after the usual work-up, was recrystallized from hexane to give 1.0 g (90%) of **29**, mp 90–91°.

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15. Found: C, 77.80; H, 9.18.

A part of **29** was converted to the perchlorate salt, mp 159–160° after recrystallization from acetone–ether.

Anal. Calcd for $C_{15}H_{22}ClNO_5$: C, 54.33; H, 6.68; N, 4.22. Found: C, 54.12; H, 6.66; N, 4.18.

Another part of **29** was dissolved in ether and treated with an excess of HCl in ethyl acetate to give 1-(2-chloroethyl)amino-1-α-hydroxybenzylcyclohexane hydrochloride (**30**), mp 216° dec, after recrystallization from ethanol–ether.

Anal. Calcd for $C_{15}H_{23}Cl_2NO$: C, 59.23; H, 7.62; N, 4.60. Found: C, 59.02; H, 7.59; N, 4.54.

Registry No.—**3**, 15817-11-5; **5**, 15817-31-9; **7**, 32515-75-6; **9**, 32515-76-7; **10** HCl, 15946-21-1; **11**, 32515-78-9; **12**, 32515-79-0; **13**, 32515-80-3; **14b**, 32515-81-4; **15a**, 32515-82-5; **15a** perchlorate, 32515-83-6; **15b**, 32515-84-7; **15b** perchlorate, 32515-85-8; **16a**, 32515-86-9; **16b**, 32515-87-0; **17**, 15817-32-0; **18**, 32515-89-2; **19**, 32515-90-5; **20** HCl, 15817-12-6; **21**, 32515-98-3; **23**, 15885-97-9; **26**, 15817-09-1; **28**, 32515-94-9; **29**, 32515-95-0; **29** perchlorate, 32515-96-1; **30**, 32515-97-2.

Acknowledgment.—The authors thank Dr. K. Grant Taylor for useful discussions. Financial support from the National Science Foundation, Grant GP 8272, is gratefully acknowledged.

A New Type of Basic Amide Hydrolysis, Characterized by Alkyl–Nitrogen Fission

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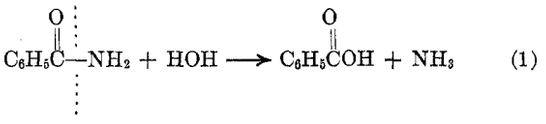
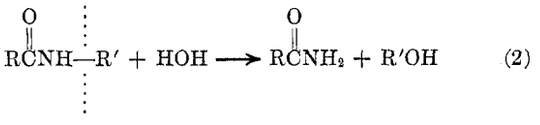
Amides of the type $RNHCH(R')C_6H_4N{=}NR^2$ [R = alkyl C=O, aryl C=O, alkyl SO_2, aryl SO_2, $H_2NC{=}O$, $C_6H_5NHC{=}O$, $(C_6H_5)_2NC{=}O$; R^1 = H, CH_3, C_6H_5; R^2 = phenyl, substituted phenyl, naphthyl] undergo basic hydrolysis under mild conditions to give RNH_2 and $R^1C(=O)C_6H_4NHNHR^2$. A similar reaction occurs when the substituents are ortho to one another. No reaction takes place when the groups are in the meta position. The effects of structural modifications on the course of the reaction were studied, and a mechanism for the reaction has been proposed.

In 1832, Liebig and Wöhler[2] described the first hydrolysis of an acyl amide in their classical paper on the benzoyl radical; the base-catalyzed reaction proceeded *via* the now familiar acyl–nitrogen cleavage (eq 1). It



(1)

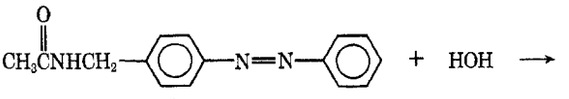
was not until 1960 that a second type of amide hydrolysis became known. In that year, Lacey[3] reported that under acid conditions some highly branched amides hydrolyze with alkyl–nitrogen fission (eq 2).



(2)

Work here has now shown that this second type of cleavage also occurs in basic solution with certain amides containing an azo group.

The "amidazo" reaction was encountered during an attempt to prepare *p*-phenylazobenzylamine by saponification of its acetyl derivative **1**; instead of the anticipated behavior, a more complicated reaction was observed (eq 3). Reaction conditions consisted of 3-hr refluxing under nitrogen in 0.36 *N* KOH in alcohol, 1.2 mol of alkali being used per mol of amide; the yields of acetamide and 4-formylhydrazobenzene (**2**) were 37 and 62%, respectively.



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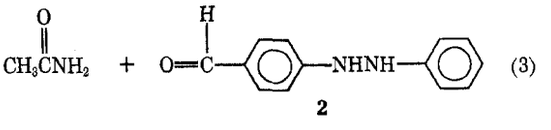
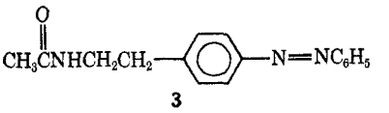


2 (3)

This novel reaction appeared to be of sufficient theoretical interest to warrant further scrutiny; so a study of its general nature was undertaken. First, some limitations of the reaction were established by demonstrating that the following compounds do not undergo alkyl–nitrogen cleavage when refluxed with alcoholic KOH.



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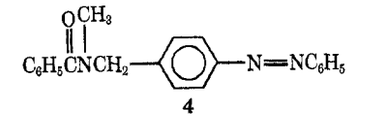

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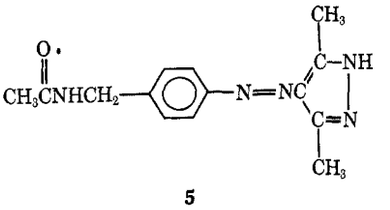

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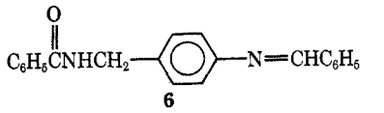

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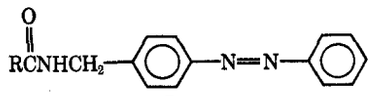
(1) This is a laboratory of the Northern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) J. von Liebig and F. Wöhler, *Justus Liebigs Ann. Chem.*, **3**, 268 (1832).

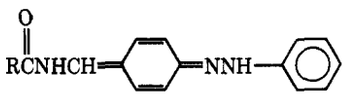
(3) R. N. Lacey, *J. Chem. Soc.*, 1633 (1960).

These preliminary experiments indicated that the amidazo reaction might be restricted to compounds of the general type **7**. However, another pos-



7

sibility became apparent when a mechanism for the reaction was postulated that included the intermediate **8**.



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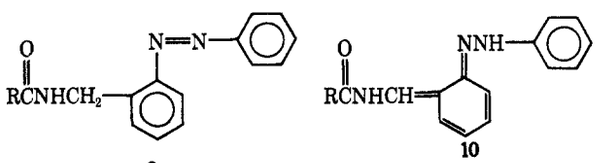
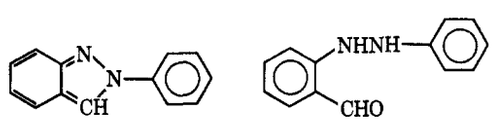
Involvement of this quinoid structure suggested that the reaction might also occur with ortho compounds of type **9** since they, too, are capable of assuming a quinoid form, as shown in **10**.



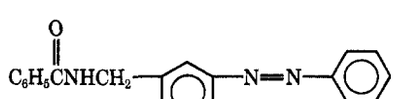
9 **10**

It was found that the ortho compounds do, indeed, undergo the amidazo reaction, the only difference being that they yield 2-phenylindazole (**11**), a dehydration product of the expected aldehyde **12**.



11 **12**

On the same basis, meta compounds would not be expected to undergo the amidazo reaction because of their inability to form quinoid structures; this reasoning was shown to be correct when **13** proved to be unaltered by alcoholic KOH under amidazo reaction conditions.

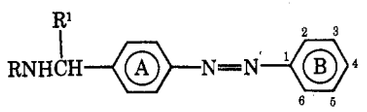


13

Next, a study of the effect of structural modifications was initiated to provide further insight into the nature of the amidazo reaction. The experiments directed toward this end were all conducted under reflux in a stream of nitrogen with 1 mmol of amide in 20 ml of 0.39 *N* KOH in 95% alcohol (7.8 mol of KOH per mol of amide). The yield of ammonia formed by hydrolysis of the primary amide product was obtained by passage of the nitrogen through standard acid; yields of aldehydes and ketones are based on isolated azo compounds (or a suitable derivative) after oxidation of the hydrazo compounds with periodic acid; yields of amides were calculated from isolated products, and of 2-phenylindazole, from the salt formed with 2,4-dinitrobenzenesulfonic acid. Reaction times ranged from 1 to 8 hr.

Results for the para and ortho series, showing the effects of varying R and R^1, and of modifying rings A and B, are the following.

A. Variations in R.—Studies on compounds having R^1 = H (rings A and B unsubstituted) demonstrated that the amidazo reaction takes place with compounds having the R groups shown in Table I. All of the compounds (except **1**) listed in this table were prepared from *p*-phenylazobenzylamine carbamate (**14**). The yields of amides from compounds **19**, **20**, and **23–26** were 45, 51, 67, 62, 27, and 6%, respectively.

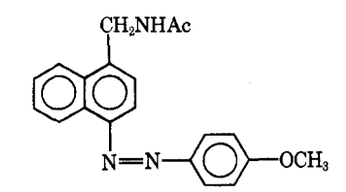


From Table I it is apparent that the amidazo reaction is quite general so far as the R group is concerned, although the nature of this group can have a marked effect on the rate of the reaction. The high yield of ammonia observed with the formyl compound **15** can, to a great extent, be accounted for by the complete hydrolysis of formamide. However, it appears likely that a part of the ammonia comes from the *p*-phenylazobenzylamine formed by ordinary acyl–nitrogen cleavage, since hydrolysis of this amine under amidazo reaction conditions gave a 20% yield of ammonia in 3 hr.

B. Variations in R^1.—Table II gives the results of modifying R^1 (rings A and B unsubstituted) in the amidazo compounds, the carbonyl products in this series being ketones instead of aldehydes. The compounds listed in Table II were prepared from α-methyl-*p*-(phenylazo)benzylamine hydrochloride (**31**) and α-phenyl-*p*-(phenylazo)benzylamine (**32**).

The low yields of azo ketones reported in Table II appear to be due merely to the slowness of the reaction; when an 8-hr hydrolysis was carried out on **34**, the yield of azo ketone was 49% (12% NH_3, 46% recovered starting material), compared to 9% for 1 hr. No attempt was made to determine the reaction time required for maximum yield. The lethargic reactions observed in this series are to be expected since it is well known that tertiary carbanions are less stable than secondary ones (see mechanism).

C. Modification of Ring A.—Compounds **41** and **42** gave no evidence of undergoing the amidazo reaction, although they were considerably altered by the alkaline treatment. It cannot be claimed, however,



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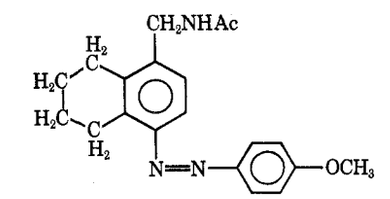

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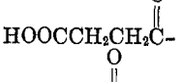
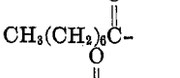
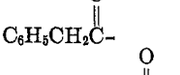
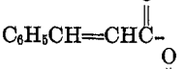
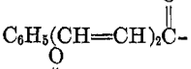
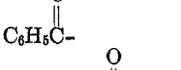
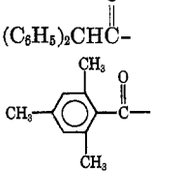
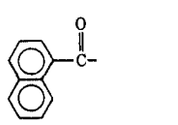
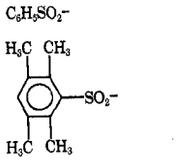
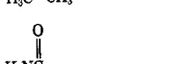
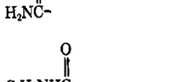
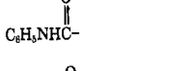
TABLE I

SYNTHESIS, PROPERTIES, AND EFFECTS OF SUBSTITUENTS ON HYDROLYSIS OF PARA SERIES COMPOUNDS[a]
(R^1 = H; RINGS A AND B UNSUBSTITUTED)

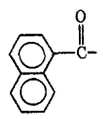
Compd	R	Time, hr	NH_3, %	*p*-$C_6H_5N{=}NC_6H_4CHO$, %	Method of preparation[b]	Crystallization solvent[c]	Mp, °C[d]
15		1	61	52	A	A	154–155
15		3	64	51			
1		1	22	70			
1		2	41	82			
1		8	78	85			
16		5	66	78	B	A	196–197
17		3	25	83	C	A	140–141
18		2	39	86	C	B	174–175
19		5	26	81	C	A	182–183
20		6	16	79	C	C	219–220
21		1	3	85	B	A	161–162
22		3	10	86	C	D	172–173
23		3	0	83	C	E	161–163
24		2	3	84	C	F	204–205
25	CH_3SO_2–	3	0	28	C	G	157–158
26	$C_6H_5SO_2$–	3	0	10	C	A	169–170
27		3	0	25	C	G	137–138[e]
28		3	3	70	D	H	248–250
29		3	0	83	E	H	229–230
30		3	0	89	C	B	150–151

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all compounds listed in the table. [b] Reagent for reaction with compound **14**: (A) formic acetic anhydride; (B) anhydride and pyridine; (C) acid chloride, 2.5 *N* NaOH and tetrahydrofuran (see compound **24** in Experimental Section for typical procedure); (D) urea nitrate; (E) phenyl isocyanate and dimethylformamide (DMF). [c] (A) 95% EtOH, (B) acetone–hexane, (C) absolute EtOH, (D) EtOH–hexane, (E) acetone, (F) EtOH–EtOAc, (G) DMF–H_2O, (H) DMF. [d] Hot stage, uncorrected. [e] Solidifies and remelts at 147–148°.

that the failure of these compounds to show alkyl–nitrogen cleavage is due entirely to the modification of ring A; the inhibiting effect of the *p*-methoxy group located on ring B (see section D) could allow other reactions to occur, leading to the extensive decomposition observed. Unfortunately, compounds of this type with ring B unsubstituted are not readily accessible.

TABLE II

SYNTHESIS, PROPERTIES, AND EFFECTS OF SUBSTITUENTS ON HYDROLYSIS OF PARA SERIES COMPOUNDS[a] (RING A AND B UNSUBSTITUTED)

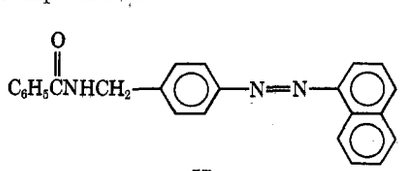
Compd	R	R¹	Time, hr	NH_3, %	p-C_6H_5N=NC_6H_4COR', %	Recovered starting material, %	Method of preparation[b]	Crystallization solvent[c]	Mp, °C[d]
33	$CH_3C(=O)-$	CH_3	3	6	15	66	A	A	155–156
34	$C_6H_5C(=O)-$	CH_3	1	1	9	87	B	B	194–195
35		CH_3	2	0	5	91	C	C	214–215
36	CH_3SO_2-	CH_3	3	0	1	95	D	D	106–107
37	$C_6H_5NHC(=O)-$	CH_3	3	4	27	46	E	E	207–208
38	$CH_3C(=O)-$	C_6H_5	3	4	13	75	F	F	186–187
39	$C_6H_5C(=O)-$	C_6H_5	1	0	5	92	G	B	205–206
40	$C_6H_5NHC(=O)-$	C_6H_5	3	8	53	37	H	B	258–260

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all compounds listed in the table. [b] (A) Ac_2O and compound **31**; (B) $(C_6H_5CO)_2O$, pyridine, and compound **31**; (C) α-naphthoyl chloride, aqueous KOH, tetrahydrofuran, and compound **31**; (D) methylsulfonyl chloride, aqueous KOH, tetrahydrofuran, and compound **31**; (E) C_6H_5NCO, DMF, and compound **31**; (F) Ac_2O and compound **32**; (G) $(C_6H_5CO)_2O$, pyridine, and compound **32**; (H) C_6H_5NCO, DMF, and compound **32**. [c] (A) 80% EtOH; (B) DMF; (C) acetone–*N*-methylpyrrolidone; (D) EtOAc–hexane; (E) DMF–80% EtOH; (F) acetone–H_2O. [d] Hot stage, uncorrected.

D. Substitution on Ring B.—The effects of substitution on ring B on the amidazo reaction are shown in Table III (R^1 = H; ring A unsubstituted).

In general, it can be stated that the effects of ring B substituents on rates (hence, yields) of the amidazo reaction are readily explainable in terms of effects of substituents on the relative stabilities of the anionic intermediates shown in the proposed mechanism.

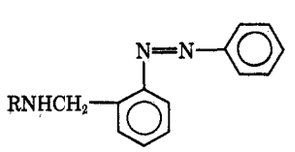
E. Replacement of Ring B by a Naphthalene Ring. The naphthalene compound **57** undergoes the amidazo reaction in much the same way that the corresponding benzene compound does.



57

4% NH_3, 79% azo, 71% benzamide; time, 1 hr.

Ortho Series.—Behavior of the ortho series of compounds in the amidazo reaction is summarized in Table IV.



The depicted mechanism, which involves addition of water to an imide type of compound, appears to rationalize the products of the amidazo reaction (Scheme I).

The behavior of compound **62** suggests that a mechanism different from the above may be in operation with ortho-substituted sulfonamides.

Experimental Section

Unless otherwise noted, melting points were determined on a Fisher[4] hot-stage apparatus and were not corrected. The capillary melting points were corrected.

***N*-*p*-Phenylazobenzylacetamide (1).**—*N*-*p*-Aminobenzylacetamide[5] (37.74 g, 0.230 mol) was dissolved in 100 ml of HOAc at 40° and nitrosobenzene (24.88 g, 0.232 mol) was added gradually to the solution. After 4 days at room temperature water was added and the solid separated (43.2 g, 74%). Crystallization from alcohol gave orange needles of 1 melting at 173–174°.

Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.1; H, 6.05; N, 16.6.

Hydrolysis of 1 to 4-Formylhydrazobenzene (2) and Acetamide.—Compound 1 (5.066 g, 0.020 mol) was dissolved in 32 ml of 95% EtOH in a 200-ml flask attached to a distilling head equipped with a gas inlet tube and a dropping funnel. Nitrogen was passed over the solution for 15 min and bubbled through 50 ml of standard acid. A solution of KOH (1.68 g, 0.030 mol) in 1.70 ml of water and 35 ml of 95% EtOH was then added to the solution of 1. The reaction mixture was refluxed gently for 3 hr under a current of nitrogen. Back titration gave a 41% yield of a base, which was identified as ammonia by conversion to benzamide (mp 126–127°, cap).

The reaction mixture was added to 300 ml of water and extracted with 500 ml of ether. The ether extract was washed with three 25-ml portions of water, the pH of the combined water fractions adjusted to 7, and the neutral solution lyophilized. Sublimation of the resulting powder at 80° and 1 mm yielded 193 mg of acetamide (mp 82–83°, cap), which was characterized as the chloral derivative (mp 162–163°, cap). Additional acetamide isolated from the lyophilization condensate raised the yield to 434 mg (37%).

The washed ether extract was concentrated to about 25 ml and 50 ml of benzene was added. Further concentration to 15 ml gave 2.03 g of crude **2** in the form of light tan bars. A second crop brought the yield of crude product to 3.16 g (75%). Recrystallization from alcohol yielded almost pure material of mp 141–143°

(4) The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

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TABLE III

SYNTHESIS, PROPERTIES, AND EFFECTS OF SUBSTITUENTS ON HYDROLYSIS OF PARA SERIES COMPOUNDS[a] (R^1 = H; RING A UNSUBSTITUTED, RING B SUBSTITUTED)

Compd	Ring B substitution	R	Time, hr	NH_3, %	Substituted aldehyde, %	Recovered starting material, %	Method of preparation[b]	Crystallization solvent[c]	Mp °C[d]
43	4-CH_3	$CH_3C(=O)-$	3	42	72		A	A	200–201
44	4-C_6H_5	$CH_3C(=O)-$	3	40	77		B	B	241–242
45	4-Cl	$CH_3C(=O)-$	3	56	85		A	C	214–215
46	4-OCH_3	$CH_3C(=O)-$	3	20	28		B	D	178–179
47	4-$OCH_2C_6H_5$	$CH_3C(=O)-$	3	13	18	56	B	E	202–204
48	4-SCH_3	$CH_3C(=O)-$	3	54	73		B	C	198–199
49	4-OH	$C_6H_5C(=O)-$	1	0	0	98	C		
50	4-OCH_3	$C_6H_5C(=O)-$	1	1	37	48	C		
51	4-NH_2	$CH_3C(=O)-$	3	4		91	C		
52	4-NMe_2	$C_6H_5C(=O)-$	1	0	0	82	C		
53	3-CF_3	$CH_3C(=O)-$	3	58	83		B	A	172–173
54	2-CH_3	$CH_3C(=O)-$	3	50	75		B	D	145–146
55	2-OCH_3	$CH_3C(=O)-$	3	58	60		B	F	143–144
56	2-C_6H_5	$CH_3C(=O)-$	3	55	59		B	G	170–171

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all compounds listed in the table. [b] (A) *p*-Aminobenzylacetamide and substituted nitrosobenzene (1 mmol of each; 1 ml of CH_3OH and 0.5 ml of HOAc; 60–70°); (B) *p*-nitrosobenzylacetamide (for preparation, see compound **5** in Experimental Section) and substituted aniline (same conditions as in A); (C) see Experimental Section. [c] (A) 95% EtOH; (B) EtOH; (C) DMF–H_2O; (D) 80% EtOH; (E) DMF; (F) EtOAc–hexane; (G) EtOAc. [d] Hot stage; uncorrected.

TABLE IV

EFFECTS OF SUBSTITUENTS ON HYDROLYSIS OF ORTHO SERIES COMPOUNDS[a]

Compd	R	NH_3, %	2-Phenylindazole, %
58	$CH_3C(=O)-$	31	67
59	$C_6H_5C(=O)-$	15	66
60	$H_2NC(=O)-$	2	72
61	$C_6H_5NHC(=O)-$	1	46
62	$C_6H_5SO_2$[b]	0	97

[a] Time, 3 hr. [b] A 98% yield of benzenesulfonamide was obtained. The high yield in this reaction contrasts sharply with the 10% value obtained with compound **26** (Table I).

(2.65 g, 63%). Two crystallizations from benzene afforded pure **2** (mp 143–144°, cap) as off-white bars.

Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.02. Found: C, 73.5; H, 5.72; N, 13.3.

4-Formylhydrazobenzene oxime was prepared by heating **2** with hydroxylamine acetate in alcohol for 10 min (mp 164–165°, cap).

Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.72; H, 5.77; N, 18.50. Found: C, 68.9; H, 5.77; N, 18.7.

4-Formylhydrazobenzene semicarbazone (mp 216–218°, cap) was prepared in the same way as the oxime.

Anal. Calcd for $C_{14}H_{15}N_5O$: C, 62.43; H, 5.61; N, 26.01. Found: C, 62.4; H, 5.40, N, 26.2.

Compound **2** was readily oxidized at room temperature by HIO_4 in alcohol to red crystals (mp 121–122°, cap), which were shown to be 4-phenylazobenzaldehyde by comparison with an authentic sample.[6] The phenylhydrazones[6] were also identical (mp 167–168°, cap).

1-*p*-Phenylazophenyl-2-acetaminoethane (3).—1-*p*-Aminophenyl-2-acetaminoethane[7] (4.43 g, 0.0249 mol) and nitrosobenzene (2.66 g, 0.0249 mol) were heated at 60° for 6 hr in 25 ml of HOAc. On crystallization from alcohol the crude product (5.23 g, 78%) gave orange needles of **3** (mp 148–149°).

Anal. Calcd for $C_{16}H_{17}N_3O$: C, 71.89; H, 6.41; N, 15.72. Found: C, 72.2; H, 6.47; N, 15.9.

***N*-*p*-Phenylazobenzyl-*N*-methylbenzamide (4).**—*N*-Methyl-*p*-nitrobenzylamine[8] was prepared from 21.6 g of *p*-nitrobenzyl bromide and 100 ml of 40% CH_3NH_2–H_2O in 200 ml of absolute EtOH (1 week at room temperature). The alcohol was removed under reduced pressure and the crystals were separated. The

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(7) M. Borovička, Z. Šedivý, J. O. Jílek, and M. Protiva, *Chem. Listy*, **49**, 231 (1955); J. Comin and W. Keller-Schierlein, *Helv. Chim. Acta*, **42**, 1730 (1959).

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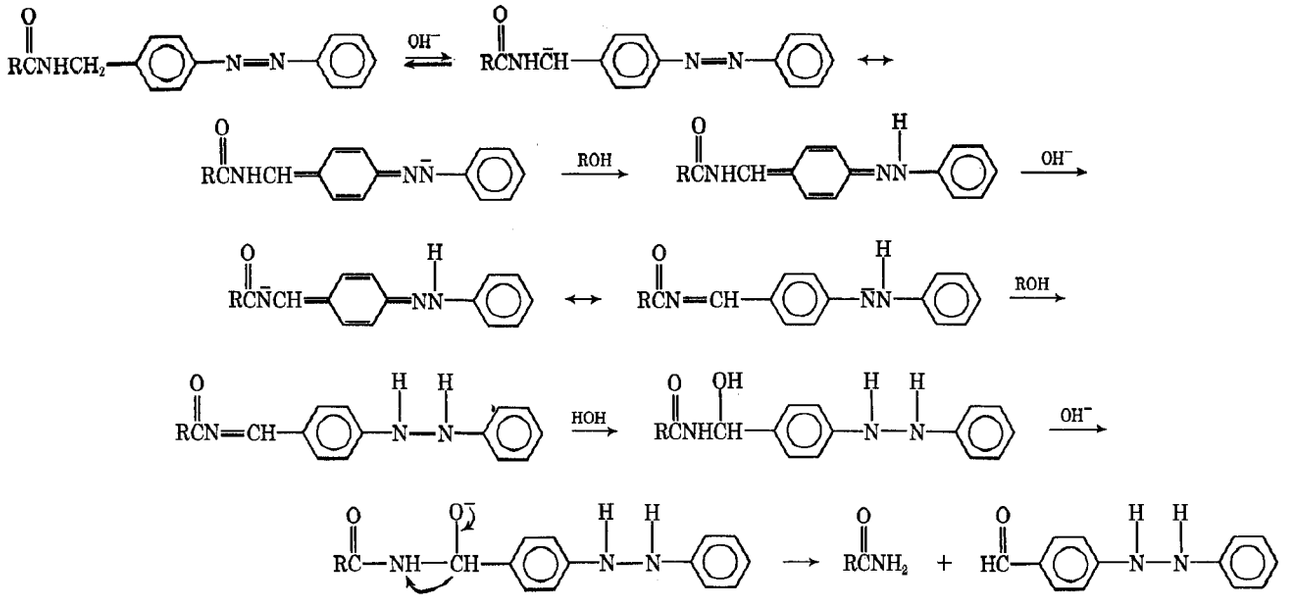
SCHEME I



filtrate was extracted with ether and the aqueous phase was made alkaline with NaOH. Extraction of the alkaline solution with ether and removal of the ether gave 14.1 g (85%) of *N*-methyl-*p*-nitrobenzylamine. Benzoylation with benzoic anhydride in pyridine gave a 95% yield of ***N*-*p*-nitrobenzyl-*N*-methylbenzamide**, which was purified by crystallization from acetone–hexane. The light tan needles melted at 95–96°.

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.37. Found: C, 66.6; H, 5.21; N, 10.3.

The benzoyl derivative was reduced to the amine (PtO_2, 95% EtOH), which was converted to the azo compound by reaction with nitrosobenzene (HOAc–CH_3OH, 70°, 6 hr). Crystallization from benzene–hexane gave orange-brown crystals of **4** (mp 90–91°).

Anal. Calcd for $C_{21}H_{19}N_3O$: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.8; H, 6.05; N, 12.5.

3,5-Dimethylpyrazole-4-azo-4′-acetaminomethylbenzene-1 (5).—*N*-*p*-Nitrosobenzylacetamide was prepared as follows. To 11.0 g of *N*-*p*-nitrobenzylacetamide[5] in 25 ml of 95% EtOH was added a solution of 2.27 g of NH_4Cl in 25 ml of 50% EtOH. Zinc dust (14.2 g) was added with stirring at a rate that maintained the temperature at 65–70° (about 25 min). The reaction mixture was filtered and the filtrate was added dropwise to a stirred solution of 38.3 g of $FeCl_3 \cdot 6H_2O$ in 300 ml of water. The solid was separated and the filtrate was extracted three times with $CHCl_3$. Removal of the solvent gave 7.66 g (76%) of tan crystals. Crystallization from $CHCl_3$–hexane yielded colorless plates (mp 122–124°, green melt) of ***N*-*p*-nitrosobenzylacetamide.**

Anal. Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66. Found: C, 60.8; H, 5.87.

The nitroso compound (890 mg, 0.005 mol) was condensed with 4-amino-3,5-dimethylpyrazole[9] (555 mg, 0.005 mol) in 5 ml of HOAc (1 hr, 70°). The crude azo compound (99%) was crystallized from ethanol–acetone to give orange needles of **5** (mp 231–232°).

Anal. Calcd for $C_{14}H_{17}N_5O$: C, 61.97; H, 6.32; N, 25.81. Found: C, 61.5; H, 6.29; N, 26.3.

***N*-Benzylidene-*p*-benzoylaminomethylaniline (6).**—*N*-*p*-Nitrobenzylbenzamide[10] (mp 158–159°) was reduced (Pd/C; absolute EtOH) to the amine, which crystallized from dilute alcohol in the form of bars. The pure ***N*-*p*-aminobenzylbenzamide** melted at 142–143°.

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 73.9; H, 6.23; N, 12.4.

A solution of the amine (1.13 g, 0.005 mol) and benzaldehyde (0.584 g, 0.0055 mol) in alcohol was heated 5 min at 95°. The product was crystallized from acetone–DMF to yield white crystals of **6** (mp 154–155°).

Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.25; H, 5.77; N, 8.91. Found: C, 80.0; H, 5.75; N, 9.00.

***m*-Phenylazobenzylbenzamide (13).**—*m*-Nitrobenzylamine hydrochloride[11] was converted to the benzoyl derivative with benzoyl chloride and aqueous KOH. Crystallization from 80% EtOH gave colorless needles of ***m*-nitrobenzylbenzamide** (mp 139–140°).

Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.61; H, 4.72; N, 10.93. Found: C, 65.9; H, 4.88; N, 10.9.

The nitro compound was reduced (PtO_2, EtOH) to the amine, which was converted to the azo compound by reaction with nitrosobenzene in HOAc (2 hr, 60°). Crystallization from 80% EtOH and from acetone–hexane gave yellow-orange crystals of **13** (mp 160–161°).

Anal. Calcd for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32. Found: C, 76.2; H, 5.50; N, 13.6.

***p*-Phenylazobenzylamine Carbamate (14).**—*N*-*p*-Aminobenzylacetamide[5] (3.28 g) was heated for 4 hr on a steam bath with 15 ml of 6 *N* HCl; evaporation to dryness gave the dihydrochloride of *p*-aminobenzylamine.[12] The dihydrochloride (8.13 g) was dissolved in 20 ml of water containing 5.2 g of KOH. Three $CHCl_3$ extractions gave an oil, which was converted to the solid carbamate with CO_2 (5.37 g).

The carbamate (28.83 g, 0.100 mol) was dissolved in a mixture of 135 ml of HOAc and 270 ml of 95% EtOH. Nitrosobenzene (23.70 g, 0.22 mol) was dissolved in the carbamate solution with stirring. After 27 hr at room temperature, 1.6 l. of ether was added and the orange precipitate of acetate was separated (42.0 g, 77%). The acetate was decomposed with 12 g of KOH in 100 ml of water, and the amine was extracted with ether. Passage of CO_2 through the ether solution gave ***p*-phenylazobenzylamine carbamate (14)** (34.98 g, 75%) as an orange powder, which melted at 87–92° with evolution of gas.

Anal. Calcd for $C_{27}H_{26}N_6O_2$: C, 69.51; H, 5.62; N, 18.02. Found: C, 69.6; H, 5.74; N, 18.4.

***N*-*p*-Phenylazobenzyl-α-naphthamide (24).**—*p*-Phenylazobenzylamine carbamate (**14**) (488 mg, 0.00096 mol) was heated for a few minutes in a silicone bath (140°) to give a clear red melt of the free amine. After cooling, the amine was dissolved in 5 ml of tetrahydrofuran, and to this solution was added 5 ml (0.0125 mol) of 2.5 *N* NaOH. A solution of α-naphthoyl chloride (366 mg, 0.00192 mol) in 5 ml of tetrahydrofuran was added and the mixture was shaken for 10 min. Addition of water gave a 91% yield of crude amide of mp 190–196°. Recrystallization from DMF–95% EtOH yielded **24** in the form of orange plates (75%, mp 204–205°).

Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.9; H, 5.17; N, 11.8.

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(12) H. Amsel and A. W. Hofmann, *Chem. Ber.*, **19**, 1284 (1886).

1-*p*-Phenylazophenylethylamine Hydrochloride (31).—*p*-Aminoacetophenone oxime[13] was reduced to the diamine by the Raney alloy method of Staskun and van Es.[14] An ether solution of the crude liquid diamine treated with 3 *N* HCl–CH_3OH gave **1-*p*-aminophenylethylamine dihydrochloride** (mp 225–230°) in the form of a white powder.

Anal. Calcd for $C_8H_{14}Cl_2N_2$: C, 45.95; H, 6.75; N, 13.40. Found: C, 46.0; H, 6.91; N, 13.3.

The free amine (6.13 g, 0.045 mol) (prepared from the dihydrochloride) and nitrosobenzene (5.08 g, 0.047 mol) were dissolved in 70 ml of 95% EtOH and 35 ml of HOAc. After 3 days at room temperature the reaction mixture was poured into water and excess alkali added. Ether extraction gave an oil, which was converted to **31** with 3 *N* HCl–CH_3OH. The hydrochloride melted at 230–232°.

Anal. Calcd for $C_{14}H_{16}ClN_3$: C, 64.24; H, 6.16; N, 16.05. Found: C, 64.4; H, 6.55; N, 15.6.

Phenyl-*p*-phenylazophenylmethylamine (32).—*p*-Aminobenzophenone was converted to a mixture of oximes,[15] which was reduced to the diamine with Raney nickel alloy and alkali.[14] The crude product was dissolved in ether and addition of 3 *N* HCl–CH_3OH gave colorless needles of **phenyl-*p*-aminophenylmethylamine dihydrochloride** (mp 235–240°).

Anal. Calcd for $C_{13}H_{16}Cl_2N_2$: C, 57.58; H, 5.95; N, 10.33; Cl, 26.15. Found: C, 57.7; H, 6.12; N, 10.1; Cl, 26.0.

The diamine (10.26 g, 0.0517 mol) and nitrosobenzene (5.81 g, 0.0543 mol) were dissolved in 75 ml of 95% EtOH and 37 ml of HOAc. After 3 days at room temperature the reaction mixture was diluted with water and excess alkali added. Ether extraction yielded 12.58 g of crude azo compound (85%). Crystallization from ether and from 95% EtOH gave **32** (mp 94–95°).

Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.3; H, 6.38; N, 14.4.

1-Acetaminomethyl-4-*p*-methoxyphenylazonaphthalene (41).—1-Methyl-4-nitronaphthalene (4.00 g, 0.0214 mol) was converted to 1-bromomethyl-4-nitronaphthalene by the method of Benigni and Minnis.[16] The crude product left after removal of CCl_4 was refluxed for 20 min with urotropine (3.00 g, 0.0214 mol) in 30 ml of $CHCl_3$. Filtration gave 6.12 g of addition compound (mp 175–180°). This product was triturated with 12 ml of 6 *N* HCl, allowed to stand at room temperature for 3.5 hr, and then steam distilled for 1 hr with 100 ml of 3 *N* HCl to remove formaldehyde. Cooling in ice and filtration yielded 2.80 g of 1-nitro-4-naphthalene methylamine hydrochloride. Acetylation gave **1-acetaminomethyl-4-nitronaphthalene** (mp 159–160°).

Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.92; H, 4.95. Found: C, 64.3; H, 4.98.

Reduction of the nitro compound (Pd/C, 95% EtOH), diazotization of the amine, coupling of the diazonium salt with phenol, and methylation of the azo phenol gave **41** (mp 200–201°).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 72.5; H, 5.94; N, 12.8.

1-Acetaminomethyl-4-*p*-methoxyphenylazo-5,6,7,8-tetrahydronaphthalene (42).—1-Acetaminomethyl-4-nitronaphthalene described above was reduced[17] (Raney nickel, 1 hr, 100°, 800 lb/in.^{2}, absolute EtOH) to **1-acetaminomethyl-4-amino-5,6,7,8-tetrahydronaphthalene**, which melted at 164–165° after crystallization from absolute EtOH.

Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.3; H, 8.45; N, 12.6.

Acetylation of the amine gave **1-acetaminomethyl-4-acetamino-5,6,7,8-tetrahydronaphthalene** (mp 227–228°).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 69.37; H, 7.76. Found: C, 69.4; H, 7.76.

1-Acetaminomethyl-4-amino-5,6,7,8-tetrahydronaphthalene (3.01 g, 0.0138 mol) was diazotized in 15 ml of 2 *N* HCl with 1.03 g of $NaNO_2$ (0.015 mol) in 5 ml of water and coupled with phenol. The resulting azo phenol was methylated with CH_2N_2–CH_3OH–ether to give compound **42**, which melts at 176–177°, solidifies, and remelts at 186–187°.

Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45. Found: C, 70.9; H, 6.95; N, 12.2.

***N*-*p*-Hydroxyphenylazobenzylbenzamide (49).**—*N*-*p*-Aminobenzylbenzamide (2.26 g, 0.010 mol; for preparation see compound **6**) was converted to the diazonium chloride (2.2 ml of concentrated HCl, 18 ml of H_2O, and 0.75 g of $NaNO_2$ in 5 ml of H_2O) and coupled with phenol (941 mg, 0.010 mol, 20 ml of 1 *N* NaOH). Crystallization from ethanol gave the red azo phenol **49** (mp 230–231°).

Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.6; H, 5.26; N, 12.5.

***N*-*p*-Methoxyphenylazobenzylbenzamide (50).**—Compound **49** was methylated with CH_2N_2–CH_3OH–ether and the unreacted phenol removed by extraction of an ether solution with 2 *N* NaOH. Crystallization from 95% EtOH gave **50** (mp 170–171°).

Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.02; H, 5.54; N, 12.17. Found: C, 72.8; H, 5.60; N, 12.0.

***N*-*p*-Aminophenylazobenzylacetamide (51).**—*N*-*p*-Nitrosobenzylacetamide (3.14 g, 0.0177 mol, for preparation see compound **5**), *p*-aminotrifluoroacetanilide (3.60 g, 0.0177 mol) [prepared by reduction (Pd/C, EtOH) of *p*-nitrotrifluoroacetanilide[18]] in 18 ml of CH_3OH and 9 ml of HOAc were heated for 1 hr at 65° to give an 85% yield of crude azo compound. Crystallization from alcohol yielded pure **1-acetaminomethylbenzene-4-azo-4′-trifluoroacetaminobenzene-1** (mp 275–276°).

Anal. Calcd for $C_{17}H_{15}F_3N_4O_2$: C, 56.04; H, 4.15; N, 15.38. Found: C, 55.6; H, 4.14; N, 15.1.

The trifluoro compound (3.64 g, 0.010 mol) was dissolved in 55 mol of 0.55 *N* NaOH and kept at room temperature for 4 days. The solution was then brought to the boiling point and cooled and the pH adjusted to 7. Addition of water gave crude amine (2.62 g, 98%) of mp 165–166°, which on crystallization from alcohol yielded **51** (mp 167–168°).

Anal. Calcd for $C_{15}H_{16}N_4O$: C, 67.14; H, 6.01; N, 20.88. Found: C, 67.42; H, 6.06; N, 20.6.

***N*-*p*-Dimethylaminophenylazobenzylbenzamide (52).**—*N*-*p*-Aminobenzylbenzamide (2.26 g, 0.010 mol; see compound **6** for preparation) was converted to the diazonium chloride (4.2 ml of 6 *N* HCl in 15 ml of H_2O and 745 mg of $NaNO_2$ in 5 ml of H_2O). To an ice-cold solution of the salt was added dropwise with stirring a solution of dimethylaniline (1.49 g, 0.0123 mol) in 5 ml of alcohol. After 30 min of stirring a solution of 2.72 g of $NaOAc \cdot 3H_2O$ was added dropwise. After 2 hr of stirring the azo compound was separated and purified on a Bio-Sil A column (EtOAc eluate). Crystallization from alcohol gave pure **52** of mp 209–210°.

Anal. Calcd for $C_{22}H_{22}N_4O$: C, 73.72; H, 6.19; N, 15.63. Found: C, 73.3; H, 6.34; N, 16.0.

***N*-*p*-α-Naphthylazobenzylbenzamide (57).**—*N*-*p*-Aminobenzylbenzamide (9.04 g, 0.040 mol; see compound **6** for preparation) was suspended in 100 ml of absolute EtOH, and 10 ml of concentrated H_2SO_4 in 50 ml of absolute EtOH was added gradually. *n*-Butyl nitrite (12 ml) was then added dropwise with stirring. After 30 min standing at room temperature the white crystals of diazonium sulfate (11.64 g) were separated and dissolved in 14 ml of water. This solution was added dropwise to a stirred solution of α-naphthylamine (5.72 g, 0.040 mol) in 150 ml of 95% EtOH. After 30 min of stirring, 12 g of $NaOAc \cdot 3H_2O$ in water was added and the stirring continued for 15 min. The azo compound was separated (12.7 g, 84%, mp 170–190°) and crystallized from DMF–EtOH to give pure **1-benzoylaminomethylbenzene-4-azo-4′-aminonaphthalene-1**, mp 198–200°.

Anal. Calcd for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73. Found: C, 76.1; H, 5.69; N, 14.8.

The amine (3.80 g, 0.10 mol) was dissolved at 95° in 50 ml of HOAc containing 1 ml of water. The solution was cooled to room temperature and 10 ml of concentrated H_2SO_4 in 20 ml of HOAc was added. The solution was cooled in ice and 800 mg of $NaNO_2$ in 1 ml of water was added, followed by 10.6 g of $Na_3PO_2 \cdot H_2O$ (0.10 mol) in 3 ml of concentrated H_2SO_4 in 20 ml of water. After 2.5 hr in ice, the reaction mixture was allowed to warm to room temperature. When the evolution of nitrogen ceased, the solution was shaken with $CHCl_3$ and water. The $CHCl_3$ solution was washed well with water and concentrated to a red-brown oil. Purification on an Al_2O_3 (grade I) column and crystallization from $CHCl_3$–hexane gave **57** (mp 175–176°) in small yield.

Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.7; H, 5.22; N, 11.3.

***N*-*o*-Phenylazobenzylacetamide (58).**—*o*-Nitrobenzyl bromide[19]

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was converted to the urotropine addition compound in $CHCl_3$. This product (78 g) was refluxed for 1.5 hr with 60 ml of concentrated NH_4OH in 360 ml of water. Formaldehyde in 40% solution (20 ml) was added to the hot reaction mixture, from which an oil had separated. On cooling, the oil solidified and the solid was separated (34.12 g). On concentration on a steam bath with 20 ml of concentrated HCl, this solid gave crystals and liquid. Trituration with absolute EtOH and filtration yielded 26.5 g (66%) of *o*-nitrobenzylamine hydrochloride,[20] mp 245–250°.

Acetylation of the hydrochloride gave *N*-*o*-nitrobenzylacetamide,[20] which was reduced (Pd/C, 95% EtOH) to *N*-*o*-aminobenzylacetamide.[21] A solution of this amine (1.71 g, 0.0104 mol) and nitrosobenzene (1.11 g, 0.0104 mol) in 10 ml of CH_3OH and 5 ml of HOAc was heated at 65° for 2 hr to yield 1.28 g of crude azo compound (mp 105–112°). Purification on a silicic acid column (Bio-Sil A, ether eluate) and crystallization from ethanol–hexane gave **58**, mp 126–127°.

Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.2; H, 5.96; N, 16.4.

N*-*o*-Phenylazobenzylbenzamide (59).**—N*-*o*-Aminobenzylbenzamide**[21] (2.16 g, 0.0084 mol) was condensed with nitrosobenzene (907 mg, 0.0084 mol) in 10 ml of HOAc (60°, 2 hr). The crude azo compound (1.79 g, 67%) was crystallized from dilute alcohol to give compound **59**, mp, 134–135°.

Anal. Calcd for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32. Found: C, 76.2; H, 5.67; N, 13.2.

***o*-Phenylazobenzylurea (60).**—*o*-Nitrobenzylurea[22] was reduced (Pd/C, 80% EtOH) to ***o*-aminobenzylurea**, which was crystallized from 95% EtOH. It melted at 190–191°.

Anal. Calcd for $C_8H_{11}N_3O$: C, 58.17; H, 6.71; N, 25.44. Found: C, 58 3; H, 7.00; N, 25.1.

A solution of the amine (1.85 g, 0.0112 mol) and nitrosobenzene (1.32 g, 0.0123 mol) in 12 ml of CH_3OH and 6 ml of HOAc was heated at 70° for 7 hr. The crude azo compound (2.46 g, 86%, mp 155–165°) was crystallized from 50% EtOH to give **60**, mp 177–178°.

Anal. Calcd for $C_{14}H_{14}N_4O$: C, 66.12; H, 5.55; N, 22.03. Found: C, 66.4; H, 5.69; N, 21.5.

1-Phenyl-3-*o*-phenylazobenzylurea (61).—To a solution of freshly prepared *o*-nitrobenzylamine (2.60 g, 0.0171 mol) in dimethylformamide was added 1.83 g (0.0154 mol) of phenyl isocyanate. The solution was heated at 95° for 30 min, cooled, and added to water. The crude product (4.12 g, 99%) was crystallized from 95% EtOH to give **1-phenyl-3-*o*-nitrobenzylurea**, mp 183–184°.

Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.83; N, 15.49. Found: C, 61.8; H, 5.03; N, 15.3.

The nitro compound was reduced (Pd/C, absolute EtOH) to the amine, which was purified by crystallization from 95% EtOH. Pure **1-phenyl-3-*o*-aminobenzylurea** melted at 208–209°.

Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.50. Found: C, 69.7; H, 6.15; N, 17.3.

A solution of the amine (4.64 g, 0.0192 mol) and nitrosobenzene (2.26 g, 0.0211 mol) in 20 ml of CH_3OH, 10 ml of HOAc, and 40 ml of 95% EtOH was heated at 60° for 12 hr. The crude azo compound (5.57 g, 88%) on crystallization from HOAc and from DMF–H_2O gave pure **61**, mp 201–202°.

Anal. Calcd for $C_{20}H_{18}N_4O$: C, 72.71; H, 5.49; N, 16.96. Found: C, 72.7; H, 5.59; N, 16.9.

***N*-*o*-Phenylazobenzylbenzenesulfonamide (62).**—*N*-*o*-Aminobenzylbenzenesulfonamide[23] (3.43 g, 0.0131 mol) and nitrosobenzene (1.54 g, 0.0144 mol) were heated for 8 hr at 65° in 13 ml of CH_3OH and 6.5 ml of HOAc. The crude azo compound was a sticky black solid (4.25 g, 93%), which was purified on a silicic acid column (Bio-Sil A, ether–EtOAc eluate) and by crystallization from EtOAc–hexane and from alcohol. Pure **62** melted at 130–131°.

Anal. Calcd for $C_{19}H_{17}N_3O_2S$: C, 64.93; H, 4.88; N, 11.96. Found: C, 64.7; H, 5.01; N, 11.9.

Millimol Hydrolyses of Amidazo Compounds.—The apparatus used for the hydrolyses was in two parts: (1) A 50-ml round-bottomed flask with a 24/40 female joint. (2) A distilling bulb (5-cm diameter) situated 4 cm above a male joint. A dropping funnel and a gas inlet tube were connected to the 4-cm portion of the tube above the joint. To the top of the distillation bulb was attached 9-mm tubing, which extended horizontally 10 cm and downward 25 cm.

For the hydrolyses 1 mmol of the amidazo compound, 10 ml of 95% EtOH, and a bubbling tube were put in the 50-ml flask. The two parts were connected (Lubriseal) and the exit tube placed in 50 ml of 0.1 *N* HCl in a 150-ml beaker. After nitrogen was passed through the system for 15 min, 1 ml of 7.8 *N* aqueous KOH and 9 ml of 95% EtOH were added through the dropping funnel. The reaction mixture was refluxed gently by heating in a silicone bath (100°), while nitrogen was slowly passed through the apparatus.

At the end of the reaction, the alcohol solution was shaken with 100 ml of water and 300 ml of ether. After three washings with water, the ether solution was concentrated to a solid.[24] This product was dissolved in a minimum of 95% EtOH at about 50° and a saturated solution of 456 mg of H_5IO_6 in 95% EtOH was added to oxidize hydrazo compounds to the azo state. After 5 min at room temperature, the solution was added to water and extracted with ether. The ether solution was washed with water, $NaHCO_3$ solution, and water. Removal of ether gave a solid, which was extracted with 20-ml portions of boiling hexane. The azo carbonyl compounds and 2-phenylindazole were readily soluble, leaving a solid residue of primary amide and unchanged starting material.

Removal of hexane yielded a solid "A Fraction," which was analyzed as described below under Analyses for Table I.

The hydrolysis products from compounds **3**, **4**, **5**, and **6** were not investigated; it was assumed that the amidazo reaction did not take place with these compounds since no ammonia was evolved. For this series, the reaction times were 3, 1, 7, and 3 hr, respectively.

Analyses for Table I.—Analytical conditions were established with pure reagents as follows. A solution of 4-phenylazobenzaldehyde of mp 120–121° (200 mg) and 4-biphenylamine (177 mg, 10% excess) in 4 ml of HOAc was heated on a steam bath for 30 min. After cooling the reaction mixture to room temperature, the crystalline precipitate of benzylidene derivative was filtered on a tared funnel. The yield was 97.4% (335 mg). Recrystallization from acetic acid raised the melting point of the ***N*-*p*-phenylazobenzylidene-4-biphenylamine** only 1° to 218–219°.

Anal. Calcd for $C_{25}H_{19}N_3$: C, 83.08; H, 5.30; N, 11.73. Found: C, 82.9; H, 5.53; N, 11.4.

The above conditions were used in the analysis of the A fractions obtained from the compounds in Table I, 50 mg of material being used if available. All of the benzylidene derivatives showed satisfactory melting points (215–218°) without recrystallization. The yields were not corrected for losses inherent in the method of analysis.

Analyses for Table II.—For compounds **33–37**, an analytical method based on the following was used. A solution of pure *p*-phenylazoacetophenone (50 mg, mp 115–116°) and 2,4-dinitrophenylhydrazine (49 mg, 10% excess) in 0.5 ml of HOAc containing 2 drops of concentrated HCl was heated on a steam bath for 10 min and then cooled to room temperature. The product was filtered and weighed (84.3 mg, 93.5%). The ***p*-phenylazoacetophenone-2,4-dinitrophenylhydrazone** melted at 244–245°.

Anal. Calcd for $C_{20}H_{16}N_6O_4$: C, 59.39; H, 3.99; N, 20.78. Found: C, 59.0; H, 4.15; N, 21.0.

The analyses were uncorrected for the inaccuracy of the analytical method.

For compounds **38–40**, *p*-phenylazobenzophenone was isolated from the A fractions and compared with an authentic sample of mp 104–105°.

Results for Compound 41.—A 65% yield of ammonia was obtained in this 8-hr reaction. Fraction A was a black tar with an odor of naphthalene. With 4-biphenylamine it gave a small yield of a black product (mp 150–160°), which was not investigated further.

Results for Compound 42.—This 8-hr reaction gave a 17% yield of ammonia; no definite products were isolated from fraction A.

Analyses for Table III.—Except for compounds **49**, **51**, and **52**, the A fractions were condensed with 4-biphenylamine as described under Analyses for Table I.

(20) S. Gabriel, *Chem. Ber.*, **20**, 2224 (1887).

(21) S. Gabriel and R. Jansen, *ibid.*, **23**, 2807 (1890).

(22) S. Gabriel and R. Jansen, *ibid.*, **24**, 3091 (1891).

(23) G. T. Morgan and F. M. G. Micklethwait, *J. Chem. Soc.*, 1158 (1906).

(24) For compounds **49**, **51**, and **52**, this solid was used directly, without further treatment, for determination of the amount of unchanged starting material.

Compound 43.—*p*-Tolylazobenzylidene-4-biphenylamine had mp 201–203°.

Anal. Calcd for $C_{26}H_{21}N_3$: C, 83.17; H, 5.64; N, 11.19. Found: C, 83.5; H, 5.93; N, 11.2.

Compound 44.—*N*-4-Biphenylazobenzylidene-4-biphenylamine melted at 292–295°.

Anal. Calcd for $C_{31}H_{23}N_3$: C, 85.10; H, 5.30; N, 9.60. Found: C, 84.7; H, 5.74; N, 9.34.

Compound 45.—*N*-*p*-Chlorophenylazobenzylidene-4-biphenylamine melted at 235–237°.

Anal. Calcd for $C_{25}H_{18}ClN_3$: C, 75.85; H, 4.58; N, 10.61. Found: C, 76.2; H, 4.78; N, 10.5.

Compound 46.—*N*-*p*-Methoxyphenylazobenzylidene-4-biphenylamine of mp 211–213° was obtained. See compound **50** for analytical data.

Compound 47.—*N*-*p*-Benzyloxyphenylazobenzylidene-4-biphenylamine melted at 232–234°.

Anal. Calcd for $C_{32}H_{25}N_3O$: C, 82.20; H, 5.39; N, 8.99. Found: C, 81.9; H, 5.29; N, 8.84.

Compound 48.—*N*-*p*-Mercaptomethylphenylazobenzylidene-4-biphenylamine melted at 231–233°.

Anal. Calcd for $C_{26}H_{21}N_3S$: C, 76.63; H, 5.19; N, 10.31. Found: C, 76.3; H, 5.32; N, 10.4.

Compound 49.—A 98% recovery of unchanged starting material (mp 230–232°) was obtained.

Compound 50.—*N*-*p*-Methoxyphenylazobenzylidene-4-biphenylamine melted at 212–213°.

Anal. Calcd for $C_{26}H_{21}N_3O$: C, 79.77; H, 5.41; N, 10.73. Found: C, 79.3; H, 5.54; N, 10.3.

Compound 51.—Acetylation of the product of this reaction gave a 91% yield of a compound of mp 227–230°, which was shown to be 1-acetaminomethylbenzene-4-azo-4′-acetaminobenzene-1 by comparison with an authentic sample of mp 230–231°.

Anal. Calcd for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05. Found: C, 65.6; H, 5.96; N, 17.7.

Compound 52.—An 82% yield of unchanged starting material (mp 205–207°) was obtained.

Compound 53.—*N*-*m*-Trifluoromethylphenylazobenzylidene-4-biphenylamine melted at 177–178°.

Anal. Calcd for $C_{26}H_{18}F_3N_3$: C, 72.72; H, 4.23; N, 9.79. Found: C, 72.8; H, 4.48; N, 9.84.

Compound 54.—*N*-*o*-Tolylazobenzylidene-4-biphenylamine melted at 169–170°.

Anal. Calcd for $C_{26}H_{21}N_3$: C, 83.17; H, 5.64; N, 11.19. Found: C, 83.2; H, 6.09; N, 11.4.

Compound 55.—*N*-*o*-Methoxyphenylazobenzylidene-4-biphenylamine melted at 154–156°.

Anal. Calcd for $C_{26}H_{21}N_3O$: C, 79.77; H, 5.41; N, 10.73. Found: C, 80.0; H, 5.52; N, 10.7.

Compound 56.—*N*-*o*-Biphenylazobenzylidene-4-biphenylamine melted at 178–179°.

Anal. Calcd for $C_{31}H_{23}N_3$: C, 85.10; H, 5.30; N, 9.60. Found: C, 85.2; H, 5.65; N, 9.43.

Compound 57.—*N*-*p*-α-Naphthylazobenzylidene-4-biphenylamine melted at 177–178°.

Anal. Calcd for $C_{29}H_{21}N_3$: C, 84.85; H, 4.91; N, 10.24. Found: C, 84.7; H, 5.28; N, 10.1.

Analyses for Table IV.—For compounds **58–62**, an analytical method based on the following was used. 2,4-Dinitrobenzenesulfonic acid (153 mg, 0.000617 mol) was dissolved in 30 ml of dry ether. This solution was added dropwise to a solution of 2-phenylindazole (100 mg, 0.000515 mol) in 5 ml of dry ether. The precipitate of fine needles was separated (221 mg, 97.2% yield, mp 177–179°). Crystallization from absolute EtOH gave pure 2-phenylindazole 2,4-dinitrobenzenesulfonate (mp 180–181°).

Anal. Calcd for $C_{19}H_{14}N_4O_7S$: C, 51.58; H, 3.19; N, 12.67. Found: C, 51.2; H, 3.34; N, 12.4.

Action of Alcoholic KOH on *p*-Phenzylazobenzylamine.—A mmol of *p*-phenylazobenzylamine (as carbamate) was hydrolyzed for 3 hr under amidazo reaction conditions. A 20% yield of NH_3 was obtained.

Registry No.—**1,** 32478-84-5; **2,** 32478-85-6; 2 oxime, 32478-86-7; 2 semicarbazone, 32478-87-8, **3,** 32478-88-9; **4,** 32478-89-0; **5,** 32478-90-3; **6,** 32478-91-4; **13,** 32527-23-4; **14,** 32479-09-7; **15,** 32478-92-5; **16,** 32478-93-6; **17,** 32478-94-7; **18,** 32478-95-8; **19,** 32478-96-9; **20,** 32478-97-0; **21,** 32478-98-1; **22,** 32478-99-2; **23,** 32479-00-8; **24,** 32479-01-9; **25,** 32479-02-0; **26,** 32479-03-1; **27,** 32479-04-2; **28,** 32479-05-3; **29,** 32479-06-4; **30,** 32479-07-5; **31,** 32479-08-6; **32,** 32479-10-0; **33,** 32479-11-1; **34,** 32479-12-2; **35,** 32479-13-3; **36,** 32479-14-4; **37,** 32479-15-5; **38,** 32479-16-6; **39,** 32479-17-7; **40,** 32479-18-8; **41,** 32479-19-9; **42,** 32479-20-2; **43,** 32479-21-3; **44,** 32479-22-4; **45,** 32479-23-5; **46,** 32479-24-6; **47,** 32479-25-7; **48,** 32479-26-8; **49,** 32479-27-9; **50,** 32479-28-0; **51,** 32479-29-1; **52,** 32479-30-4; **53,** 32479-31-5; **54,** 32479-32-6; **55,** 32478-55-0; **56,** 32478-56-1; **57,** 32478-57-2; **58,** 32478-58-3; **59,** 32478-59-4; **60,** 32478-60-7; **61,** 32478-61-8; **62,** 32478-62-9; *N*-*p*-nitrobenzyl-*N*-methylbenzamide, 32478-63-0; *N*-*p*-nitrosobenzylacetamide, 32478-64-1; *N*-*p*-aminobenzylbenzamide, 32478-65-2; *m*-nitrobenzylbenzamide, 32478-66-3; 1-*p*-aminophenylethylamine hydrochloride, 32478-67-4; phenyl-*p*-aminophenylmethylamine dihydrochloride, 5580-53-0; 1-acetaminomethyl-4-nitronaphthalene, 32527-24-5; 1-acetaminomethyl-4-amino-5,6,7,8-tetrahydronaphthalene, 32478-69-6; 1-acetaminomethyl-4-acetamino-5,6,7,8-tetrahydronaphthalene, 32478-70-9; 1-acetaminomethylbenzene-4-azo-4′-trifluoroacetaminobenzene-1, 32478-71-0; 1-benzoylaminomethylbenzene-4-azo-4′-aminonaphthalene-1, 32478-72-1; *o*-aminobenzylurea, 32478-73-2; 1-phenyl-3-*o*-nitrobenzylurea, 32478-74-3; 1-phenyl-3-*o*-aminobenzylurea, 32478-75-4; *N*-*p*-phenylazobenzylidene-4-biphenylamine, 32478-76-5; *p*-phenylazoacetophenone 2,4-DNPH, 32478-77-6; *p*-tolylazobenzylidene-4-biphenylamine, 32478-78-7; *N*-4-biphenylazobenzylidene-4-biphenylamine, 32478-79-8; *N*-*p*-chlorophenylazobenzylidene-4-biphenylamine, 32478-80-1; *N*-*p*-methoxyphenylazobenzylidine-4-biphenylamine, 32478-54-9; *N*-*p*-benzyloxyphenylazobenzylidene-4-biphenylamine, 32478-81-2; *N*-*p*-mercaptomethylphenylazobenzylidene-4-biphenylamine, 32478-82-3; *N*-*m*-trifluoromethylphenylazobenzylidene-4-biphenylamine, 32478-83-4; *N*-*o*-tolylazobenzylidene-4-biphenylamine, 32478-49-2; *N*-*o*-methoxyphenylazobenzylidene-4-biphenylamine, 32478-50-5; *N*-*o*-biphenylazobenzylidene-4-biphenylamine, 32478-51-6; *N*-*p*-α-naphthylazobenzylidene-4-biphenylamine, 32478-52-7; 2-phenylindazole 2,4-DNP, 32478-53-8.