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INTRAMOLECULAR DIAZO COUPLING AND MOLECULAR REARRANGEMENT OF *o*-AMINOPHENYLCARBINOLS[1]

ROBERT L. COHEN[2] AND ANTHONY J. SISTI
Department of Chemistry, Adelphi University, Garden City, Long Island, New York
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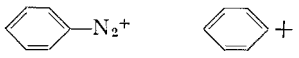
ABSTRACT

A number of 1-(2-aminophenyl)-1-(substituted aryl)ethanols were deaminated, yielding ketones, formed by a molecular rearrangement and, in some instances, azo ketones formed by intramolecular coupling and cleavage. The sensitivities of these two reactions, one characteristic of the aryl cation and the other of the diazonium group, to relatively small changes in the electrical nature of the migrating group were determined.

The products of decomposition of the aromatic diazonium ion (I) may be classified as resulting from the aryl cation (II) (produced by the irreversible loss of nitrogen from I),

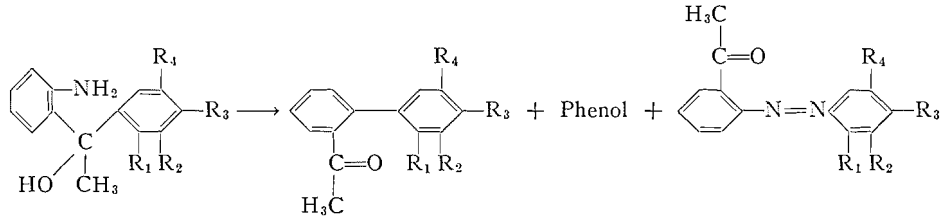


I II

or from the diazonium group functioning as an electrophile. The available data in the literature indicate that the aryl cation (II) is a highly reactive, non-selective moiety (1, 2). Thus, the heterolytic acid-catalyzed decomposition of diazonium salts normally leads to substitution by solvent or other nucleophiles (3, 4), but in certain instances molecular rearrangement (2) and elimination, yielding benzyne intermediate (2, 5, 6), have been observed.

The well-known coupling reaction of aromatic diazonium ions yielding azo compounds illustrates the electrophilic property of the diazonium group. Other reactions indicating this property have been discussed elsewhere (7, 4 (p. 424 ff.)).

Recently, an interesting intramolecular coupling and cleavage of a diazotized amine was reported (8). Namely, when 1-*o*-aminophenyl-1-(2,5-dimethyl-4-methoxyphenyl)-ethanol (III, $R_1 = R_4 = CH_3$, $R_3 = OCH_3$) was treated with nitrous acid, in addition to phenol and the expected rearrangement product (2) (IV), an 18% yield of azo ketone (V)

[1] 

III IV V

was isolated (eq. 1). The intermolecular application of the aforementioned reaction led to an excellent synthesis of aldehydes and ketones (9, 10, 11).

[1]*Taken in part from the Ph.D. thesis of Robert L. Cohen, Adelphi College, 1963; presented at American Chemical Society Meeting, New York, N.Y., September 9–13, 1963.*

[2]*Present address: Jackson Laboratory, Organic Chemicals Department, E.I. du Pont de Nemours and Company, Inc., P.O. Box 525, Wilmington 99, Delaware.*

The present paper deals with a study of the factors (steric and (or) electrical) which promote the novel rearrangement of the anisyl group yielding azo ketone. It is also of interest to note that compounds of type III afford an excellent opportunity to study simultaneously the reactivity and selectivity of the aryl cation (II) and the diazonium group (I) with minor changes in the electrical nature of the migrating group (eq. 1).

RESULTS

The amino alcohols listed in Table I were prepared by treatment of the appropriately substituted *o*-aminobenzophenones with methylmagnesium iodide. The *o*-aminobenzophenones were prepared by conventional Friedel–Crafts acylations. Each compound was diazotized in acidic aqueous dioxane and the resulting diazonium salts were decomposed at room temperature. Three products were isolated: alkali-soluble material presumably phenol, ketones resulting from molecular rearrangement, and azo ketones (when produced) resulting from intramolecular coupling and cleavage. The two ketones were separated chromatographically on an alumina-packed column.

The results of the diazotization of various 1-(2-aminophenyl)-1-(substituted aryl)-ethanols (III), yielding ketone (IV) and azo ketone (V), are given in Table II (eq. 1). No fluorenol resulting from ring closure (2) could be isolated. The ketones (IV and V) were identified by infrared spectra and elemental analysis. Structure determinations were not carried out since ketones (2) and the azo ketone previously isolated (8) from similar reactions were synthesized unequivocally.

DISCUSSION

Inspection of the results presented in Table II reveals that *azo ketone* (V) was produced *only* by those amines which contain alkylated anisole rings (III*f*–III*i*). Significant amounts were produced from the diazotization of amines which bore two alkyl substituents in the anisole nucleus (compare III*e* and III*f* with III*g*–III*i*). The effect of the *ortho*-substituent (R_1) in promoting azo ketone formation cannot be primarily steric in nature (compare III*g* and III*i* with III*j* and III*k*). Specifically it should be noted that the azo coupling of the electrophilic diazonium group is particularly sensitive to the electrical changes in the migrating anisyl group (compare III*g*, III*h*, and III*i* with III*e* and III*f*, and with III*j* and III*k*). A rationalization for the results is best presented by assuming that the transition state for intramolecular azo coupling resembles the intermediate presented in equation 2. Maximum stabilization for the transition state is furnished by the *p*-methoxyl group, however, this substituent is not sufficient to yield a significant amount of coupling product. If the inductive stabilizing effect of the 1-methyl and 2- or 4-methyl groups are added, the rate of intramolecular azo coupling is fast enough to produce reasonable yields of the azo ketone. This interpretation of the results is in complete agreement with previously reported studies (12). The rate of coupling of *p*-nitrobenzenediazonium sulphate with various alkylated anisoles increased in the following order: *m*-methylanisole, 2,3-dimethylanisole, 2,5-dimethylanisole, and 3,5-dimethylanisole (anisole and *o*-methylanisole do not couple at all). Competitive coupling studies of phenols and substituted phenols with *p*-nitrobenzenediazonium sulphate revealed that chlorine and bromine deactivate whether *ortho* or *meta* to the coupling position (coupling occurs *para* to —OCH_3 or —OH group). Thus, the methyl, chloro, and bromo groups, which are sterically similar, whether *ortho* or *meta* to the coupling site exert effects consistent with their respective inductive electrical properties. A rationale for migration is therefore

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TABLE I

Amino alcohols

	M.p.	Yield,* %	Calc. C	Calc. H	Calc. N	Found C	Found H	Found N
1-(2-Amino-4,5-dimethylphenyl)-1-(2-chlorophenyl)-ethanol (III*c*)	106–107	71	69.69	6.53	5.08	69.73	6.58	5.05
1-(2-Amino-4,5-dimethylphenyl)-1-(2-bromophenyl)-ethanol (III*d*)	112–112.5	48	60.01	5.66	4.37	60.13	5.60	4.45
1-(2-Aminophenyl)-1-(2-methyl-4-methoxyphenyl)-ethanol (III*f*)	145–147	67	74.68	7.44	5.44	74.55	7.32	5.41
1-(2-Aminophenyl)-1-(2,3-dimethyl-4-methoxyphenyl)-ethanol (III*h*)	178–180	33	75.24	7.80	5.16	75.24	7.67	5.31
1-(2-Aminophenyl)-1-(5-methyl-2-ethyl-4-methoxyphenyl)ethanol (III*i*)	110–112	26	75.76	8.12	4.91	75.73	8.02	4.97
1-(2-Aminophenyl)-1-(2-chloro-5-methyl-4-methoxyphenyl)ethanol (III*j*)	120–122	52	65.86	6.22	4.80	65.85	6.27	4.83
1-(2-Aminophenyl)-1-(2-bromo-5-methyl-4-methoxyphenyl)ethanol (III*k*)	124–126	56	57.15	5.40	4.17	57.33	5.34	4.28
2-Aminophenyldi-(2,5-dimethyl-4-methoxyphenyl)-carbinol† (VI)	161–163	20	76.69	7.47	3.58	76.62	7.37	3.52

*Yields refer to reactions of substituted *o*-aminobenzophenones with methylmagnesium iodide.
†Prepared from methyl anthranilate and the Grignard reagent from 2,5-dimethyl-4-methoxyiodobenzene.

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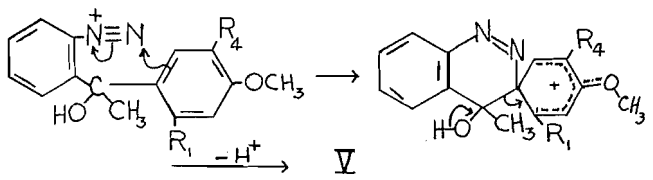
TABLE II

Yields of ketones, azo ketones, and phenols from diazonium salts

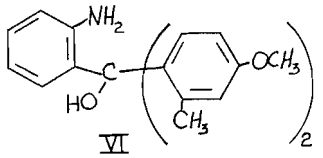
	Amine III							
	R_1	R_2	R_3	R_4	% ketone (IV)*		% azo ketone (V)†	% phenol
(*a*)‖	$-CH_3$	—H	$-CH_3$	—H		10§	0	—
(*b*)‖	—H	—H	—H	—H		3.0§	0	—
(*c*)‡	—Cl	—H	—H	—H	1.34	0.8§§	0	—
(*d*)‡	—Br	—H	—H	—H	1.4	1.4§	0	—
(*e*)‖	—H	—H	$-OCH_3$	—H	—	4.4§	0	—
(*f*)	$-CH_3$	—H	$-OCH_3$	—H	17.2	13.4§	1.7	30
(*g*)‖	$-CH_3$	—H	$-OCH_3$	$-CH_3$	16	(13)	18	22
(*h*)	$-CH_3$	$-CH_3$	$-OCH_3$	—H	18.4	(12)	16.5	17
(*i*)	$-CH_2CH_3$	—H	$-OCH_3$	$-CH_3$	—	(14.2)	15.6	20
(*j*)	—Cl	—H	$-OCH_3$	$-CH_3$	15.0	(11.7)	0	60
(*k*)	—Br	—H	$-OCH_3$	$-CH_3$	15.8	(13.1)	0	40

*Yields in parentheses refer to recrystallized ketone; those without parentheses to chromatographed yield.
†Yields refer to crystallized material.
‡1-(2-Amino-4,5-dimethylphenyl)-1-(substituted aryl)ethanol (VI).
§Yield of 2,4-dinitrophenylhydrazone.
‖The results of these compounds were reported previously (ref. (2)).

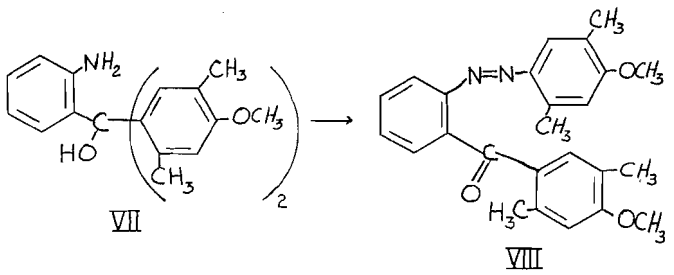
envisaged as an intramolecular electrophilic attack by the diazonium group upon the anisyl group (eq. 2).

[2] 

In a previously reported result (2), azo ketone was not isolated when amino alcohol VI was deaminated. Further substantiation of the selectivity and sensitivity of the electro-



philic diazonium group to relatively minor electrical changes was obtained upon diazotization of the amino alcohol (VII) which resulted in the isolation of a 7% yield of azo ketone (VIII) (eq. 3).*

[3] 

Further inspection of Table II reveals that the yields of ketone (IV), produced by migration of the aryl group to an electron-deficient carbon (2) (aryl cation), were essentially *constant* (III*f*–III*k*). These constant yields are significant since in those cases in which negligible amounts of azo ketone were produced (III*f*, *j*, and *k*), the increased portion of the reaction via aryl cation gave mainly phenol. Thus, the aryl cation is relatively insensitive to these electrical changes in the migrating group. Since it has been demonstrated that the lifetime of the aryl cation is very short (13) these results are not completely unexpected. However, they strongly support the mechanism previously offered for the formation of ketone (2). Thus, the electron-donor group (—OCH_3) in the *para*-position of the migrating group assists rearrangement provided an *ortho*-substituent is present (compare III*c*, *d*, and *e* with III*f*–*k*). This electrical assistance is to be expected in this type of rearrangement. Provided the *p*-methoxyl group is present, the yield of ketone is related to the number of free *ortho*-positions (III*f*–*k*). When the *p*-methoxyl group is absent the effect of an *o*-substituent upon ketone formation appears to be electrical (III*a*–III*d*). The rate of ketone formation, therefore, appears largely determined by the number of free *ortho*-positions, and the ground state electron density, of the migrating

*2,5-Dimethyl-4-methoxy-2'-(2,5-dimethyl-4-methoxyphenyl)benzophenone (27%) and 1,4-dimethyl-3-methoxy-9-(2,5-dimethyl-4-methoxyphenyl)-9-fluorenol (15.3%) were also isolated.

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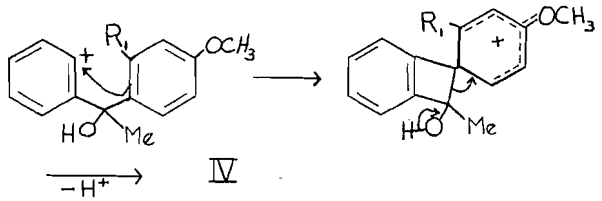
aryl group. As previously presented (2), the following reaction path is in accord with the data (eq. 4).

[4] 

EXPERIMENTAL

Synthesis of o-Aminobenzophenones

The following ketones were synthesized by the method of Kranzlein (14): 2′-chloro-4,5-dimethyl-2-aminobenzophenone, m.p. 121.5–123° (reported (14), 120°); *2′-bromo-4,5-dimethyl-2-aminobenzophenone*, m.p. 111–112.5°; yield, 61%, crystallized from 95% ethanol. Anal. Calc. for $C_{15}H_{14}BrNO$: C, 59.22; H, 4.64; N, 4.61. Found: C, 59.26; H, 4.62; N, 4.53.

2-Amino-4′methoxy-2′-methylbenzophenone

This was prepared according to the procedure of Sternbach *et al.* (15) by treating the Grignard reagent prepared from 4-iodo-3-methylanisole (16) with acetyl anthranil (17); yield, 17%; m.p. 60–61°, crystallized from aqueous ethanol. Anal. Calc. for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.26; N, 5.81. Found: C, 74.53; H, 6.34; N, 5.69.

The following series of substituted benzophenones were prepared according to the procedure of Lothrup (18): 2,3-dimethyl-4-methoxy-2′-aminobenzophenone, m.p. 147–149° (reported (18), 144–145°); *2-ethyl-4-methoxy-5-methyl-2′-aminobenzophenone*, m.p. 116–118°; yield 49%, crystallized from 95% ethanol. Anal. Calc. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.67; H, 7.16; N, 5.33.

2-Chloro-4-methoxy-5-methyl-2′-aminobenzophenone

2-Chloro-4-methoxy-5-methyl-2′-aminobenzophenone, m.p. 124–126°; yield, 29%, crystallized from absolute ethanol. Anal. Calc. for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08. Found: C, 65.20; H, 5.20; N, 5.15.

2-Bromo-4-methoxy-5-methyl-2′-aminobenzophenone

2-Bromo-4-methoxy-5-methyl-2′-aminobenzophenone, m.p. 139–141°; yield, 22%, crystallized from 95% ethanol. Anal. Calc. for $C_{15}H_{14}BrNO_2$: C, 56.26; H, 4.41; N, 4.37. Found: C, 56.21; H, 4.25; N, 4.52.

The following anisoles were prepared by treating the corresponding phenols with methyl iodide for 5 hours in refluxing alcoholic potassium hydroxide: 2,3-dimethylanisole, b.p. 195–198° at 760 mm (reported (19), 199° at 760 mm), yield, 73%; 5-ethyl-2-methylanisole, b.p. 77–80° at 4.3 mm (reported (20), 96° at 16 mm), yield 81%; 5-chloro-2-methylanisole, b.p. 204–207° at 760 mm (reported (21), 206–208° at 760 mm), yield, 64%; 5-bromo-2-methylanisole, b.p. 75° at 1.4 mm (reported (22), 108° at 15 mm), yield, 83%. 2,3-Dimethylphenol was a commercial product, the other phenols were prepared by the methods described: 5-ethyl-2-methylphenol, b.p. 89° at 2.5 mm (reported (23), 224° at 760 mm); 5-chloro-2-methylphenol, m.p. 70–75° (reported (21), b.p. 225° at 760 mm); 5-bromo-2-methylphenol, m.p. 78–80° (reported (24), 78°).

Synthesis of Amino Alcohols

All of the amino alcohols listed in Table I were prepared from the appropriately substituted *o*-aminobenzophenone and methylmagnesium iodide, except compound VII which was prepared by treating the Grignard reagent of 4-iodo-2,5-dimethylanisole with methyl anthranilate. *4-Iodo-2,5-dimethylanisole* was prepared from 2,5-dimethylanisole by the procedure of Oki and Sato (25), m.p. 46–48°, yield, 60%. Anal. Calc. for $C_9H_{11}OI$: C, 41.25; H, 4.20. Found: C, 41.35; H, 4.36.

In each instance the ethereal solution of the Grignard reagent was cooled in an ice bath during addition of the carbonyl compound. The reactions were completed by refluxing for approximately 24 hours, with the exception of the preparation of VII in which case the reaction mixture was stirred overnight at room temperature. Hydrolysis was effected with aqueous ammonium chloride. All amino alcohols were crystallized from benzene – petroleum ether with the exception of III*h* which was crystallized from 95% ethanol.

Diazotizations

The amino alcohols (5–20 mmoles) were dissolved in a minimum quantity of *p*-dioxane and added to 100–200 ml of 5–10% sulphuric acid solution. The resulting solution or suspension was diazotized with stirring by the dropwise addition of an excess of sodium nitrite dissolved in 10 ml of water. The solution was allowed to stand from ½ hour to 3 hours at 0–10°; it was then permitted to warm to room temperature and stand overnight. The decomposition was completed by warming to 40–50°. The reaction mixture was extracted three times with ether, and the combined ether extracts washed, first with two 100-ml portions of 5% aqueous sodium hydroxide, and then with water, to remove phenolic material, which was not further

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characterized. The neutral ether solution was dried over calcium sulphate, the solvent removed under vacuum, and the residue in each case treated as described below.

Products from IIIc

The residue was dissolved in 15% benzene – petroleum ether and placed on the column. Elution with 45% benzene – petroleum ether yielded 0.063 g (1.34%) of oil, ν 1692 cm^{-1} (chloroform). The ketone was completely converted to its 2,4-dinitrophenylhydrazone. There was obtained 0.062 g of hydrazone, m.p. 235–236°. This was equivalent to 0.036 g (0.8%) of *2-(2-chlorophenyl)-4,5-dimethylacetophenone*. Anal. Calc. for $C_{22}H_{19}ClN_4O_4$: C, 60.21; H, 4.36; N, 12.77. Found: C, 60.10; H, 4.41; N, 12.69. Further elution of the column produced only highly colored oils.

Products from IIId

The residue was dissolved in 20% benzene – petroleum ether, placed on a column, and eluted with 1:1 benzene – petroleum ether. There was obtained 0.066 g (1.4%) of oil, ν 1690 cm^{-1} (chloroform). It was completely converted to its 2,4-dinitrophenylhydrazone, which after purification, yielded 0.104 g of hydrazone, m.p. 231–234° (decomp.). This was equivalent to 0.065 g (1.4%) of *2-(2-bromophenyl)-4,5-dimethylacetophenone*. Anal. Calc. for $C_{22}H_{19}BrN_4O_4$: C, 54.67; H, 3.96; N, 11.59. Found: C, 55.46; H, 4.29; N, 11.98. Further elution of the column produced only highly colored oils.

Products from IIIf

The residue was dissolved in 30% benzene – petroleum ether, placed on a column, and eluted with the same solvent. There was obtained 0.845 g (17%) of light yellow oil, ν 1687 cm^{-1} (chloroform). The oil was completely converted to its 2,4-dinitrophenylhydrazone yielding 1.13 g of hydrazone, m.p. 150–152.5°, equivalent to 0.655 g (13.4%) of *2-(2-methyl-4-methoxyphenyl)acetophenone*. Anal. Calc. for $C_{22}H_{20}N_4O_5$: C, 62.85; H, 4.79; N, 13.33. Found: C, 62.64; H, 4.85; N, 13.20.

Elution of the column with chloroform gave a red oil which crystallized from aqueous ethanol to yield 0.095 g (1.7%) of red needles, m.p. 71–72.5°, ν 1685 cm^{-1} (chloroform). On the basis of previous work (8) it was assigned the structure of *2-acetyl-2'-methyl-4'-methoxyazobenzene*. Anal. Calc. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.78; H, 6.19; N, 10.73.

Products from IIIh

The residue was dissolved in 1:1 benzene – petroleum ether, placed on a column, and eluted with petroleum ether. There was obtained 0.862 g (18.4%) of an oil, ν 1685 cm^{-1} (chloroform). The oil was crystallized from benzene – petroleum ether yielding 0.560 g (12%) of *2-(2,3-dimethyl-4-methoxyphenyl)acetophenone*, m.p. 60.5–61.5°. Anal. Calc. for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.17; H, 7.28. The 2,4-dinitrophenylhydrazone melted at 163–165°. Anal. Calc. for $C_{24}H_{22}N_4O_5$: C, 63.58; H, 5.11; N, 12.90. Found: C, 63.39; H, 5.03; N, 13.00.

Elution of the column with 1:1 benzene – petroleum ether gave a red oil which crystallized from ethanol to yield 0.808 g (15.6%) of *2-acetyl-2',3'-dimethyl-4'-methoxyazobenzene*, m.p. 134–135°, ν 1687 cm^{-1} (chloroform). Anal. Calc. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 71.96; H, 6.32; N, 9.80.

Products from IIIi

The residue was dissolved in petroleum ether, absorbed on the column, and eluted with 10% benzene – petroleum ether. There was obtained 0.622 g (14.2%) of *2-(5-methyl-2-ethyl-4-methoxyphenyl)acetophenone*, m.p. 68–70°, ν 1683 cm^{-1} (chloroform), which was crystallized from petroleum ether. Anal. Calc. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.53; H, 7.59. The 2,4-dinitrophenylhydrazone melted at 170–171.5°. Anal. Calc. for $C_{24}H_{24}N_4O_5$: C, 64.27; H, 5.39; N, 12.50. Found: C, 64.07; H, 5.38; N, 12.38.

Elution of the column with 1:1 benzene – petroleum ether gave a red oil which crystallized in red needles from 80% aqueous ethanol to yield 0.799 g (16.5%) of *2-acetyl-5'-methyl-2'-ethyl-4'-methoxyazobenzene*, m.p. 49–51°, ν 1687 cm^{-1} (chloroform). Anal. Calc. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.06; H, 6.69; N, 9.41.

Product from IIIj

The residue was dissolved in 45% benzene – petroleum ether, placed on a column, and eluted with 25% benzene – petroleum ether. There was obtained 0.704 g (15%) of a light yellow oil. The oil was crystallized from ethanol to yield 0.550 g (11.7%) of *2-(2-chloro-5-methyl-4-methoxyphenyl)acetophenone*, m.p. 114–115°, ν 1697 cm^{-1} (chloroform). Anal. Calc. for $C_{16}H_{15}ClO_2$: C, 69.94; H, 5.50. Found: C, 69.92; H, 5.52. The 2,4-dinitrophenylhydrazone melted at 184–186°. Anal. Calc. for $C_{22}H_{19}ClN_4O_4$: C, 58.08; H, 4.21; N, 12.32. Found: C, 57.99; H, 4.15; N, 12.20. Further elution of the column produced only highly colored oils.

Products from IIIk

The residue was dissolved in 30% benzene – petroleum ether, placed on a column, and eluted with 40% benzene – petroleum ether. There was obtained 0.740 g (15.8%) of an oil. The oil was crystallized from benzene – petroleum ether yielding 0.610 g (13.1%) of *2-(2-bromo-5-methyl-4-methoxyphenyl)acetophenone*, m.p. 123–124°, ν 1686 cm^{-1} (chloroform). Anal. Calc. for $C_{16}H_{15}BrO_2$: C, 60.20; H, 4.74. Found: C, 59.98;

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H, 4.72. The 2,4-dinitrophenylhydrazone melted at 195–197°. Anal. Calc. for $C_{22}H_{19}BrN_4O_5$: C, 52.91; H, 3.84; N, 11.22. Found: C, 52.69; H, 3.70; N, 11.18. Further elution of the column produced only highly colored oils.

Products from VII

The residue was dissolved in 1:1 benzene – petroleum ether, placed on the column, and eluted with 2:1 benzene – petroleum ether. There was obtained 0.714 g (38%) of a light yellow oil, ν 1660 cm^{-1} (chloroform). The oil was crystallized from petroleum ether yielding 0.502 g (27%) of *2,5-dimethyl-4-methoxy-2'-(2,5-dimethyl-4-methoxyphenyl)benzophenone*, m.p. 97–99°. Anal. Calc. for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 79.98; H, 7.07.

Elution of the column with benzene produced a red oil which crystallized from ethanol to give 0.156 g (7.4%) of *2-(2,5-dimethyl-4-methoxybenzoyl)-2',5'-dimethyl-4'-methoxyazobenzene*, m.p. 133–134°, ν 1660 cm^{-1} (chloroform). Anal. Calc. for $C_{25}H_{26}N_2O_3$: C, 74.60, H, 6.51; N, 6.96. Found: C, 74.44; H, 6.58; N, 6.86.

Further elution of the column with 2:1 chloroform–benzene yielded an oil which crystallized from benzene – petroleum ether to give 0.286 g (15.3%) of *1,4-dimethyl-3-methoxy-9-(2,5-dimethyl-4-methoxyphenyl)-9-fluorenol*, m.p. 231–233°, ν 3600 cm^{-1} (chloroform). Anal. Calc. for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 80.29; H, 7.07.

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