tions were used as the chemical actinometer for which a quantum yield of 0.38 was used[43] giving a reproducible light intensity of 2.10×10^{16} quanta sec^{-1}. Analyses were performed on a Hewlett-Packard Model 5750 gas chromatograph using a 10% FS-1265 Diasaport S column at 210–235.[6] The mole ratio:area ratio response of the instrument was calibrated for each aroylimine and internal standard used, so that yields of product could be measured accurately. The conversions were run to 10% or less. The mass balance in these runs were generally better than 95%.

Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer equipped with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. The emission spectra were measured in a methanol–ethanol (4:1) or methylcyclohexane glass. The solvent was checked for emission each time a spectra was recorded. No interference due to solvent was found at any time. All compounds having short radiative lifetimes were measured by photographing the decay curve on an oscillograph. The chopper speed was adjusted manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted vs. time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime (τ_0).

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Registry No.—**9**, 36728-20-8; **12**, 55030-00-7; **13**, 55030-01-8; **14**, 55030-02-9; **15**, 55030-03-0; **16**, 55030-04-1; **17**, 55030-05-2; **18**, 55030-06-3; *n*-butyl bromide, 109-65-9; benzonitrile, 100-47-0; benzoyl chloride, 98-88-4; bromobenzene, 108-86-1; 2,2-dimethylbutyronitrile, 20654-46-0; 2,2-dimethylvaleronitrile, 20654-47-1; *p*-anisoyl chloride, 100-07-2.

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A Convenient Synthesis of Protiated and Specifically Deuterated Secondary Azoalkanes

P. L. Grizzle,[1a] D. W. Miller,[1b] and S. E. Scheppele*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

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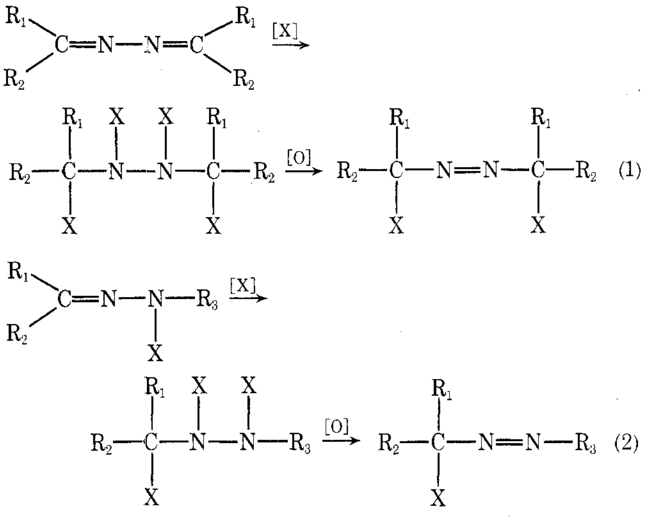
A convenient synthesis of secondary azo compounds is reported. The method involves addition of chlorine to the azine or hydrazone in CH_2Cl_2 followed by reduction of the dichloro- or chloroazoalkane with $LiAlH_4$ or $LiAlD_4$ in ether. The preparation of a variety of symmetrical secondary azoalkanes demonstrates the applicability of the technique. The procedure is applicable to the synthesis of (*sec*-alkylazo)alkanes and presumably of (*sec*-alkylazo)-2,4,6-trichlorobenzenes. The isotope purity of the azoalkane is fixed by that of the azine or hydrazone precursor and of the $LiAlD_4$.

Secondary deuterium isotope effects[2] in and the rates[3] of thermolysis of secondary azoalkanes have been extensively utilized in investigations of the mechanism of azo compound pyrolysis and of the effect of substituents on the energetics of free-radical formation. We report a convenient synthesis of secondary azoalkanes and their specifically deuterated congeners possessing essentially the maximum number of atoms of deuterium.

The classical method (Scheme I) for the synthesis of symmetrical (eq 1) or unsymmetrical (eq 2) secondary azoalkanes involves catalytic reduction of the corresponding azine or hydrazone to the hydrazine followed by oxidation;

Scheme I



X = H or D

usual oxidizing reagents are yellow mercuric oxide,[2a,f,g,3c,i,4] hydrogen peroxide,[3b,c,5] and cupric chloride.[3i]

However, a number of complications have been observed with Scheme I. Rather vigorous conditions have been required for the reduction of some azines to the hydrazines,[3b,c,4] e.g., ring-substituted acetophenone azines.[3b,4] Reduction of *tert*-butyl phenyl ketazine (**1**) in ethanol with Pd at room temperature gave only hydrazone; reduction of the hydrazone in glacial acetic acid yielded both the hydrazine and 2,2-dimethyl-1-phenylpropylamine. All attempts to reduce 2,2-dimethylpropiophenone methylhydrazone (**2**) and phenylhydrazone (**3**) failed. Similarly, low-pressure hydrogenation of benzophenone phenylhydrazone was unsuccessful.[3d] Difficulties have also been encountered with the oxidation step in reaction rate and product yield.[6]

Scheme I imposes limitations on the synthesis of specifically deuterated azo compounds. Generally some fraction of the sample is not specifically labeled because some exchange of aliphatic protium (deuterium) normally accompanies reduction with $D_2(H_2)$;[2a,c,d,g,i] exchange of aromatic protium (deuterium) in the reduction is usually negligible.[2a,c,d,g,i,j,7] Furthermore, in catalytic deuteration the number of atoms of D introduced is variable and less than the maximum.[2a,c,g,h,j] This result presumably reflects catalytic exchange between the deuterium gas and hydroxylic protium; water present in the solvent or absorbed on the walls of the hydrogenation vessel and exchangeable protium in the solvent constitute sources of the latter.

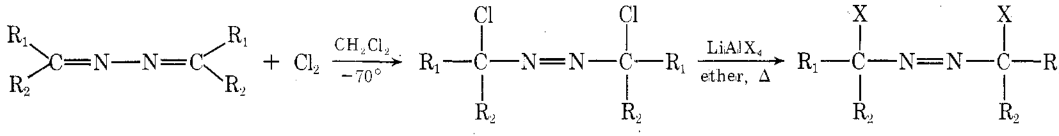
Lithium aluminum hydride and deuteride are ideal reagents to obviate problems in the reduction step of Scheme I. Although some success has been realized in the reduction of hydrazones (eq 2) with these reagents,[2b,3d] the $LiAlH_4$ reduction of azines to hydrazines (eq 1) has been remarkably unsuccessful[3c,8] except in the case of simple aliphatic azines.[9]

Consequently, a chlorine addition–metal hydride reduction method was developed. The general reaction scheme and the azoalkanes so prepared are given in Table I. The addition–reduction method bypasses the oxidation step in Scheme I and incorporates (a) the desirable properties of $LiAlH_4$ ($LiAlD_4$), (b) the propensity of ketazines to undergo 1,4 addition of Cl_2 to form 1,1′-dichloroazoalkanes,[10] and (c) the facileness with which the latter undergo nucleophilic substitution.[10b,c,11] Azine and excess Cl_2 were combined in CH_2Cl_2, usually at −70°. After removal of the CH_2Cl_2 the 1,1′-dichloroazoalkane, depending upon its stability, was either purified before reaction with the metal hydride or immediately treated with the hydride in refluxing diethyl ether. The general utility of this approach is demonstrated by the variety of azines which were converted to the corresponding azoalkanes; see Table I.

The structures of 1,1′-dichloro-1,1′-diphenylazobutane and 1,1′-dichloro-1,1′,3,3,3′,3′-hexaphenylazopropane were confirmed by NMR and MS; their reduction to **9** and **10** also provides confirmation of structure.

As reported[10d] **1** smoothly added Cl_2 (3 hr) to give 1,1′-dichloro-2,2,2′,2′-tetramethyl-1,1′-diphenylazopropane (**13**). In contrast to the reaction of **1** with H_2/Pd (see eq 1), reaction of **13** with $LiAlH_4$ ($LiAlD_4$) for 4 hr gave **11** (**12**). 4-Bromoacetophenone azine (**14**) and 3,3-diphenylpropiophenone azine (**15**) were smoothly and rapidly converted to **5** and **10** analogously. It is noteworthy that **5** could not be

Table I
Symmetrical Azoalkanes Synthesized via Chlorine Addition–Metal Hydride Reduction



X = H or D

Compd	X	R_1	R_2	Mp or bp, °C (mm)[a]	Atoms of D	% yield[b]
3[c]	H	CH_3	C_6H_5	72–73		52
4	D	CH_3	C_6H_5	72–73	1.960 ± 0.002[d]	64
5[e]	H	CH_3	p-Br-C_6H_4	107.5–108		41
6[f]	H	CH_3	p-CH_3-C_6H_4	78–79		48
7[g]	H	CH_3	2-$C_{10}H_7$	144–144.5		58
8[h]	H	CH_3	C_2H_5	48–49 (25)		63
9[i]	H	C_3H_7	C_6H_5	60–61		42
10[j]	H	$(C_6H_5)_2CHCH_2$	C_6H_5	146.5–147.5		60
11[k]	H	t-C_4H_9	C_6H_5	155.5–156.5		61
12	D	t-C_4H_9	C_6H_5	156–156.5	1.998 ± 0.003[d]	63

[a] Melting points and boiling points are not corrected. [b] Yield based on azine. [c] W. A. Schulze and H. L. Lochte, *J. Am. Chem. Soc.*, 48, 1030 (1926). [d] Determined by duplicate combustion analysis; uncertainty is average deviation. [e] Anal. Calcd for $C_{16}H_{16}N_2Br_2$: C, 48.51; H, 4.07; N, 7.07; Br, 40.34. Found: C, 48.61; H, 4.11; N, 7.13; Br, 40.32. [f] Reference 3b. [g] Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.22; H, 6.74; N, 8.06. [h] Reference 3h. [i] Reference 2j. [j] Anal. Calcd for $C_{42}H_{38}N_2$: C, 88.38; H, 6.71; N, 4.91. Found: C, 87.94; H, 6.60; N, 5.38. [k] Anal. Calcd for $C_{22}H_{30}N_2$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.81; H, 9.07; N, 9.06.

prepared via eq 1 because attempts to reduce **14** were unsuccessful. Furthermore, in the synthesis of **10** via eq 1, low-pressure hydrogenation (Pd to azine ratio in grams was 3:1) required from 15 to 48 hr depending upon the solvent, and oxidation of the hydrazine with yellow mercuric oxide required 24 hr. Pure **7** was easily obtained via chlorine addition–metal hydride reduction but not via eq 1. The low-pressure catalytic hydrogenation of methyl 2-naphthyl ketazine continued after uptake of 2 mol of H_2 per mole of azine; one or more of the double bonds in the 2-naphthyl moiety evidently underwent reduction. The applicability of the chlorine addition–metal hydride reduction method to the preparation of aliphatic secondary azoalkanes was demonstrated by the conversion of 2-butanone azine to **8**.

If substitution of Cl_2 competed appreciably with its addition, the chlorine addition–metal hydride reduction method would not be a satisfactory route to deuterated azo compounds because $LiAlD_4$ cleavage of carbon–chlorine bonds other than the C-1–Cl and C-1′–Cl bonds would result in substitution of deuterium for protium. Similarily, in the conversion of deuterated azines to the corresponding azo compounds, use of $LiAlH_4$ would result in substitution of protium for deuterium. The hydrogenolysis of bonds linking chlorine to an aromatic ring with metal hydride would not be expected.[12]

The following evidence reveals that such substitution is negligible. The chemical shifts observed in and the proton ratios obtained upon integration of the NMR spectra of the chloroazoalkanes were consistent with the presence of chlorine only at C-1 and C-1′. Mass spectra were obtained for the chloroazoalkane precursors to **3** (**4**), **6**, **7**, **9**, and **10**. These spectra were characterized by ions formally derived from formation and subsequent fragmentation of the substituted alkyl radicals from C–N bond homolysis. Neither the ion intensities nor the high-resolution data showed any evidence for the presence of chlorine at positions other than C-1 and C-1′. Finally, **4** and **12** containing 1.960 and 1.998 atoms of D, respectively, were obtained upon $LiAlD_4$ reduction of 1,1′-dichloro-1,1′-diphenylazoethane (**16**) and **13**. The same $LiAlD_4$ was used in preparation of **12** and benzyl alcohol-α,α-d_2.[13] It is thus noteworthy that the atom % D of the former as determined by combustion, 99.9 ± 0.3, is in good agreement with the value for the latter as determined by low-voltage mass spectrometry,[13] 99.3 ± 0.3. Different $LiAlD_4$ was used in synthesis of **4**. Since **4** and **12** do not contain in excess of two atoms of D, either the formation of or the reduction of chlorine-substituted 1,1′-dichloroazoalkanes must be negligible. These conclusions concerning the extent to which substitution of chlorine accompanies its addition to azines are supported by the results of Malament and McBride.[10d]

Pyrolysis of recrystallized **11** in ethylbenzene yielded only 81.6% of the theoretical quantity of nitrogen gas.[14] This result was attributed to the presence of a trace amount of **16** in the sample. Although the thermal decomposition of 1,1′-dichloroazoalkanes proceeds predominantly by C–N bond homolysis,[10,15] there may be some C–Cl bond cleavage, which under our conditions would lead to formation of traces of HCl. The HCl would catalyze the isomerization of **11** to hydrazone; the uv spectrum of the residue from pyrolysis displayed absorption characteristic of the hydrazone. The 99.1% yield of nitrogen obtained upon heating a mixture of pyridine[16] and **11** (6:1 mole ratio) in ethylbenzene supports this explanation.

Since 1,1′-dichloroazoalkanes undergo hydrolysis,[10b-d,17] the crude azoalkanes were solvolyzed homogeneously in ether–acetone–water containing equimolar amounts of $AgNO_3$; in all cases formation of traces of AgCl was observed. The azoalkane was then purified by column chromatography over silica gel followed by recrystallization. The chromatography step, which is not unique to the chloride addition–metal hydride reduction method, and which may have been unnecessary, was introduced to facilitate removal of colloidal silver and silver salts. After purification, a 99.2 and 99.7% yield of nitrogen was obtained upon pyrolysis of **11** and **12**, respectively, in ethylbenzene. Similar results were obtained for decomposition of **3** and **4** prepared by both chlorine addition–metal hydride reduction and eq 1.[14]

(*sec*-Alkylazo)benzenes cannot be prepared by chlorine addition–metal hydride reduction because substitution of chlorine for aromatic hydrogen is known to accompany its addition to phenylhydrazones.[18] However, (2,2-dimethyl-1-phenylpropyl)azomethane (**17**, $R_1 = C_6H_5$; $R_2 = (CH_3)_3C$; $R_3 = CH_3$) and (2,2-dimethyl-1-phenylpropyl-1-*d*)azomethane (**18**) were prepared from **2** via chlorine addition–metal hydride reduction. Deuterium analysis of **18** yielded 1.072 atoms of D, indicating that 0.092 atoms of H (1.072 − 1.960/2) had been replaced by chlorine in the addition step. This extent of deuterium–protium exchange is in almost all cases less than that observed in the catalytic deuteration of azines or hydrogenation of deuterated azines. Thus it appears that chlorine addition–metal hydride reduction is applicable to the synthesis of (*sec*-alkylazo)alkanes and (*sec*-alkylazo)-2,4,6-trichlorobenzenes, since Moon[18] has demonstrated that 2,4,6-trichlorophenylhydrazones react with Cl_2 to form [(1-chloroalkyl)azo]-2,4,6-trichlorobenzenes.

Experimental Section

General. NMR spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are reported with respect to tetramethylsilane. Mass spectra were obtained using a CEC 21-110B spectrometer at 70 eV. Elemental and deuterium analyses were performed by Galbraith Laboratories, Inc., and Mr. Josef Nemeth, Urbana, Ill., respectively.

Butyrophenone (Aldrich), 4-bromoacetophenone (Aldrich), 4-methylacetophenone (Aldrich), methyl 2-naphthyl ketone (Eastman), acetophenone (Baker), and 2-butanone (Mallinckrodt) were commercial samples and used without further purification. 3,3-Diphenylpropiophenone was prepared by the procedure of Vörlander and Friedberg.[19]

Preparation of 2,2-Dimethylpropiophenone. In a 1-l. four-necked flask equipped with an additional funnel, mechanical stirrer, reflux condenser, and a section of Gooch tubing for solid introduction were placed 60 ml of dry ether and 36 ml of an ethereal solution of phenylmagnesium bromide (Arapaho, 0.1082 mol). The flask was cooled to 0° and anhydrous cadmium chloride (10.35 g, 0.0565 mol) was slowly added via the Gooch tubing to the stirred solution. The mixture was allowed to warm to room temperature and refluxed for 20 min. The major portion of the ether was removed by distillation and 120 ml of dry benzene was added. Distillation was continued until the distillate was ether free, as analyzed by gas chromatography. The flask and its contents were then cooled to 10°, 2,2-dimethylpropanoyl chloride (10.0 g, 0.0833 mol, Aldrich) in 30 ml of dry benzene was slowly added, and the resulting mixture was stirred for 4 hr. The reaction mixture was hydrolyzed at 5–7° by addition of 140 ml of 20% sulfuric acid. The organic phase was separated, washed twice with a saturated solution of sodium bicarbonate and repeatedly with water, and dried over anhydrous magnesium sulfate. The solution was filtered and the benzene distilled. Distillation at 91–93° (6.5 mm) [lit.[20] bp 103–104° (13 mm)] afforded 11 g (82%) of product.

Preparation of Ketazines. All ketazines were prepared by the method of Cohen et al.[3b] Acetophenone azine,[21] 4-bromoacetophenone azine,[22] 4-methylacetophenone azine,[23] methyl 2-naphthyl ketazine,[24] 2-butanone azine,[3h] 2,2-dimethylpropiophenone azine,[10d] and butyrophenone azine[2j] have been previously described.

Preparation of 3,3-Diphenylpropiophenone Azine. 3,3-Diphenylpropiophenone (30 g, 0.105 mol) and 95% hydrazine (1.71 g, 0.0525 mol) were refluxed for 6 hr in absolute ethanol (50 ml) containing 10 drops of glacial acetic acid. The reaction mixture was cooled to room temperature and filtered. The crude azine was recrystallized twice from a 9:1 mixture of absolute ethanol and benzene: 26.8 g (90%); mp 137.5–138°; mass spectrum, M$^+$ m/e 568.288 (calcd for $C_{42}H_{36}N_2$, 568.288); NMR ($CDCl_3$) δ 3.33 (d, 4 H), 4.34 (t, 2 H), 6.92–7.38 (m, 30 H).

Preparation of 2,2-Dimethylpropiophenone Methylhydrazone. 2,2-Dimethylpropiophenone (10 g, 0.0617 mol) and methylhydrazine (3.5 g, 0.0761 mol) were refluxed for 5 days in absolute ethanol (30 ml) containing 5 drops of glacial acetic acid. The crude product, obtained upon removal of the ethanol at reduced pressure, was taken up in ether, washed with a saturated solution of sodium bicarbonate and with water, dried over anhydrous magnesium sulfate, and filtered. Removal of the ether at reduced pressure and recrystallization of the crude product from hexanes yielded 7.0 g (60%) of product: mp 54.5–55°; mass spectrum, M$^+$ m/e 190.147 (calcd for $C_{12}H_{18}N_2$, 190.147); NMR ($CDCl_3$) δ 1.14 (s, 9 H), 2.76 (s, 3 H), 4.25 (broad, 1 H), 7.05 and 7.36 (m, total 5 H).

General Procedure for the Addition of Chlorine to Ketazine. The method was essentially the one described by Moon.[18] A 5% solution of the ketazine in methylene chloride was cooled to −70° in a Dry Ice–acetone bath. Liquid chlorine (2 mol/mol ketazine) at −70° was rapidly added in the dark to the stirred solution. The mixture was stirred at −70° for 2 hr and then at −40° for an additional 1 hr. The excess chlorine and the methylene chloride were removed at reduced pressure. The crude chloroazo compounds were purified when possible by recrystallization from acetone, hexanes, or a binary acetone–hexanes solvent.

The preparation of 1,1′-dichloro-1,1′-diphenylazoethane,[10a] 1,1′-dichloro-1,1′-bis(4-bromophenyl)azoethane,[10b] 1,1′-dichloro-1,1′-bis(4-methylphenyl)azoethane,[10b] 1,1′-dichloro-1,1′-di(2-naphthyl)azoethane,[10d] 1,1′-dichloro-2,2′-azobutane,[10c] and 1,1′-dichloro-2,2,2′,2′-tetramethyl-1,1′-diphenylazopropane[10d] have been reported previously. The following new 1,1′-dichloroazoalkanes were prepared.

1,1′-Dichloro-1,1′-diphenylazobutane. Butyrophenone azine was quantitatively converted to this azo compound by the above procedure. The crude product was recrystallized from hexanes: mp 85.5–86.0° dec; NMR ($CDCl_3$) δ 0.81 (t, 6 H), 1.29 (m, 4 H), 2.47 (m, 4 H), 7.37 and 7.65 (m, total 10 H).

1,1′-Dichloro-1,1′,3,3,3′,3′-hexaphenylazopropane. Addition of liquid chlorine to 3,3-diphenylpropiophenone azine by the general procedure afforded a quantitative yield. Recrystallization from hexanes yielded material melting with decomposition at 227–228°; NMR ($CDCl_3$) δ 3.26 (m, 4 H), 4.07 (t, 2 H), 6.80–7.36 (m, 30 H).

(2,2-Dimethyl-1-chloro-1-phenylpropyl)azomethane. Addition of liquid chlorine to 2,2-dimethylpropiophenone methylhydrazone by the general procedure yielded an unstable, yellow, viscous oil. The NMR spectrum of the product in $CDCl_3$ changed rapidly with time. Short exposure to the atmosphere resulted in the rapid evolution of gas. Owing to instability of this product no quantitative data were obtained.

General Procedure for the $LiAlH_4$ Reduction of the 1,1′-Dichloroazoalkanes. Each of the 1,1′-dichloroazoalkanes was reduced with excess lithium aluminum hydride to the corresponding secondary azoalkanes (Table I). The reflux time varied with the compound; completion of the reaction was taken as the disappearance of the green color in the reaction mixture. The preparation of 2,2′-azobutane illustrates the general procedure.

In a 500-ml three-necked flask equipped with an addition funnel, condenser, and mechanical stirrer were placed 2.5 g (0.066 mol) of lithium aluminum hydride and 50 ml of dry ether. The stirred solution was cooled to 0° and 11 g (0.052 mol) of 1,1′-dichloro-2,2′-azobutane in 200 ml of dry ether was added in ca. 15 min. The mixture was allowed to warm to room temperature and then refluxed for 19 hr. The aqueous and organic phases obtained upon hydrolysis of the ice-cooled mixture by the slow addition of a saturated solution of sodium potassium tartrate (100 ml) with vigorous stirring were separated. The former phase was removed and extracted three times with ether, and the ether extracts were combined with the latter phase. The ethereal solution was washed twice with water, dried over anhydrous magnesium sulfate, filtered, and freed of ether under reduced pressure. Distillation of the crude yellow oil yielded 4.8 g (63%) of **8**, bp 48.5–49.0° (25 mm) [lit.[3h] bp 49–52° (27 mm)].

1,1′-Bis(4-bromophenyl)azoethane (5). Using a reflux time of 19 hr, **5** was prepared by the general procedure. A 41% yield was obtained after recrystallization from methanol: mp 107.5–108°; NMR ($CDCl_3$) δ 1.46 (d, 6 H), 4.52 (q, 2 H), 7.22 (d, 4 H), 7.44 (d, 4 H).

1,1′-Di(2-naphthyl)azoethane (7). Using a reflux time of 20 hr, **7** was prepared by the general procedure. A 58% yield was obtained after recrystallization from a 3:1 mixture of methanol and acetone: mp 144–144.5°; NMR ($CDCl_3$) δ 1.60 (d, 6 H), 4.83 (q, 2 H), 7.48 (m, 6 H), 7.80 (m, 8 H).

1,1′,3,3,3′,3′-Hexaphenylazopropane (10). Using a reflux time of 18 hr, **10** was prepared by the general procedure. A 60% yield was obtained after recrystallization from methanol: mp 146.5–147.5° dec; NMR ($CDCl_3$) δ 2.78 (m, 4 H), 3.53 (m, 2 H), 4.42 (m, 2 H), 6.82–7.50 (m, 30 H).

1,1′-Diphenyl-2,2,2′,2′-tetramethylazopropane (11). Using a reflux time of 4 hr, **11** was prepared by the general procedure. A 61% yield was obtained after recrystallization from methanol: mp 155.5–156.5°; NMR ($CDCl_3$) δ 1.00 (s, 18 H), 4.17 (s, 2 H), 7.11 (s, 10 H).

1,1′-Diphenyl-2,2,2′,2′-tetramethylazopropane-*1,1′-d*$_2$ (12). Using lithium aluminum deuteride instead of lithium aluminum hydride in the general procedure, **12** was prepared with a reflux time of 4 hr. A 63% yield was obtained upon recrystallization from methanol: mp 156–156.5°; NMR ($CDCl_3$) δ 1.00 (s, 18 H), 7.11 (s, 10 H).

(2,2′-Dimethyl-1-phenylpropyl)azomethane (17). Using the procedure for the reduction of 1,1′-dichloroazoalkanes, **17** was prepared with a reflux time of 15 hr. Crude **17** was purified by column chromatography (column dimensions, 4.7 × 60 cm) using Baker AR grade silica gel as the substrate and a 2:1 mixture of benzene and hexanes as the eluting solvent followed by distillation: yield 56%; bp 52–54° (0.7 mm); NMR ($CDCl_3$) δ 0.94 (s, 9 H), 3.70 (s, 3 H), 4.10 (s, 1 H), 7.29 (m, 5 H).

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.75. Found: C, 75.76; H, 9.56; N, 14.38.

(2,2-Dimethyl-1-phenylpropyl-*1-d*)azomethane (18). Using lithium aluminum deuteride, **18** was prepared and purified by the procedure described for **17**: yield 60%; bp 50–51° (0.6 mm): NMR ($CDCl_3$) δ 0.94 (s, 9 H), 3.70 (s, 3 H), 7.29 (m, 5 H).

Purification Procedure for Secondary Azo Compounds. Azo compounds and silver nitrate (mole ratio 1:1) were added to a ternary solution of ether, acetone, and water. The resulting solution was stirred in the dark for 24 hr. The ether and acetone were removed under reduced pressure and the azo compound was taken up in ether. The ether solution was washed twice with a saturated solution of sodium carbonate and then with water, dried over anhydrous magnesium sulfate, filtered, and freed of ether at reduced pressure. The crude product was purified by column chromatography (column dimensions, 4.7 × 60 cm) using silica gel as the substrate and either benzene, hexanes, or a binary mixture of benzene–hexanes as an eluting solvent, followed by distillation or recrystallization.

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Registry No.—**1**, 55043-54-4; **2**, 55043-55-5; **3**, 5661-68-7; **4**, 55043-56-6; **5**, 55043-57-7; **6**, 32234-13-2; **7**, 55043-58-8; **8**, 3742-58-3; **9**, 35115-95-8; **10**, 55043-59-9; **11**, 55043-60-2; **12**, 55043-61-3; **13**, 55043-62-4; **14**, 21399-36-0; **15**, 55043-63-5; **16**, 19727-23-2; **17**, 55043-64-6; **18**, 55043-65-7; acetophenone azine, 729-43-1; 4-methylacetophenone azine, 21399-33-7; methyl 2-naphthyl ketazine, 55043-66-8; 2-butanone azine, 5921-54-0; butyrophenone azine, 17745-98-1; 2,2-dimethylpropiophenone azine, 55043-67-9; 3,3-diphenylpropiophenone, 606-86-0; 2,2-dimethylpropiophenone, 938-16-9; phenyl bromide, 108-86-1; hydrazine, 302-01-2; methylhydrazine, 60-34-4; 1,1′-dichloro-1,1′-diphenylazobutane, 55043-68-0; 1,1′-dichloro-1,1′,3,3,3′,3′-hexaphenylazopropane, 55043-69-1; (2,2-dimethyl-1-chloro-1-phenylpropyl)azomethane, 55043-70-4; 1,1′-dichloro-2,2′-azobutane, 52406-48-1.

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Intramolecular 1,3-Dipolar Cycloadditions of Aryl Azides Bearing Alkenyl, Alkynyl, and Nitrile Groups

Raffaello Fusco,* Luisa Garanti, and Gaetano Zecchi

Istituto di Chimica Industriale dell'Universitá, Centro del C.N.R. per la Sintesi e Stereochimica di Speciali Sistemi Organici, 20133 Milano, Italy

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Azido compounds **1** containing dipolarophile groups, such as C=C, C≡C, and C≡N bonds, were synthesized from the corresponding anilines and thermally decomposed in aromatic hydrocarbon solvents. Bridgehead nitrogen aziridines **3** were obtained from **1a–c**, probably through an intramolecular cycloaddition leading to unstable Δ^2-1,2,3-triazolines. From **1d–g**, the corresponding 1,3-cycloaddition products, namely the fused-ring triazoles **7** and tetrazoles **8**, were isolated in good yields.

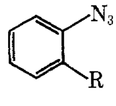
1,3-Dipoles bearing an additional function able to behave as a dipolarophile appear to be very interesting substrates. In fact, the intramolecular cycloaddition of a properly functionalized 1,3-dipole represents a general scheme for the synthesis of fused ring heterocycles. Nevertheless, in spite of the copious literature on 1,3-dipolar cycloadditions, intramolecular examples have as yet received little attention.

With azides, intramolecular cycloadditions have been occasionally reported,[1,2] but systematic data are available only for a series of azidoalkenes.[3] Also, a mechanism involving an intramolecular 1,3-dipolar cycloaddition to the carbonyl function is possibly operating in the formation of 3-arylanthranils from 2-azidobenzophenones, as proposed on the basis of a kinetic investigation.[4].

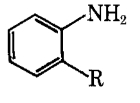
The present paper describes the results which we obtained from a series of structurally related aryl azides bearing different dipolarophile groups.

Results and Discussion

Azido compounds **1** were synthesized from the corresponding anilines **2** by diazotization and treatment of the intermediate diazonium salts with sodium azide.



1a, R = $OCH_2CH{=}CH_2$
b, R = $OCH_2C(Me){=}CH_2$
c, R = $OCH_2CH{=}CHPh$
d, R = $OCH_2C{\equiv}CH$



2e, R = $OCH_2C{\equiv}CPh$
f, R = OCH_2CN
g, R = CH_2CH_2CN

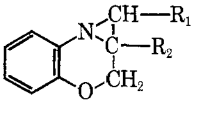
Reaction yields as well as physical and spectral data are collected in Table I.

All the compounds studied were decomposed by refluxing in aromatic hydrocarbon solvents. Temperatures were chosen on the basis of the different substrate reactivities. Each run was continued until all the starting material was consumed as indicated by thin layer chromatographic analyses of the reaction mixture.

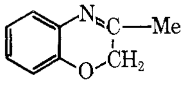
Experimental conditions and reaction products, which are summarized in Table II, will now be considered and discussed for the different kinds of substrates.

Aryl Azides Bearing an Alkenyl Substituent. The decomposition of azides **1a**, **1b**, and **1c** was performed in boiling benzene, the reaction time being respectively 6, 11, and 16 hr. In the case of **1a**, the crude product was a mixture of two components, which were isolated by column chromatography and identified as 1,1a-dihydro-2*H*-azirino[2,1-c][1,4]benzoxazine (**3a**) and 3-methyl-2*H*-1,4-benzoxazine (**4**).[5] However, the reactions of **1b** and **1c** gave essentially only the aziridines **3b** and **3c**, respectively.

Structures **3a–c** were assigned on the basis of elemental analyses, NMR spectra, and chemical behavior. The chemical shifts found for the protons of the aziridine ring in these



3a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = Me$
c, $R_1 = Ph$; $R_2 = H$



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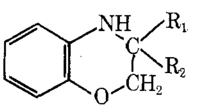

5a, $R_1 = H$; $R_2 = Me$
b, $R_1 = R_2 = Me$
c, $R_1 = H$; $R_2 = CH_2Ph$