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CHEMISTRY OF DIANIONS
I. FORMATION OF ANIONIC SPECIES DERIVED FROM AZO COMPOUNDS AND THEIR REACTIONS WITH TRIORGANOCHLOROSILANES

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The addition of alkali metals to electron-accepting unsaturated compounds to form reactive metal adducts has been known since 1914[1]. Schlenk and Bergmann[2] report on the addition of sodium to azobenzene in diethyl ether to form an unidentified precipitate. Later Wittig had prepared the disodium adduct of 1,10-dimethyldibenzopyridazine[3] and the disodium and dilithium adducts of dibenzopyridazine[4] in diethyl ether. The dilithium adduct of azobenzene, however, was prepared by a metal hydrogen exchange reaction employing hydrazobenzene and methyllithium[5]. In a systematic study of the addition of alkali metals, lithium, sodium and potassium to azobenzene, Reesor and Wright[6] have shown that nearly quantitative yields of the dimetal adducts can be obtained by shaking excess of the alkali metal with azobenzene in 1,2-dimethoxyethane. Subsequent workers[7,8,9] have shown that these metal adducts can be conveniently prepared in tetrahydrofuran.

We have now examined the addition of lithium to several substances containing the nitrogen–nitrogen double bond. Thus, 3,3′-dimethylazobenzene, 3,3′-dimethoxyazobenzene, 4-methylazobenzene, 4-methoxyazobenzene, 4,4′-dimethylazobenzene, 4,4′-dimethoxyazobenzene, 4,4′-diisopropylazobenzene, 4,4′-di-tert-butylazobenzene, 4,4′-diphenylazobenzene and dibenzopyridazine were treated with excess of lithium in tetrahydrofuran. In each case the monometal adduct (anion radical)** was formed initially which was converted to the dimetal adduct on prolonged shaking (within about six to eight hours). In contrast to the deep green or red colours of the monometal adducts, the dianions were generally yellow. The dilithium adduct of 4,4′-diphenylazobenzene, however, was blue-violet and that of dibenzopyridazine, red brown in tetrahydrofuran. The colour of these dimetal adducts varied considerably with the alkali metals and of the solvents[13]. The dilithium adduct of azobenzene, for example, has been reported to be practically colourless in diethyl ether[5], whereas, the same adduct is light yellow in tetrahydrofuran[6,8,9]. Similarly, the dilithium adduct of dibenzopyridazine is red brown in tetrahydrofuran, blue-green in dioxane and grey-blue in diethyl ether[13]. These differences in colour could be attributed to the differing degree of solvation of these adducts in various solvents[6]. (For evidence of solvation of the alkene–dimetal adducts, see refs. 14 and 15.)

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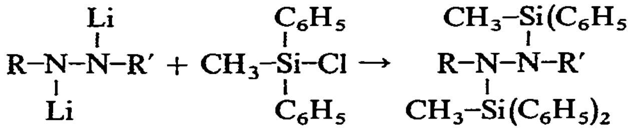
** For ESR studies of anion radicals derived from azo compounds, see refs. 10–12.

Dianions derived from aryl-substituted olefins are powerful nucleophiles. Thus, the dilithium adduct of stilbene readily reacts with alkyl halides to give tri- and tetrasubstituted ethanes[16]. These dianions could also react as strong bases in removing protons from any weaker bases present including solvent or they may transfer their extra electrons to an acceptor, returning to starting material and metal cations. Similarly, the dianions derived from azobenzene have been found to react with alkyl halides or dimethyl sulfate giving disubstituted hydrazobenzenes; however, these dianions were somewhat less reactive than the carbon dianions[6]. In previous studies we have observed that the dimetal adducts of azobenzene are capable of bringing about nucleophilic displacements on silicon[7,8,9]. Thus, the reaction of azobenzene–dilithium adduct with chlorotriphenylsilane gave a mixture of N,N'-diphenyl-N-(triphenylsilyl)hydrazine and N,N'-diphenyl-N,N'-bis(triphenylsilyl)-hydrazine[7]. Similar reactions of the same dimetal adduct with other chlorosilanes, on the other hand, gave chiefly disilyl-substituted hydrazobenzenes[9].

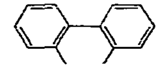
We have also examined the reactions of several dianions derived from various azo compounds with chlorodiphenylmethylsilane, with a view to evolving a general procedure for the preparation of disilyl-substituted hydrazobenzenes. (For an alternative procedure for preparing disilylhydrazines, see ref. 17.) Thus, the dilithium adducts of 3,3'-dimethylazobenzene, 3,3'-dimethoxyazobenzene, 4-methylazobenzene, 4-methoxyazobenzene, 4,4'-dimethylazobenzene, 4,4'-dimethoxyazobenzene, 4,4'-diisopropylazobenzene, 4,4'-di-tert-butylazobenzene, 4,4'-diphenylazobenzene and dibenzopyridazine were treated with chlorodiphenylmethylsilane. These dianions reacted in an expected manner giving rise to diaryl-disilyl-substituted hydrazines (IV–XIII) in good yields.



$$\text{R}-\underset{\text{Li}}{\text{N}}-\overset{\text{Li}}{\text{N}}-\text{R}' + \text{CH}_3-\underset{\text{C}_6\text{H}_5}{\overset{\text{C}_6\text{H}_5}{\text{Si}}}-\text{Cl} \longrightarrow \text{R}-\underset{\text{CH}_3-\text{Si}(\text{C}_6\text{H}_5)_2}{\text{N}}-\overset{\text{CH}_3-\text{Si}(\text{C}_6\text{H}_5)_2}{\text{N}}-\text{R}'$$

(III), R = R' = C_6H_5–; (IV), R = R' = m-$CH_3C_6H_4$–; (V), R = R' = m-$CH_3OC_6H_4$–; (VI), R = p-$CH_3C_6H_4$–, R' = C_6H_5–; (IX), R = R' = p-$CH_3OC_6H_4$–; (X), R = R' = p-$(CH_3)_2CHC_6H_4$–; (XI), R = R' = p-$(CH_3)_3CC_6H_4$–; (XII), R = R' = p-$C_6H_5C_6H_4$–;

(XIII), R,R' =



The ultraviolet spectrum of hydrazobenzene shows two absorption maxima in ethanol, one at 245 mμ(log ε 4.31) and the other at 291 mμ (log ε 3.60)[18,19]. We have examined the ultraviolet spectra of several disilyl-substituted hydrazines in tetrahydrofuran (Table 1) and find that the spectra of these compounds resemble closely that of hydrazobenzene.

EXPERIMENTAL

All melting points are uncorrected. In general, reactions were carried out under an atmosphere of dry, oxygen-free[20] nitrogen. Tetrahydrofuran boiling at 65–66° was freed from peroxides and moisture before use by refluxing over sodium followed by distillation over lithium aluminum hydride. Silicon analyses were carried

TABLE 1

ULTRAVIOLET SPECTRA OF DISILYLHYDRAZINES IN TETRAHYDROFURAN

Compound	λ_{max}*(log* ε*)*	*Compound*	λ_{max}*(log* ε*)*
(III)	254 (4.39), 291 (3.71)	(VIII)	253 (4.36), 296 (3.80)
(IV)	252 (4.36), 292 (3.79)	(IX)	253 (4.50), 315 (3.81)
(V)	250 (4.37), 292 (3.82)	(X)	252 (4.39), 292 (3.86)
(VI)	250 (4.38), 292 (3.84)	(XI)	254 (4.43), 291 (3.70)
(VII)	247 (4.38), 295 (3.81)	(XIII)	254 (4.72), 302 (3.46), 344 (3.52)

out using a previously reported procedure[21]. Ultraviolet spectra were determined using a Cary 14 spectrometer. Molecular weights were determined in a Vapour Pressure Osmometer (Mechrolab, Inc.) using benzene as solvent.

Azo compounds

3,3'-Dimethylazobenzene, m.p. 53–54° (yield 62%), was prepared by the reduction of *m*-nitrotoluene to 3,3'-dimethylhydrazobenzene using zinc dust and sodium hydroxide, followed by air-oxidation of the hydrazo compound[14]. UV spectrum (in ethanol): λ_{max} in mμ (log ε): 330 (4.2) and 446 (2.8).

3,3'-Dimethoxyazobenzene, m.p. 78–79° (yield 55%) was prepared from *m*-nitroanisole, employing a standard procedure[22]. UV spectrum (in ethanol): λ_{max} in mμ (log ε): 320 (4.2) and 430 (3.5).

4-Methylazobenzene, m.p. 70–71° (yield 72%) was prepared by treatment of *p*-toluidine with nitrosobenzene in glacial acetic acid[23]. UV spectrum (in ethanol): λ_{max}in mμ (log ε): 330 (4.2) and 445 (2.9).

Treatment of *p*-anisidine with nitrosobenzene in glacial acetic acid gave *p*-methoxyazobenzene, m.p. 64–65° (yield 66%)[24]. UV spectrum (in ethanol): λ_{max} in mμ (log ε): 340 (4.39) and 444 (2.80).

Reduction of *p*-nitrotoluene using sodium stannite[25] gave 4,4'-dimethylazobenzene, m.p. 144–146° in 85% yield. UV spectrum (in ethanol): λ_{max} in mμ (log ε): 335 (4.3) and 445 (3.1).

4,4'-Dimethoxyazobenzene, m.p. 160–161° was obtained in 54% yield by the oxidation of *p*-anisidine using active manganese dioxide[26]. UV spectrum (in ethanol): λ_{max} in mμ (log ε): 355 (4.2) and 430 (3.4).

4,4'-Diisopropylazobenzene[27], m.p. 106–107° (yield 50%), was prepared from 4-nitrocumene by a standard procedure[22]. UV spectrum (in ethanol): λ_{max} in mμ (log ε): 336 (4.5) and 435 (2.94).

Lithium aluminum hydride reduction of 4,4'-di-tert-butylazoxybenzene (kindly supplied by Dr. C. Rüchardt, Universität München) in tetrahydrofuran gave a 75% yield of 4,4'-di-tert-butylazobenzene, m.p. 182–183° (lit.[28] m.p. 184°). UV spectrum (in ethanol): λ_{max} in mμ (log ε): 335 (4.53) and 436 (2.94).

4,4'-Diphenylazobenzene[29], m.p. 254–256° (yield 70%) was prepared from *p*-nitrobiphenyl by a standard procedure[22]. The ultraviolet absorption spectrum of this material in tetrahydrofuran was characterized by the following absorption maxima in mμ (log ε): 368 (4.6) and 446 (3.2).

Dibenzopyridazine[30], m.p. 152–153° was prepared (yield 88%) by the reduction of 2,2'-dinitrobiphenyl using lithium aluminum hydride in tetrahydrofuran. The

UV spectrum of this compound showed the following absorption maxima in mμ (log ε): 356 (3.0) and 368 (3.0), in agreement with the earlier reported[31] values of 355 (3.2) and 370 (3.2) in ethanol.

Preparation of the dianions

The preferred procedure for preparation of the dianions has been to shake the requisite amount of the azo compound with excess of lithium in tetrahydrofuran inside a modified Schlenk tube[16] filled with nitrogen. Few clean, broken glass pieces were added to ensure effective cleaning of the metal surface during shaking. Formation of the dianion was nearly complete within 6–8 h of shaking in each case, as was indicated by the change of the initial dark green colour due to anion-radicals to a deep yellow or orange yellow colour. In the case of 4,4′-diphenylazobenzene, the initial colour was red which changed to blue-violet when the dianion formation was completed. Similarly the dilithium adduct of dibenzopyridazine was red-brown in tetrahydrofuran.

Preparation of the bis(diphenylmethylsilyl)-substituted hydrazines

N,N′-Di-m-tolyl-N,N′-bis(diphenylmethylsilyl)hydrazine (IV). A solution of N,N′-dilithium-3,3′-dimethylhydrazobenzene was prepared by shaking 2.1 g (0.01 mole) of 3,3′-dimethylazobenzene with 0.63 g (0.04 g-atom) of lithium in 15 ml of tetrahydrofuran, for 6 h. The dilithium adduct was added, dropwise, to a solution of 4.65 g (0.02 mole) of chlorodiphenylmethylsilane in 10 ml of tetrahydrofuran, over a period of 30 min, with stirring. Removal of the solvent under vacuum gave a residue which was extracted with hot benzene. The benzene-insoluble portion was identified as lithium chloride. Removal of the solvent from the benzene extract and treatment of the residue with methanol gave 4.9 g (81 %) of impure N,N′-di-*m*-tolyl-N,N′-bis(diphenylmethylsilyl)hydrazine (IV), m.p. 168–172°. Two crystallizations from a mixture of benzene and petroleum ether (b.p. 60–70°) gave a product which melted at 174–175°. (Found: C, 79.40; H, 6.80; N, 4.51; Si, 9.55; mol. wt., 596. $C_{40}H_{40}N_2Si_2$ calcd.: C, 79.47; H, 6.62; N, 4.64; Si, 9.27 %; mol. wt., 604.)

N,N′-Di-m-anisyl-N,N′-bis(diphenylmethylsilyl)hydrazine (V). To a solution of 4.65 g (0.02 mole) of chlorodiphenylmethylsilane in 10 ml of tetrahydrofuran was added 0.01 mole of N,N′-dilithium-3,3′-dimethoxyhydrazobenzene [prepared from 2.42 g (0.01 mole) of 3,3′-dimethoxyazobenzene and 0.28 g (0.04 g-atom) of lithium] in 15 ml of tetrahydrofuran over 30 min. Removal of the solvent and work-up as in the previous case gave 4.6 g (72 %) of N,N′-di-*m*-anisyl-N,N′-bis(diphenylmethylsilyl)hydrazine (V), m.p. 142–43°. Repeated crystallizations from cyclohexane gave a pure product, m.p. 156–57°. (Found: C, 75.48; H, 6.50; N, 4.40; Si, 8.94; mol. wt., 647. $C_{40}H_{40}N_2O_2Si_2$ calcd.: C, 75.44; H, 6.29; N, 4.40; Si, 8.81 %; mol. wt., 636.)

N-Phenyl-N′-p-tolyl-N,N′-bis(diphenylmethylsilyl)hydrazine (VI). A solution of 0.007 mole of N,N′-dilithium-4-methylhydrazonbenzene, prepared from 1.4 g (0.007 mole) of 4-methylazobenzene, 0.2 g (0.03 g-atom) of lithium and 15 ml of tetrahydrofuran was added to 3.3 g (0.014 mole) of chlorodiphenylmethylsilane in 5 ml of tetrahydrofuran. Removal of the solvent under vacuum, extraction of the residue with hot benzene and subsequent work-up gave 2.6 g (60 %) of N-phenyl-N′-*p*-tolyl-N,N′-bis(diphenylmethylsilyl)hydrazine (VI), m.p. 142–145°. Several recrystallizations from cyclohexane gave a pure product, m.p. 151–152°. (Found: C, 79.69; H, 6.8; N, 5.14; Si, 9.22; mol.wt., 584. $C_{39}H_{38}N_2Si_2$ calcd.: C, 79.32; H, 6.44; N, 4.75; Si, 9.49%; mol.wt., 590.)

N-Phenyl-N'-p-anisyl-N,N'-bis(diphenylmethylsilyl)hydrazine (VII). A solution of 0.01 mole of N,N'-dilithium-4-methoxyhydrazobenzene in 15 ml of tetrahydrofuran was added to 4.65 g (0.02 mole) of chlorodiphenylmethylsilane in 10 ml of tetrahydrofuran. Work-up in the usual manner gave 4.5 g (75%) of N-phenyl-N'-*p*-anisyl-N,N'-bis(diphenylmethylsilyl)hydrazine (VII), m.p. 120–123°. Several crystallizations from a mixture of benzene and petroleum ether (b.p. 60–80°) gave a product, m.p. 125–126°. (Found: C, 77.13; H, 6.6; N, 4.9; Si, 9.48; mol.wt., 613. $C_{39}H_{38}N_2OSi_2$ calcd.: C, 77.23; H, 6.27; N, 4.62; Si, 9.24%; mol.wt., 606.)

N,N'-Di-p-tolyl-N,N'-bis(diphenylmethylsilyl)hydrazine (VIII). To a stirred solution of 4.65 g (0.02 mole) of chlorodiphenylmethylsilane in 10 ml of tetrahydrofuran was added 0.01 mole of N,N'-dilithium-4,4'-dimethylhydrazobenzene [prepared from 2.1 g (0.01 mole) of 4,4'-dimethylazobenzene, 0.28 g (0.04 g-atom) of lithium and 15 ml of tetrahydrofuran]. Work-up as in the previous cases gave 4.8 g (72%) of N,N'-di-*p*-tolyl-N,N'-bis(diphenylmethylsilyl)hydrazine (VIII), m.p. 156–159°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–80°) raised the melting point to 160–162°. (Found: C, 79.58; H, 6.94; N, 4.85; Si, 9.48; mol.wt., 582. $C_{40}H_{40}N_2Si_2$ calcd.: C, 79.47; H, 6.62; N, 4.65; Si, 9.27%; mol.wt., 604.)

N,N'-Di-p-anisyl-N,N'-bis(diphenylmethylsilyl)hydrazine (IX). A solution of 0.05 mole of N,N'-dilithium-4,4'-dimethoxyhydrazobenzene was prepared by treatment of 1.2 g (0.005 mole) of 4,4'-dimethoxyazobenzene and 0.14 g (0.02 g-atom) of lithium, in 10 ml of tetrahydrofuran. The dilithium adduct was added slowly to a solution of 2.32 g (0.01 mole) of chlorodiphenylmethylsilane in 15 ml of tetrahydrofuran. Removal of the solvent under vacuum and work-up in the usual manner gave 1.9 g (60%) of N,N'-di-*p*-anisyl-N,N'-bis(diphenylsilyl)hydrazine (IX), m.p. 145–150°. A pure product, m.p. 157–158° was obtained by recrystallization from benzene/petroleum ether (b.p. 60–80°) mixture. (Found: C, 75.62; H, 6.33; N, 4.73; Si, 8.63; mol.wt., 616. $C_{40}H_{40}N_2O_2Si_2$ calcd.: C, 75.44; H, 6.29; N, 4.40; Si, 8.81%; mol.wt., 636.)

N,N'-Bis(4-isopropylphenyl)-N,N'-bis(diphenylmethylsilyl)hydrazine (X). A solution of N,N'-dilithium-4,4'-diisopropylhydrazobenzene was prepared by shaking 2.65 g (0.01 mole) of 4,4'-diisopropylazobenzene with 0.28 g (0.04 g-atom) of lithium in 15 ml of tetrahydrofuran. This dilithium adduct was added to a tetrahydrofuran solution (10 ml) of chlorodiphenylmethylsilane (0.02 mole). The solvent was removed under vacuum and the residue was extracted with hot benzene to remove the lithium chloride. Removal of the solvent from the benzene extract gave a viscous mass which was treated with methanol to give 4.0 g (60%) of N,N'-bis(4-isopropylphenyl)-N,N'-bis(diphenylmethylsilyl)hydrazine (X), m.p. 128–132°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–80°) raised the melting point to 135–136°. (Found: C, 80.20; H, 7.60; N, 4.40, Si, 8.76; mol.wt., 673. $C_{44}H_{48}N_2Si_2$, calcd.: C, 80.00; H, 7.27; N, 4.24; Si, 8.49%; mol.wt., 660.)

N,N'-Bis(4-tert-butylphenyl)-N,N'-bis(diphenylmethylsilyl)hydrazine (XI). To a solution of 1.6 g (0.007 mole) of chlorodiphenylmethylsilane in 5 ml of tetrahydrofuran was added 0.0035 mole of N,N'-dilithium-4,4'-di-tert-butylhydrazobenzene [prepared from 1.1 g (0.0035 mole) of 4,4'-di-tert-butylazobenzene and 0.1 g (0.14

g-atom) of lithium in 10 ml of tetrahydrofuran]. Work-up of the reaction mixture as in the previous cases gave 1.5 g (63%) of N,N'-bis(4-tert-butylphenyl)-N,N'-bis-(diphenylmethylsilyl)hydrazine (XI), m.p. 182–190°. Recrystallization from a mixture of cyclohexane and petroleum ether (b.p. 60–80°) gave a pure product, m.p. 194–5°. (Found: C, 80.65; H, 7.9; N, 4.08; Si, 8.61; mol.wt., 682. $C_{46}H_{52}N_2Si_2$ calcd.: C, 80.24; H, 7.56; N, 4.07; Si, 8.12%; mol.wt., 688.)

N,N'-Di-4-biphenylyl-N,N'-bis(diphenylmethylsilyl)hydrazine (XII). A solution of 0.005 mole of N,N'-dilithium-4,4'-diphenylhydrazobenzene in 10 ml of tetrahydrofuran was prepared by shaking 1.7 g (0.005 mole) of 4,4'-diphenylazobenzene with 0.14 g (0.02 g-atom) of lithium in 10 ml of tetrahydrofuran for 6 h. Initially the colour of the solution changed from orange yellow to red due to the formation of the anion-radical. On further shaking, the solution became blue and remained as such. Treatment of 0.005 mole of this dilithium adduct with 2.32 g (0.01 mole) of chlorodiphenylmethylsilane in 15 ml of tetrahydrofuran and work-up as in the previous cases gave 1.9 g (52%) of N,N'-di-4-biphenylyl-N,N'-bis(diphenylmethylsilyl)hydrazine (XII), m.p. 208–212°. Crystallization from a mixture of benzene and cyclohexane gave a pure product, m.p. 214–215°. (Found: C, 82.58; H, 6.01; N, 3.94; Si, 7.67; mol.wt., 716. $C_{50}H_{44}N_2Si_2$ calcd.: C, 82.42; H, 6.04; N, 3.85; Si, 7.70%; mol.wt., 728.)

N,N'-Bis(diphenylmethylsilyl)dihydrodibenzopyridazine (XIII). A solution of the dilithium adduct of dibenzopyridazine was prepared by treating 1.8 g (0.01 mole) of dibenzopyridazine with 0.28 g (0.04 g-atom) of lithium in 15 ml of tetrahydrofuran. The solution became deep green at first, due to the formation of the anion-free radical and later it turned red. Treatment of 0.01 mole of this dilithium adduct with 4.65 g (0.02 mole) of chlorodiphenylmethylsilane in 10 ml of tetrahydrofuran and work-up of the mixture as in the previous cases gave 4.3 g (76%) of N,N'-bis(diphenylmethylsilyl)dihydrodibenzopyridazine (XIII), m.p. 111–116°. Crystallization from petroleum ether (b.p. 60–80°) raised the melting point to 117–118°. (Found: C, 79.20; H, 6.20; N, 5.08; Si, 9.62; mol.wt., 582. $C_{38}H_{34}N_2Si_2$ calcd.: C, 79.44; H, 5.92; N, 4.88; Si, 9.76%; mol.wt., 574.)

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SUMMARY

Dianions derived from 3,3'-dimethylazobenzene, 3,3'-dimethoxyazobenzene, 4-methylazobenzene, 4-methoxyazobenzene, 4,4'-dimethylazobenzene, 4,4'-dimethoxyazobenzene, 4,4'-diisopropylazobenzene, 4,4'-di-tert-butylazobenzene, 4,4'-diphenylazobenzene and dibenzopyridazine were prepared by treatment with excess of lithium in tetrahydrofuran. Reaction of these dianions with chlorodiphenylmethylsilane gave disilylsubstituted hydrazines. The ultraviolet spectra of these silylhydrazines resemble that of hydrazobenzene.

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