotometrically,[4] the proportions of isomers being assumed to be the same as in the products of the simple nitrations. This enabled us to treat the product from each competitive nitration as a binary mixture. Diphenylmethane and dibenzofuran were compared with

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[4] Dewar and Urch, *J.*, 1957, 345.

[5] Staedel, *Annalen*, 1878, **194**, 363.

[6] Morgan and Thomason, *J.*, 1926, 2691; Anantakrishnan and Hughes, *J.*, 1935, 1607; Courtot, *Ann. Chim.* (*France*), 1930, **14**, 5.

[7] Weissberger, personal communication.

[8] Suter, *J. Amer. Chem. Soc.*, 1929, **51**, 2583.

[9] Dewar and Urch, *J.*, 1957, 345.

[10] Ryan and Ryan, *Proc. Roy. Irish Acad.*, 1917—19, *B*, **34**, 195, 198, 213.

[11] Cf. Jones and Culbertson, *Proc. Iowa Acad. Sci.*, 1942, **49**, 287.

[12] Morgan and Mitchell, *J.*, 1931, 3283; Lindemann, *Ber.*, 1924, **57**, 555.

diphenyl, and carbazole with perylene; the reactivities of diphenyl and perylene at 25° relative to benzene are known.[2] Diphenyl ether was compared with dibenzofuran, diphenylamine with carbazole, and fluorene with diphenyl ether. In this way we obtained the relative overall reactivities (benzene = 6) given in the first column of Table 2; and these together with the isomer ratios of Table 1 led to the partial rate factors (corrected for statistical factors) shown in the remaining columns of Table 2. The errors in these are uncertain; in the analogous work on hydrocarbons [2] it appeared that the values obtained were not in error by more than 50%.

TABLE 1. *Proportions of isomers in mononitro-derivatives formed by nitration in acetic anhydride at 0° and 25°.*

	At 0°				At 25°			
Isomer:	1	2	3	4	1	2	3	4
Diphenylmethane	—	52	—	48	—	38	—	62
Fluorene	—	63	3	34	—	69	2	29
Diphenyl ether	—	51	—	49	—	50	—	50
Dibenzofuran [8]	25	39	36	—	19	40	41	—
Diphenylamine	—	76	—	24	—	71	—	29
Carbazole	29	1	70	—	28	2	70	—

TABLE 2. *Overall reactivities and partial rate factors for nitration in acetic anhydride at 25°.*

Compound	Overall reactivity (C_6H_6 = 6)	Partial rate factors for position			
		1	2	3	4
Diphenylmethane	117	—	13	—	32
Fluorene	608	—	2040	60	944
Diphenyl ether	936	—	117	—	23
Dibenzofuran	470	47	94	94	—
Diphenylamine	4,430,000	—	831,000	—	575,000
Carbazole	222,000	32,100	1100	77,600	—

Molecular-orbital treatment of these reactions will be described in a later paper; attention may be drawn to the comparisons diphenyl ether–dibenzofuran and diphenylamine–carbazole, which indicate that closure of the five-membered ring in each case lowers the overall reactivity.

EXPERIMENTAL

Materials.—Chromatography was carried out with Peter Spence's alumina (type "H", 100/200 mesh). Solvents were distilled before use. Fluorene was purified by chromatography from light petroleum (b. p. 40—60°) on alumina, and had m. p. 117—117·5°. Perylene was prepared by decarboxylation of perylenetetracarboxylic acid and purified by recrystallisation to m. p. 271—272°. Carbazole was prepared by dehydrogenation [13] of tetrahydrocarbazole and purified by chromatography from benzene on alumina; it had m. p. 244—245°. Nitric acid (*d* 1·5), acetic anhydride, diphenyl, diphenyl ether, diphenylmethane, and dibenzofuran were commercial specimens, used without further purification. The preparation and spectra (in 95% EtOH) of reference compounds are listed in Table 3.

3-Nitrofluorene was not prepared; the spectrum reported by Hayashi and Nakayama [21] was used in the analysis. Likewise we used for 4-nitrofluorene the spectrum reported by Weissburger and Weissburger.[22]

The preparation of 1- and 3-nitrocarbazole presented special features. 3-Nitrocarbazole was prepared by Lindemann's method [23] and purified by recrystallisation six times from acetic acid, and then five times from ethanol; it then formed yellow crystals, m. p. 215·5—216·5°.

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[13] Gabriel and Stelzner, *Ber.*, 1896, **29**, 1303.

Slow crystallisation from benzene gave a dark wine-red allotropic form, m. p. 213—215°, converted into the yellow form by recrystallisation from ethanol. Both forms had identical ultraviolet spectra. 1-Nitrocarbazole was isolated from the mother-liquors from the first recrystallisation of the 3-isomer; after it had been chromatographed three times from benzene on alumina it formed bright yellow needles, m. p. 186—187°.

TABLE 3. *Spectra of reference compounds, and references to methods of preparation.*

			Spectrum in 95% ethanol (except where stated)	
Compound	Ref.	M. p.	$\lambda_{\text{max.}}$ (mμ) ($\log_{10}\varepsilon$)	$\lambda_{\text{min.}}$ (mμ) ($\log_{10}\varepsilon$)
2-Nitrodiphenylmethane	13	Oil	254(3·663)	238(3·580)
3-Nitrodiphenylmethane	14	Oil	264(3·881)	236(3·574)
4-Nitrodiphenylmethane	15	30—31°	278(4·020)	234(3·465)
2-Nitrofluorene	16	155—156	332(4·254), 234(3·980)	265(3·202), 222(3·920)
2-Nitrodiphenylamine	17	75·5—76	428(3·820), 259(4·150), 220(4·125), shoulder at 282(4·05)	325(2·631), 238(4·016), 214(4·107)
3-Nitrodiphenylamine	17	113—114	367(3·167), 282(4·209), 265(4·258) (in light petroleum, b. p. 40—60°)	320(2·718), 278(4·205)
4-Nitrodiphenylamine	17	132·5—133	391(4·293), 258(3·978), 228(3·818)	308(3·156), 234(3·807), 222(3·811)
N-Acetyl-2-nitrodiphenylamine	18	135—136	234(4·237), shoulders at 308(3·184), 266(3·671)	218(4·147)
N-Acetyl-3-nitrodiphenylamine	18	66—66·5	317(3·117), 244(4·318) (in light petroleum, b. p. 40—60°)	300(3·046), 220(3·990)
N-Acetyl-4-nitrodiphenylamine	18	100—101	310(3·981), 228(4·091)	262(3·609), 218(4·081)
N-Acetyldiphenylamine	18	101—102	236(4·041)	222(3·954)
2-Nitrodiphenyl ether	19	Oil	313(3·337)	286(3·253)
4-Nitrodiphenyl ether	19	31—31·5°	303(4·088)	250(3·420)
1-Nitrocarbazole	See below	186—187	403(3·855), 301(4·127), 260(3·957), 222(4·682)	316(3·239), 281(3·814), 256(3·944)
2-Nitrocarbazole	20	165—60	340(4·151), 281(3·867), 250(4·353), 212(4·362), shoulders at 259(4·290), 241(4·250), 222(4·104)	300(3·640), 271(3·792), 228(4·029)
3-Nitrocarbazole	See below	See below	366(3·985), 308(4·130), 279(4·374), 231(4·451), shoulder at 270(4·180)	330(3·777), 289(3·987), 254(3·640), 218(4·296)
4-Nitrocarbazole	20	181—20	361(3·765), 222(4·698), shoulder at 290(3·757)	312(3·364)

Nitrations.—A weighed amount of substance was dissolved in acetic anhydride (300 c.c.). The required amount of nitric acid (*d* 1·5) in acetic anhydride (50 c.c.) was added, and the flask containing the nitric acid solution rinsed into the reaction mixture with acetic anhydride (50 c.c.). All the solutions had previously been brought to the required temperature (0° or 25°) in an ice-bath or thermostat. After a suitable period the solution (usually yellow) was poured with stirring into ice-water (1 l.). When hydrolysis was complete, the organic material was isolated with chloroform and chromatographed on an alumina column (20 × 4 cm.). After excess of starting material had been eluted with light petroleum, the nitro-compounds were eluted with ether and rechromatographed 3—6 times. The combined fractions of starting material were evaporated, weighed, and analysed by ultraviolet spectrophotometry;[4] the combined nitro-compound fractions were similarly treated. Solutions in 95% ethanol were used

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[14] Becker, *Ber.*, 1882, **15**, 2091.
[15] Basler, *Ber.*, 1883, **16**, 2716.
[16] Kuhn, *Org. Synth.*, 1933, **13**, 74.
[17] Schopff, *Ber.*, 1890, **23**, 1840; Ullman and Nadai, *Ber.*, 1908, **41**, 1872.
[18] Cf. Kehrmaren and Baumgartner, *Helv. Chim. Acta*, 1926, **9**, 673.
[19] Brewster and Groening, *Org. Synth.*, 1934, **14**, 66.
[20] Barclay and Campbell, *J.*, 1945, 530.
[21] Hayashi and Nakayama, *J. Soc. Chem. Ind. Japan*, 1933, **36**, 127.
[22] Weissburger and Weissburger, *J. Org. Chem.*, 1954, **19**, 968.
[23] Lindemann, *Ber.*, 1924, **57**, 555.

TABLE 4. *Products from nitration in acetic anhydride at* 0° *and* 25°.

Material	Wt. (g.)	Temp.	HNO_3 (g.)	Time (hr.)	Products and wts. (g.)	
Diphenylmethane ...	1·684	0°	0·63	65	CH_2Ph_2	1·346
					2-NO_2-deriv.	0·047
					4-NO_2-deriv.	0·043
					$COPh_2$	0·012
,, ...	1·687	25	0·63	16	CH_2Ph_2	1·390
					2-NO_2-deriv.	0·032
					4-NO_2-deriv.	0·052
					$COPh_2$	0·006
Fluorene	1·664	0	0·315	72	Fluorene	1·304
					2-NO_2-deriv.	0·165
					3-NO_2-deriv.	0·008
					4-NO_2-deriv.	0·089
,, ...	1·660	25	0·315	16	Fluorene	1·320
					2-NO_2-deriv.	0·198
					3-NO_2-deriv.	0·007
					4-NO_2-deriv.	0·084
Diphenyl ether	1·707	0	0·63	65	Ph_2O	1·134
					2-NO_2-deriv.	0·245
					4-NO_2-deriv.	0·235
,, ...	1·702	25	0·63	16	Ph_2O	1·243
					2-NO_2-deriv.	0·250
					4-NO_2-deriv.	0·249
Diphenylamine	0·339	0	0·063	20	$NHPh_2$	0·171
					N-Ac deriv.	0·049
					2-NO_2-deriv.	0·028
					N-Ac-2-NO_2-deriv.	0·054
					4-NO_2-deriv.	0·015
					N-Ac-4-NO_2-deriv.	0·010
,, ...	0·339	25	0·063	5	$NHPh_2$	0·184
					N-Ac deriv.	0·048
					2-NO_2-deriv.	0·027
					N-Ac-2-NO_2-deriv.	0·032
					4-NO_2-deriv.	0·015
					N-Ac-4-NO_2-deriv.	0·008
Carbazole	0·827	0	0·158	24	Carbazole	0·692
					N-Ac deriv.	0·001
					1-NO_2-deriv.	0·059
					2-NO_2-deriv.	0·002
					3-NO_2-deriv.	0·146
,, ...	0·836	25	0·158	6	Carbazole	0·752
					N-Ac deriv.	0·001
					1-NO_2-deriv.	0·032
					2-NO_2-deriv.	0·002
					3-NO_2-deriv.	0·079

TABLE 5. *Competitive nitrations.*

Material	Wt. (g.)	Temp.	HNO_3 (g.)	Time (hr.)	Products and wts. (g.)	
Diphenylmethane	1·681	0°	0·63	60	CH_2Ph_2	1·433
Diphenyl	1·540				NO_2-derivs.	0·066
					Ph_2	1·303
					NO_2-derivs.	0·060
Diphenylmethane	1·681	25	0·63	24	CH_2Ph_2	1·483
Diphenyl	1·542				NO_2-derivs.	0·061
					Ph_2	1·361
					NO_2-derivs.	0·090
Dibenzofuran	1·684	0	0·63	65	Dibenzofuran	1·499
Diphenyl	4·617				NO_2-derivs.	0·206
					Ph_2	4·387
					NO_2-derivs.	0·240
Dibenzofuran	1·682	25	0·63	17	Dibenzofuran	1·240
Diphenyl	4·621				NO_2-derivs.	0·284
					Ph_2	3·443
					NO_2-derivs.	0·252
Diphenyl ether	1·705	0	0·63	65	Ph_2O	1·396
Dibenzofuran	1·680				NO_2-derivs.	0·355
					Dibenzofuran	1·357
					NO_2-derivs.	0·187

in 0·5 cm. silica cells on a Unicam S.P. 500 spectrophotometer. The results are summarised in Table 4.

Competitive Nitrations.—The competitive nitrations were carried out in the same way as the simple nitrations, except that in the comparison carbazole–perylene a larger volume of acetic anhydride (1 l.) had to be used. The mixture of mononitro-compounds was analysed[4] as a binary mixture on the assumption that the isomer ratios were the same as in the simple nitrations. The results are shown in Table 5.

TABLE 5. (*Continued.*)

Material	Wt. (g.)	Temp.	HNO_3 (g.)	Time (hr.)	Products and wts. (g.)	
Diphenyl ether	1·702	25°	0·63	17	Ph_2O	1·381
Dibenzofuran	1·681				NO_2-derivs.	0·458
					Dibenzofuran	1·349
					NO_2-derivs.	0·222
Fluorene	1·661	0	0·315	72	Fluorene	1·431
Diphenyl ether	1·700				NO_2-derivs.	0·241
					Ph_2O	1·453
					NO_2-derivs.	0·044
Fluorene	1·664	25	0·315	16	Fluorene	1·407
Diphenyl ether	1·664				NO_2-derivs.	0·294
					Ph_2O	1·425
					NO_2-derivs.	0·044
Perylene	0·504	0	0·063	21	Perylene	0·492
Carbazole	0·335				NO_2-derivs.	0·007
					Carbazole	0·295
					NO_2-derivs.	0·004
Perylene	0·504	25	0·063	5	Perylene	0·497
Carbazole	0·670				NO_2-derivs.	0·005
					Carbazole	0·655
					NO_2-derivs.	0·004
Diphenylamine	0·338	0	0·063	17	$NHPh_2$	0·231
Carbazole	3·346				NO_2-derivs.	0·048
					Carbazole	3·303
					NO_2-derivs.	0·028
Diphenylamine	0·338	25	0·063	5	$NHPh_2$	0·190
Carbazole	3·344				NO_2-derivs.	0·062
					Carbazole	3·332
					NO_2-derivs.	0·010

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