mole) of isobutyraldehyde, there was obtained 10 g. (18% yield) of **1,1,1-trichloro-3-methyl-2-butanol**, b.p. 88–89° (20 mm.), $n^{25}D$ 1.4737. The physical constants are in agreement with those of Normant and Ficini[11] who prepared it by another method. The infrared spectrum showed ν_{max} (liq. film between salt plates) 3575–3350, 3000, 2900, 1495, 1405, 1380, 1305, 1250, 1180, 1150, 1110, 1055, 1020, 920, 855–800, 780–750, and 660–640 cm.$^{-1}$.

Anal. Calcd. for $C_5H_9Cl_3O$: C, 31.34; H, 4.73; Cl, 55.58. Found: C, 31.58; H, 4.92; Cl, 55.30.

Using potassium hydroxide as the base, the yield was 12% of theory.

Acknowledgment.—We are grateful to Dr. Ellis Lippincott and Dr. Francis Powell for their assistance in obtaining and interpreting the infrared spectra. The financial support provided by the National Institutes of Health is deeply appreciated.

The Thermal Decomposition of 2-Azidobenzylideneamines

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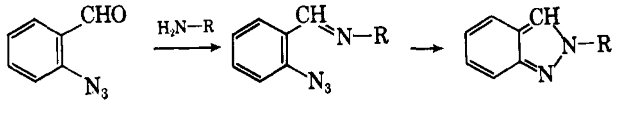
The synthesis and thermal decomposition of a series of 2-azidobenzylideneamines are described. In every case the reaction resulted in an intramolecular cyclization to yield a five-membered ring structure possessing the indazole nucleus.

Thermal- or photo-induced decompositions of biaryl azides which result in intramolecular cyclization with a loss of nitrogen are well-known. For example, Smith and co-workers[1] have reported that the decomposition of 2-azidobiphenyl produced carbazole in high yield. This reaction has been extended to vinyl azides by Smolinsky[2] who obtained 2-phenylazirine upon pyrolysis of α-azidostyrene. The decomposition of 2,2′-diazidoazobenzene has been reported by Carboni and Castle[3] to yield 1,3a,4,6a-tetraazapentalene. The decomposition of azides has been shown by several workers[4] to be capable of intramolecular cyclization at saturated centers. These products can be explained readily by a mechanism involving a univalent, uncharged nitrogen atom frequently called an azene. This intermediate also has been called nitrene, imene, and imine.

Analogous cyclization reactions proceeding presumably through the azene intermediate have also been effected by the reduction of a nitroso or nitro group. Thus, 2-nitrobenzylideneaniline[5] upon treatment with triethyl phosphite was reduced to 2-phenylindazole, and, similarly, 2-nitroso-[6] and 2-nitrobiphenyls[7] were converted to the corresponding carbazoles. The reductive cyclization of 2-nitrophenylpyridine[8] also has been reported.

In this report there are described the thermal decompositions of 2-azidobenzylideneamines in an inert solvent to yield cyclized products. The synthesis of the starting azido compounds with one exception were conveniently effected by the condensation of 2-azidobenzaldehyde with the appropriate amine. These azides are listed in Table I. The decomposition of the azide was carried out in either 1,2-dichloro- or 1,2,4-trichlorobenzene at a temperature (approximately 150°) where a smooth liberation of nitrogen was observed. In every case a high yield of the corresponding 2-substituted indazole was obtained. The results of the thermal decompositions of 2-azidobenzylideneamines together with several azines are summarized in Table II.



The decompositions of 2-azidobenzylideneaniline (I) and 4-nitro(2-azidobenzylidene)aniline (II) yielded 2-phenylindazole[9] and 2-(4-nitrophenyl)indazole, respectively. In the case of the pyrolysis of 2,4-dinitro-(2-azidobenzylidene)aniline (III) the presence of the indazole nucleus in the product, 2-(2,4-dinitrophenylamino)indazole, was substantiated by reductive cleavage to indazole.

Upon heating a solution of 2,2′-diazidobenzylideneazine (V) in either di- or trichlorobenzene, the decomposition occurred in two discrete stages. One mole of nitrogen was released at a temperature of 120–130° to yield 2-(2-azidobenzylideneamino)indazole (VI). At a temperature of 150–155°, a second mole of nitrogen was evolved and 2,2′-biindazole (VII) was produced in high yield. Both stages of the decomposition can be effected by heating V to 150° in an inert solvent producing VII in 93% yield.

A similar cyclization reaction to form the indazole nucleus was also carried out with 2-azido-2′-nitrobenzylideneazine (IV). The decomposition of IV at 150° in dichlorobenzene occurred smoothly producing a 97% yield of 2-(2-nitrobenzylideneamino)-indazole (VIII). The structural similarity of VIII and the azidoindazole (VI) mentioned earlier was established by catalytic reduction of these compounds to 2-(2-aminobenzylideneamino)indazole (IX). Further confirmation of structure IX was obtained by the conversion of the two reduction products to the identical acetamide. The possibility that a skeletal rearrange-

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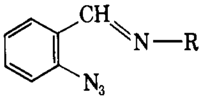
TABLE I

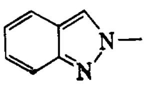
2-AZIDOBENZYLIDENEAMINES

No.	Azide	Yield, %	M.p., °C., dec.	Empirical formula	% carbon Calcd.	% carbon Found	% hydrogen Calcd.	% hydrogen Found	% nitrogen Calcd.	% nitrogen Found
I	2-Azidobenzylideneaniline	44	83	$C_{13}H_{10}N_4$	70.25	70.34	4.54	4.56	25.20	25.00
II	4-Nitro(2-azidobenzylidene)aniline	66	155	$C_{13}H_9N^5O_2$	58.43	58.49	3.40	3.54	26.21	26.20
III	2,4-Dinitro(2-azidobenzylidene)aniline	83	288	$C_{13}H_9N_7O_4$	47.72	47.80	2.77	2.39	29.97	29.90
IV	2-Azido-2′-nitrobenzylideneazine	50	148	$C_{14}H_{10}N_6O_2$	57.14	57.30	3.43	3.83	28.56	28.65
V	2,2′-Diazidobenzylideneazine	~100	160	$C_{14}H_{10}N_8$	57.92	58.13	3.48	3.40	38.60	38.60

TABLE II

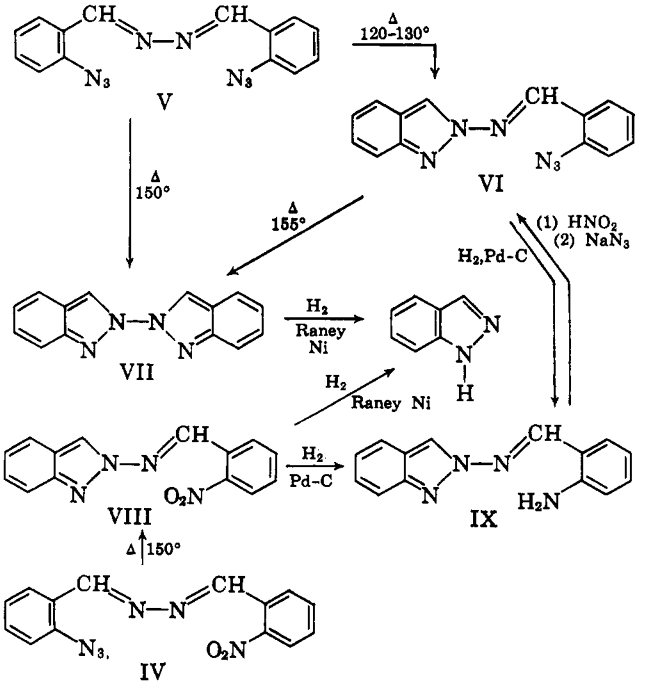
DECOMPOSITION OF 2-AZIDOBENZYLIDENEAMINES



No.	R	Dec. temp., °C.	Solvent	Product	Yield, %	M.p., °C.	Empirical formula	% carbon Calcd.	% carbon Found	% hydrogen Calcd.	% hydrogen Found	% nitrogen Calcd.	% nitrogen Found
I	C_6H_5-	150	DCB[a]	2-Phenylindazole	75	82-83[b]	$C_{13}H_{10}N_2$		[c]		[c]		[c]
II	4-$NO_2C_6H_4$-	155	TCB[d]	2-(4-Nitrophenyl)-indazole	93	225	$C_{13}H_9N_3O$	65.27	65.26	3.80	3.65	17.56	17.50
III	2,4-$(NO_2)_2C_6H_3NH$-	150	TCB	2-(2,4-Dinitrophenyl-amino)indazole	94	118	$C_{13}H_9N_5O_4$	52.18	52.19	3.03	3.21	23.41	23.55
IV	2-$NO_2C_6H_4CH{=}N$-	150	DCB	2-(2-Nitrobenzylidene-amino)indazole	97	138	$C_{14}H_{10}N_4O_2$	63.15	63.49	3.79	3.96	21.04	21.10
V	2-$N_3C_6H_4CH{=}N$-	120-130	DCB	2-(2-Azidobenzylidene-amino)indazole	79	122	$C_{14}H_{10}N_6$	64.12	64.26	3.84	3.96	32.05	32.00
V	2-$N_3C_6H_4CH{=}N$-	150	DCB	2,2′-Biindazole	93	268	$C_{14}H_{10}N_4$	71.77	71.84	4.31	4.40	23.92	23.80
VI		155	DCB	2,2′-Biindazole	90	268	$C_{14}H_{10}N_4$						

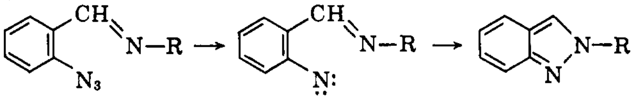
[a] 1,2-Dichlorobenzene. [b] Lit.[9] m.p. 81–82°. [c] Analyses were obtained only for new compounds. [d] 1,2,4-Trichlorobenzene.

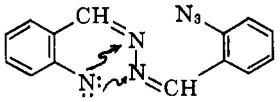
ment might have occurred during either of these reductions was conclusively ruled out by the conversion of IX back to VI. Compound VI, obtained in this manner, was identical with that obtained by the partial decomposition of V and, upon decomposition in dichlorobenzene, also yielded biindazole VII. The reduction of VII with Raney nickel yielded indazole, however, only in 40–50% yield. Apparently a significant amount was lost during the removal of the solvent.



Indazole was also obtained by the Raney nickel reduction of VIII. Thus, the above sequence of reactions indicated that the indazole nucleus was present in VI, VII, VIII, and IX. The assignment of 2,2′-biindazole for the structure of VII was based on the isolation of indazole from the catalytic reduction of VII and VIII, coupled with the establishment of the empirical formula, $C_{14}H_{10}N_4$, and the absence of the NH absorption in the infrared spectrum.

In the present study, the results of the thermal decomposition of 2-azidobenzylideneamines are explained readily by a mechanism involving an electron-deficient azene intermediate formed by the loss of nitrogen. The azene is then believed to attack the nitrogen atom of the azomethine linkage to form the 2-substituted indazoles. The pyrolysis of 2,2′-diazidobenzylideneazine (V) was of special interest. It can readily be seen that the azene derived from V can attack the the nitrogen atom of the azomethine linkage to yield either a five of a six-membered ring. The two possible sites of attack are very similar except for the effect of the azene *vs.* the azido group. The fact that the only products isolated were those possessing the indazole nucleus indicates the high degree of preference for the





five-membered ring formation in the ring closure reactions of azenes. In view of the high yield (93%) of the biindazole obtained with V, the formation of benzotriazine (six-membered ring) occurred to only a small extent, if at all.

Decomposition reactions of 2-azidodiphenylmethane derivatives are presently being investigated to determine whether a six-membered ring closure can be effected.

Experimental[10,11]

With the exception of 2-(2-azidobenzylideneamino)indazole (VI) all azides used in this study were prepared by the condensation of 2-azidobenzaldehyde with the appropriate amines. The azides prepared in this manner are summarized in Table I. A typical example of the synthesis of azides is given below.

2-Azido-2′-nitrobenzylideneazine (IV).—A solution of 5.0 g. of 2-azidobenzaldehyde[12] in 50 ml. of ethanol was added to a solution of 5.0 g. of 2-nitrobenzylidenehydrazine[13] in 100 ml. of ethanol. A few drops of acetic acid were added, and the mixture was stirred for a few minutes. The yellow precipitate which separated was collected and dried, yielding 5.0 g. (50%) of 2-azido-2′-nitrobenzylideneazine, melting at 145–148° dec. An analytical sample was prepared by recrystallization from ethanol, yielding yellow needles, m.p. 148° dec.

2-(2-Azidobenzylideneamino)indazole (VI).—A solution of 3.5 g. of 2,2′-diazidobenzylideneazine (V) in 200 ml. of dichlorobenzene was heated to 120–130° for 2 hr. During this heating period considerable evolution of gas was observed and the solution turned dark brown. The solvent then was removed at approximately 100° under reduced pressure. The residue was recrystallized from ethanol, yielding 2.5 g. (79%) of yellow 2-(2-azidobenzylideneamino)indazole, m.p. 116–118° dec. An analytical sample, m.p. 122° dec., was prepared by dissolving the product in cold benzene, filtering, and reprecipitating by the addition of ethanol.

Thermal decompositions of all the azides were carried out under essentially the same conditions. The results are summarized in Table II. Pyrolysis of 2-(2-azidobenzylideneamino)indazole is described below as a representative example.

2,2′-Biindazole (VII).—A solution of 1.5 g. of 2-(2-azidobenzylideneamino)indazole (VI) in 150 ml. of dichlorobenzene was heated to 155° for 2 hr. The solution darkened to dark brown and gas was evolved. The solvent then was removed under reduced pressure at 100°. The residue was recrystallized from toluene, yielding 1.2 g. (90%) of 2,2′-biindazole, m.p. 260–264°. Further recrystallizations from toluene yielded an analytical sample melting at 268°.

2-(2-Aminobenzylideneamino)indazole (IX). A.—A solution of 1.7 g. of 2-(2-nitrobenzylideneamino)indazole in 250 ml. of ethanol was hydrogenated with 1.0 g. of 5% palladium on charcoal on a Parr shaker for 1 hr. at 30 p.s.i. The mixture was filtered and the solvent was removed at reduced pressure. The residue was recrystallized from ethanol, yielding 1.0 g. (66%) of yellow 2-(2-aminobenzylideneamino)indazole, m.p. 165–167°. Further recrystallizations from ethanol yielded an analytical sample melting at 167–167.5°.

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.02; H, 5.10; N, 23.90.

B.—A suspension of 1.0 g. of 2-(2-azidobenzylideneamino)-indazole (VI) in 200 ml. of ethanol was hydrogenated at 40–50° with 1.0 g. of 5% palladium on charcoal on a Parr shaker at 50 p.s.i. for 2 hr. The mixture was filtered and the solvent was removed at reduced pressure. The residue was recrystallized from alcohol to yield 0.7 g. (78%) of 2-(2-aminobenzylideneamino)indazole melting at 165–167°. Mixture melting point with the reduction product of 2-(2-nitrobenzylideneamino)indazole showed no depression.

2-(2-Acetamidobenzylideneamino)indazole.—A mixture of 0.1 g. of 2-(2-aminobenzylideneamino)indazole (IX) and 5 ml. of acetic anhydride was heated gently for 10 min. After cooling, the mixture was poured into 50 ml. of ice-cold water. The crystals which separated were collected and dried, yielding 0.1 g. (82%) of 2-(2-acetamidobenzylideneamino)indazole, m.p. 205–212°. An analytical sample melting at 212° was prepared by recrystallizations from ethanol.

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.04; H, 5.07; N, 20.14. Found: C, 68.88; H, 5.14; N, 20.20.

2-(2-Azidobenzylideneamino)indazole (VI) from Amine IX.—A solution of 1.0 g. of 2-(2-aminobenzylideneamino)indazole (IX) in 75 ml. of glacial acetic acid and 25 ml. of concentrated hydrochloric acid was cooled to 0°. To the cold mixture a solution of 0.35 g. of sodium nitrite in 5 ml. of water was added. The resulting mixture was stirred for 10 min. at 0°, and 150 ml. of ice-cold water was added followed by a solution of 1.0 g. of sodium azide in 10 ml. of water. The mixture was diluted further by the addition of 150 ml. of water and then extracted with ether. The ethereal extract was washed first with water, then with 5% sodium hydroxide solution, and dried over sodium sulfate. After the removal of the solvent under reduced pressure at 30°, the solid residue was recrystallized from ethanol yielding 0.5 g. (45%) of 2-(2-azidobenzylideneamino)indazole, m.p. 117–118° dec. A mixture melting point with the partial decomposition product of 2,2-diazidobenzylideneazine (V) showed no depression.

Reductive Cleavage of 2-(2,4-Dinitrophenylamino)indazole.—A suspension of 2.0 g. of 2-(2,4-dinitrophenylamino)indazole in 200 ml. of ethanol was hydrogenated with 0.5 g. of 5% palladium on charcoal on a Parr shaker at 40 p.s.i. for 2 hr. The mixture was separated and the solvent was removed at reduced pressure. A solution of the residue in benzene was placed on an alumina-packed chromatography column and eluted with a mixture of benzene and cyclohexane to yield 0.3 g. (38%) of indazole, melting at 147°; picrate, m.p. 137° (lit.[14] m.p. 148°; picrate, m.p. 136°).

Reductive Cleavage of 2,2′-Biindazole (VII).—A suspension of 1.0 g. of 2,2′-biindazole in 300 ml. of ethanol was hydrogenated with Raney nickel catalyst on a Parr shaker at 40–50° for 0.5 hr. The mixture was separated and the solvent was removed at 60–70°. The residue was recrystallized from water yielding 0.5 g. (50%) of indazole melting at 145–146°, m.m.p. 146–147°.

Reductive Cleavage of 2-(2-Nitrobenzylideneamino)indazole.—A solution of 1.5 g. of 2-(2-nitrobenzylideneamino)indazole in 250 ml. of ethanol was hydrogenated at 40–50° with Raney nickel catalyst for 0.5 hr. The mixture was worked up as above yielding 0.4 g. (60%) of indazole, m.p. 146°.

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(10) All melting points are uncorrected.

(11) Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

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