546. *Compounds of Silicon. Part I. Silicon Derivatives of β-Amino-αγ-diphenylcrotononitrile.*

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Spectroscopic evidence shows that the crystalline dimer of benzyl cyanide is β-amino-αγ-diphenylcrotononitrile and not the tautomeric ketimine, and that the former is also the predominant tautomer in solution. From these data and further physical and chemical evidence, it appears that in the organosilicon compounds, derived by condensing trialkylhalogenosilanes with the sodium derivative of the above amino-nitrile, the trialkylsilyl group is linked to nitrogen rather than to carbon.

In pursuance of previous studies on organosilicon compounds derived by substitution at reactive C–H bonds,[1, 2] attempts were made to prepare benzyl cyanide derivatives. Under the experimental conditions employed, however, condensation of the sodium derivative of the nitrile with trialkylhalogenosilanes always yielded trialkylsilyl derivatives of the dimerised form, β-amino-αγ-diphenylcrotononitrile (I).

Before discussing the possible structures of these silanes, some spectroscopic evidence on the tautomerism of the parent aminonitrile is presented. This compound was first isolated by Atkinson and Thorpe,[3] who described it as 2-imino-1-cyano-1 : 3-diphenylpropane (II). More recently, however, the enamine (I) was suggested as the predominant form to account for results of hydrogenation and Raman spectra,[4] as well as for the exaltation of the refractive index and dispersion.[5] Spectroscopic measurements confirm this. Whilst the ultraviolet absorption of β-oxo-αγ-diphenylbutyronitrile (III) in *n*-hexane ($\lambda_{max.}$ 258 mμ, ε 1850) resembles closely that of benzyl cyanide ($\lambda_{max.}$ 255 mμ, ε 1450),[6] the former is predominantly enolised in alcohol ($\lambda_{max.}$ 271 mμ, ε 15,900).[7] Because of the isoelectronic structure of keto- and ketimino-groups, the spectrum of the ketimine (II) should be very similar to that of the keto-form of (III) (cf. fluorenone [8] and 9-iminofluorene [1]).

(I) $CH_2Ph\cdot C(NH_2){:}CPh\cdot CN$ $CH_2Ph\cdot C({:}NH)\cdot CHPh\cdot CN$ (II)

(III) $CH_2Ph\cdot CO\cdot CHPh\cdot CN$ $CH_2Ph\cdot CO\cdot CHPh\cdot CO\cdot NH_2$ (IV)

The spectrum of the benzyl cyanide dimer in *n*-hexane ($\lambda_{max.}$ 277 mμ, ε 15,800) and in alcohol ($\lambda_{max.}$ 285 mμ, ε 16,000) [the change observed ($\Delta\lambda$ + 8 mμ, $\Delta\varepsilon$ − 200) is probably a solvation effect rather than a shift of the tautomeric equilibrium] is, however, very similar to that of the enolised form of the keto-nitrile (III), as would be expected from an ω-aminostyrene derivative, such as (I). Introduction of an amino-group at the terminal carbon atom of a conjugated system results in pronounced bathochromic and hyperchromic shifts.[9] 1-Phenylbutadiene [10] has an absorption maximum at 280 mμ, which well agrees with the figures (277 and 285 mμ) obtained for the enamine (I). The presence of an amino-group is confirmed by the infrared spectra of the solid and its solution in carbon tetrachloride. The ultraviolet spectrum of β-oxo-αγ-diphenylbutyramide (IV) ($\lambda_{max.}$ 258 mμ, ε 5780), and its colour reaction with ferric chloride,[11] show that the amide must contain at least some of the enol form in alcoholic solution. Similar results on ketimine–enamine and keto–enol tautomerism were obtained by Glickman and Cope,[12] who examined ultraviolet absorption spectra and exaltation of molecular refraction.

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[1] Eaborn and Shaw, *J.*, 1955, 1420.

[2] *Idem, ibid.*, p. 3306.

[3] Atkinson and Thorpe, *J.*, 1906, **89**, 1906.

[4] Adkins and Whitman, *J. Amer. Chem. Soc.*, 1942, **64**, 150.

[5] von Auwers and Wunderling, *Ber.*, 1931, **64**, 2758.

[6] Bruylants, Braye, and Schonne, *Helv. Chim. Acta*, 1952, **35**, 1127.

[7] Wariyar, personal communication.

[8] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," J. Wiley & Sons Inc., New York, 1951.

[9] Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45.

[10] Braude, *Ann. Reports*, 1945, **42**, 105.

[11] Staudinger, *Ber.*, 1911, **44**, 539.

[12] Glickman and Cope, *J. Amer. Chem. Soc.*, 1945, **67**, 1017.

As the ultraviolet spectrum of the triethylsilyl derivative of the benzyl cyanide dimer greatly resembles that of its parent compound, substitution at $C_{(1)}$ can be excluded with reasonable certainty, leaving the alternative structures (V) and (VI) to be considered.

(V) $CH_2Ph\cdot C(NH\cdot SiEt_3){:}CPh\cdot CN$ $CHPh(SiEt_3)\cdot C(NH_2){:}CPh\cdot CN$ (VI)

Although alkylation of the sodium derivatives of compounds similar to (I) [3] took place first, and in some cases only, at $C_{(3)}$, Hauser and his co-workers [13] carried out *N*-acylations of the magnesium derivatives of the enamine (I) by means of acyl halides. Because of the similar behaviour of groups attached to silicon and to carbonyl,[14] in many chemical reactions, in particular of silicon and acyl halides,[15] the silylamine (V) would be, by analogy, the more likely structure.

Support for the silylamine structure (V) is provided by the infrared spectra of the solid and its solution in carbon tetrachloride, which clearly indicate a secondary amino-group. Although spectroscopic data on N–H vibrations, where the nitrogen is attached to silicon, are scarce, all the available evidence indicates that SiN–H and CN–H vibrations behave qualitatively in the same manner. Thus diaminodi-*tert.*-butoxysilane [16] has frequencies of 3546, 3390, and 1686 cm.$^{-1}$, which can be assigned to a primary amino-group,[17] whilst hexa-*tert.*-butoxy*cyclo*trisilazane [16] (3413 cm.$^{-1}$) and hexamethyldisilazane [18] (3380 cm.$^{-1}$) exhibit the normal behaviour of secondary amines.[17]

The silane [the term being used without prejudice to structures (V) and (VI)] was stable for prolonged periods to cold, aqueous alcohol, and could be recrystallised from the boiling solvent. It should be pointed out that any decomposition of the silane in reactions involving prolonged heating must be treated with reserve, as it could be due to a thermal depolymerisation analogous to that of the enamine (I).[3,19] Boiling alcoholic alkali yielded phenylacetic acid. The silane, as well as the enamine (I), dissolved readily in cold, concentrated aqueous hydrochloric acid, but both solutions precipitated the keto-nitrile (III) almost at once. The absence of silicon in the product is in agreement with the Si–N structure (V), but is by itself not a definite proof, as Si–C bonds are in some cases readily cleaved in acid solution.[2,20] Dilute alcoholic hydrogen chloride gave the same product. The silane, as well as the enamine (I), on prolonged contact with hydrogen chloride in ether gave the keto-amide (IV) and ammonium chloride (cf. Robinson and his co-workers [21]).

The silane reacted readily with one equivalent of *N*-bromosuccinimide in boiling carbon tetrachloride. Longer refluxing with two equivalents appeared to cause no further reaction. This monobromo-derivative, an oil containing silicon, resisted attempts at further purification. This substance is unlikely to contain a N–Br bond, as it reacted readily with sodium iodide or silver nitrate to give sodium bromide or silver bromide respectively.

The novel type of Si–C cleavage reaction recently discovered by Eaborn and Shaw,[1] in which an α-bromoalkylsilane was converted by sodium iodide into a ketone, with loss of the silicon residue, was tried on the bromo-derivative. The reaction, although not conclusive, certainly produced no evidence in favour of an α-bromoalkylsilane structure such as (VII; $R = Et_3Si$, $R' = H$). The infrared spectrum of the product (S.1, p. 2783) showed no carbonyl frequency.

(VII) $CPhRBr\cdot C(NHR'){:}CPh\cdot CN$ (R and $R' = H$ or $SiEt_3$)

When the bromo-derivative was chromatographed on alumina an elimination reaction took place and only one product (S.2, p. 2783), $C_{32}H_{24}N_4$, was obtained. α-Bromobenzyl

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[13] Reynolds, Humphlett, Swamer, and Hauser, *J. Org. Chem.*, 1951, **16**, 165.

[14] Shaw, Thesis, London, 1955.

[15] Hughes, personal communication; Eaborn, personal communication.

[16] George, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1953, **75**, 6308.

[17] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954.

[18] Cerato, Lauer, and Beachell, *J. Chem. Phys.*, 1954, **22**, 1.

[19] Bary, *Bull. Soc. chim. belges*, 1922, **31**, 397.

[20] Hauser and Hance, *J. Amer. Chem. Soc.*, 1952, **74**, 5091.

[21] Richardson, Robinson, and Seijo, *J.*, 1937, 835.

cyanide under alkaline conditions yields a *trans*-stilbene derivative.[22] By analogy the γ-bromo-nitrile (VII) could yield one of the geometric isomers (or their tautomers) of 2 : 5-diamino-1 : 6-dicyano-1 : 3 : 4 : 6-tetraphenylhexa-1 : 3 : 5-triene (see Experimental section).

The solvent shifts, on passing from *n*-hexane to alcohol, for the enamine (I) ($\Delta\lambda$ 8 mμ), the alumina reaction product S.2 ($\Delta\lambda$ 9 mμ, for the long-wave maximum), and the silyl amine (V) ($\Delta\lambda$ 2 mμ) are also consistent with the trialkylsilylamine structure (V), where steric, as well as electronic, effects may hinder solvation.

Just as in the more widely studied alkoxysilanes, where structures resistant to hydrolysis were found,[23] examples of Si–N bonds stable in aqueous or alcoholic media are known.[24] In structures of the type $R_3Si{\cdot}NHR'$, the stability towards solvolysis seems to increase considerably with the increasing size of the hydrocarbon residue R′.[25] [In the silylamine (V) $R' = CN{\cdot}CPh{:}C(CH_2Ph){\cdot}$.] The influence, on the Si–N linkage, of olefinic unsaturation adjacent to the nitrogen atom introduces another factor about the effect of which in solvolytic reactions nothing appears to be known.

Thus it can be stated that, whilst the trialkylarylsilane structure (VI) cannot be entirely dismissed on present evidence, infrared measurements strongly support the silylamine structure (V), and nothing in the chemical evidence is incompatible with this.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Laboratory, Imperial College of Science and Technology, London.

Solvents.—Ether and benzene were dried with sodium wire.

$\alpha\gamma$-Diphenyl-β-triethylsilylaminocrotononitrile (V).—(*a*) Sodamide was prepared from sodium (8·3 g., 0·36 g.-atom) in liquid ammonia (250 ml.). Ether (150 ml.) was added whilst the ammonia was evaporated under an infrared lamp. The ether suspension was then refluxed until free from ammonia and allowed to cool, and a further quantity of ether (100 ml.) was added. Slow addition (10 min.) of benzyl cyanide (42 g., 0·36 mole) in ether (100 ml.) was accompanied by liberation of heat and evolution of ammonia. Boiling under reflux was continued for a further ½ hr. and then triethylfluorosilane (49 g., 0·365 mole) in ether (50 ml.) was added dropwise (20 min.), heat being liberated. (The fluorosilane was prefered to the more reactive chlorosilane, as the latter gave, with any residual ammonia, ammonium chloride which was troublesome to remove.) Boiling under reflux was continued for a further 4½ hr. (The mixture was stirred throughout the preparation.) The ether was then replaced by benzene, " Hyflo " filter aid was added, and the mixture was boiled for ½ hr. and then filtered. The residue was twice extracted with boiling benzene, the solvent was removed from the combined benzene extracts, and the residue was distilled in a vacuum. After a forerun of a mixture of benzyl cyanide and hexaethyldisiloxane and/or hexaethyldisilazane (8·7 g.), a fraction (42 g.) of b. p. 200—220°/0·2 mm. was obtained, which solidified. This was repeatedly recrystallised from alcohol, to give *$\alpha\gamma$-diphenyl-β-triethylsilylaminocrotononitrile* (V) (22 g., 35%), m. p. 91·5° [from alcohol, benzene, or light petroleum (b. p. 60—80°)] [Found: C, 76·15; H, 7·65; N, 8·1%; *M*, 348 (Rast). $C_{22}H_{28}N_2Si$ requires C, 75·8; H, 8·05; N, 8·05%; *M*, 348].

(*b*) Benzyl cyanide (12 g., 0·10 mole) in ether (50 ml.) was added slowly to an ether (100 ml.) suspension of finely powdered, commercial sodamide (5 g., 0·13 mole). Heat was liberated, ammonia was evolved, and the solution became deep red. It was then boiled under reflux for 4 hr., then allowed to cool, and triethylfluorosilane (13·5 g., 0·10 mole) in ether (50 ml.) was added slowly. A gelatinous precipitate was formed and the red colour was discharged. After filtration, the residue was washed with ether, the solvent was removed from the combined ether-extracts, and the residue was distilled under reduced pressure. The fraction (8 g.) of b. p. 203—216°/0·2 mm. (which solidified) was recrystallised from alcohol, to give the nitrile (V) (5 g., 29%), m. p. 91·5°. This did not deteriorate in 18 months in glass tubes closed by rubber bungs, but if the latter were replaced by corks slow decomposition to a yellow oil took place.

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[22] Rügheimer, *Ber.*, 1882, **15**, 1625; Linstead, *J.*, 1953, 2873; Timmons and Wallwork, *Chem. and Ind.*, 1955, 62.

[23] B.P. 670,630/1952; B.P. 716,323/1954.

[24] Larsson and Bjellerup, *J. Amer. Chem. Soc.*, 1953, **75**, 995; Reynolds, Bigelow, and Kraus, *ibid.*, 1929, **51**, 3070; Schwarz and Weigel, *Z. anorg. Chem.*, 1952, **268**, 291; Gilman and Smart, *J. Org. Chem.*, 1951, **16**, 424.

[25] Larsson and Tansjö, personal communication.

αγ-Diphenyl-β-trimethylsilylaminocrotononitrile.—This was prepared by the procedure (*b*) above, from an ether (50 ml.) suspension of sodamide (8 g., 0·20 mole), benzyl cyanide (25 g., 0·21 mole) in ether (50 ml.), and chlorotrimethylsilane (23 g., 0·21 mole) in ether (50 ml.). The reaction was more vigorous than with the fluorosilane, and the precipitate was filtered off more readily (after being kept overnight). Distillation yielded a fraction (7 g.), b. p. 196—205°/0·4 mm., which solidified slowly and on recrystallisation from ether gave *αγ-diphenyl-β-trimethylsilylaminocrotononitrile* (4 g., 13%), m. p. 110° (Found: C, 74·55; H, 7·3; N, 9·0. $C_{19}H_{22}N_2Si$ requires C, 74·55; H, 7·2; N, 9·2%).

Reactions of the Silane (V).—(a) *Aqueous alcohol at room temperature.* The silane (0·12 g.) was dissolved in 95% alcohol (35 ml.) and set aside for 18 hr. Excess of water was then added, and the precipitate was filtered off and dried to give the starting material (0·11 g., 92%), m. p. and mixed m. p. 90—91°.

(b) *Boiling aqueous alcohol.* The silane (0·11 g.) was refluxed with 95% alcohol (25 ml.) and recovered as under (a). After 1 hr. the m. p. was 50—76°; after 4 hr. ether-extraction yielded an oil which could not be purified.

(c) *Alcoholic alkali.* The silane (0·27 g.) was dissolved in alcohol (200 ml.), and potassium hydroxide (0·5 g.) in water (1 ml.) added. The solution was set aside for 24 hr., and then excess of water was added. Ether-extraction followed by removal of the solvent gave an oil. This was treated with the same reagents for 6 hr. at the b. p. The solution was ether-extracted, and the aqueous layer acidified and again ether-extracted. The latter extract, after removal of solvent, yielded phenylacetic acid (0·14 g., 65%), m. p. and mixed m. p. 73—75°.

(d) *Concentrated, aqueous hydrochloric acid.* The silane (0·23 g.) was finely powdered and dissolved in concentrated hydrochloric acid (10 ml.). The initially clear solution soon became cloudy and a precipitate was formed. This was filtered off and was dried, to give β-oxo-αγ-diphenylbutyronitrile (III) (0·15 g., 97%), m. p. 82° (Atkinson and Thorpe[3] report m. p. 86°) (Found: C, 82·0; H, 5·7; N, 6·0. Calc. for $C_{16}H_{13}ON$: C, 81·7; H, 5·6; N, 5·95%).

(e) *Dilute, alcoholic hydrochloric acid.* The silane (0·19 g.) was dissolved in alcohol (50 ml.), and concentrated hydrochloric acid (2 ml.) was added. The solution was set aside for 18 hr. and excess of water was then added. Ether-extraction, followed by removal of solvent, gave an oil which was taken up in alcohol. Colourless keto-nitrile (III) (0·09 g., 70%) separated, having m. p. and mixed m. p. [with the compound from (d)] 81—82°.

(f) *Hydrogen chloride.* The silane (0·83 g.) was dissolved in ether (50 ml.), and hydrogen chloride passed through the solution for 3 hr., during which the solution became yellow and a white precipitate appeared. After 3 days at −5°, during which more solid separated, the ether was removed under reduced pressure, and the residue was extracted with hot chloroform and was filtered from the ammonium chloride (0·08 g., 62%). The filtrate was evaporated and the residue dissolved in a little benzene. β-Oxo-αγ-diphenylbutyramide (IV) (0·45 g., 74%), m. p. and mixed m. p. 161—162°, very slowly separated.

Reaction of αγ-Diphenyl-β-trimethylsilylaminocrotononitrile with Concentrated Sulphuric Acid.—This silane (2·46 g.) was dissolved in concentrated sulphuric acid (10 ml.), cooled by an ice-bath, and worked up by the method of Atkinson and Thorpe[3] to give pale straw-coloured crystals of 1 : 3-diamino-2-phenylnaphthalene (1·76 g., 72%), m. p. 112·5—113·0° (Atkinson and Thorpe[3] report m. p. 116°; Lesslie and Turner[26] report m. p. 112·5—113·5°) (Found: C, 81·4; H, 5·5; N, 11·7. Calc. for $C_{16}H_{14}N_2$: C, 82·05; H, 6·0; N, 12·0%). This diamine was converted into the acetate,[3] m. p. 182—183°, of the acetyl derivative (Atkinson and Thorpe[3] report m. p. 185°).

β-Amino-αγ-diphenylcrotononitrile (I).—This was prepared by the method of Hauser and his co-workers[13] from benzyl cyanide and had m. p. 114°. The behaviour on storage was the same as that of the silane (V).

Reactions of the Amino-nitrile (I).—(a) *Concentrated, aqueous hydrochloric acid.* Finely powdered nitrile (I) (0·10 g.) was dissolved in concentrated hydrochloric acid (5 ml.) and, by the same procedure as for the silane (V), the keto-nitrile (III) (0·08 g., 80%), m. p. and mixed m. p. 81—82°, was isolated.

(b) *Hydrogen chloride.* The nitrile (I) (0·71 g.) was dissolved in ether (50 ml.) and, by the same procedure as for the silane (V), ammonium chloride (0·09 g., 56%) and the keto-amide (IV) (0·52 g., 69%) of m. p. 161—162° were isolated (Rising and Swartz[27] report m. p. 163·5—164·0°) (Found: C, 75·8; H, 6·1. Calc. for $C_{16}H_{15}O_2N$: C, 75·9; H, 6·0%).

Reaction of the Silane (V) *with Nitromethane.*—The compound (0·93 g.) was dissolved in

[26] Lesslie and Turner, *J.*, 1929, 1516.

[27] Rising and Swartz, *J. Amer. Chem. Soc.*, 1932, **54**, 2021.

nitromethane (25 ml.) and benzene (15 ml.). The solution was set aside for 36 hr. No evolution of ammonia could be detected.[1] Diethylamine (0·2 ml.) was then added and the solution boiled [28] under reflux for ¼ hr. Removal of solvents under reduced pressure gave a solid of m. p. 73—83°. This was recrystallised from alcohol, to give the starting material (0·68 g., 73%), m. p. and mixed m. p. 90—91°.

Reaction of the Silane (V) *with* N-*Bromosuccinimide.*—(a) *With one equivalent.* The silane (1·51 g., 4·35 mmole) in carbon tetrachloride (10 ml.) was boiled under reflux for 20 min. (reaction complete) with *N*-bromosuccinimide (0·78 g., 4·37 mmole). The cold solution was filtered and the residue of succinimide (0·39 g., 90%) was washed with carbon tetrachloride. The solvents was removed under reduced pressure from the combined carbon tetrachloride extracts, to leave a yellow-brown oil (VII) containing silicon and bromine, which did not crystallise at −5° or from benzene, ether, or light petroleum (b. p. 60—80°). Attempts to distil it under reduced pressure resulted in decomposition.

(b) *With two equivalents.* The silane (1·35 g., 3·9 mmole) in carbon tetrachloride (15 ml.) was boiled under reflux for 2 hr. with *N*-bromosuccinimide (1·43 g., 8·0 mmole). The mixture was worked up as under (a) to give a mixture of *N*-bromosuccinimide, succinimide (1·08 g., *i.e.*, only 1 equivalent had reacted), and a yellow oil (VII), which again could not be purified.

Reactions of the Bromo-derivative (VII).—(a) *Alumina.* The derivative (VII), prepared as above from the silane (V) (1·51 g., 4·35 mmole), was dissolved in benzene and chromatographed on alumina with benzene–chloroform (3 : 1) as eluant. A colourless solid (S.2), presumably 2-*amino*-1 : 6-*dicyano*-5-*imino*-1 : 3 : 4 : 6-*tetraphenylhexa*-1 : 3-*diene* (0·52 g., 52%) was obtained which on recrystallisation from benzene had m. p. 187° (Found : C, 82·9; H, 5·5; N, 12·2. $C_{32}H_{24}N_4$ requires C, 82·7; H, 5·2; N, 12·1%). 1 : 6-Diphenylhexa-1 : 3 : 5-triene absorbs at 349 mμ,[10] whilst S.2 has its long-wave maximum in *n*-hexane and alcohol at 315 and 324 mμ respectively. This hypsochromic shift could be caused by crossed conjugation,[10] by steric hindrance to coplanarity, or by tautomerisation of one of the enamino-groups to the ketimino-form as suggested above. The infrared spectrum provides some support for the last possibility. The information from N–H stretching and deformation modes is indecisive, but absorption in the double-bond region is strong and two new bands have appeared there : one at 1660 cm.$^{-1}$ (the band of highest frequency in the double-bond region of the compounds examined) might well be due to a carbon–nitrogen double bond.[17]

(b) *Sodium iodide.* The bromo-derivative (VII), prepared from the silane (V) (1·15 g., 3·3 mmole), was dissolved in acetone (10 ml.), and sodium iodide (0·51 g., 3·4 mmole) in acetone (5 ml.) was added. A precipitate appeared immediately and iodine was slowly liberated. After ½ hr. in the dark, the sodium bromide (0·16 g., 47%) was filtered off. The filtrate was set aside for a further 24 hr. in the dark; no further precipitate appeared, but the iodine colour deepened. The solution was poured into excess of water, ether was added, and the two layers were decolorised with sodium thiosulphate. The ether layer was separated, the aqueous layer was twice extracted with ether, and the combined ether-extracts were dried (Na_2SO_4). Removal of the solvent left a dark oil with a strong, pleasant odour. As all attempts to crystallise this failed, it was chromatographed in benzene on alumina. Benzene eluted a fraction, which on recrystallisation from the same solvent gave needles, m. p. 161·5° (S.1). The quantity was insufficient for analysis. Benzene–chloroform (3 : 1) eluted oils, whilst with ethyl acetate as eluant a small quantity of solid of m. p. 125—130° was obtained. The amount was insufficient for further purification.

Ultraviolet Absorption Spectra.—Solutions in *n*-hexane (H) or 95% ethanol (E) were examined with a Unicam S.P. 500 Spectrophotometer. (Absolute ethanol = E′.)

Compound	$\lambda_{max.}$ (mμ) (ε)	Solvent
Benzyl cyanide	255 (1450)	E′ [6]
Enamine (I)	277 (15,800)	H
	285 (16,000)	E
Keto-nitrile (III)	253 (1810), 258 (1850)	H
	271 (15,900)	E′ [7]
Keto-amide (IV)	258 (5800)	E
Silylamine (V)	287 (19,300)	H
	289 (18,500)	E
Alumina reaction product (S.2)	232 (37,100), 282 (22,500), 291·5 (23,500), 315 (8900)	H
	231 (34,700), 253 (18,900), 286·5 (24,600), 293·5 (25,300), 324 (8970)	E

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[28] Leonard, Leubner, and Burk, *J. Org. Chem.*, 1950, **15**, 979.

A solution of S.1 ($8{\cdot}7 \times 10^{-2}$ g./l.) in *n*-hexane had an absorbance of 0·650 at 238 mμ, and of 1·350 at 323·5 mμ.

Infrared Absorption Spectra.—The compounds were studied in potassium chloride discs (K), and in two cases also in saturated carbon tetrachloride solution (C), by means of a modified Hilger D 209 double-beam spectrophotometer. A rock-salt prism was used in the 2—15 mμ region, and some compounds were further examined in the 3 mμ region with a quartz prism (frequencies in parentheses). Estimated accuracy: Quartz prism ±5 cm.$^{-1}$; rock-salt prism 3300 region ±25 cm.$^{-1}$; 1600 region ±5 cm.$^{-1}$.

Compound	Frequencies (cm.$^{-1}$) with assignments	Method
Enamine (I)	3420, 3300, 3215 NH_2; 2174 C⋮N; 1635 NH_2	K
	3450, 3340, 3220 (3476, 3370, 3236) NH_2; 2174 C⋮N; 1620 NH_2	C
Silylamine (V)	3260 NH; 2174 C⋮N; 783 Et_3Si	K
	3320 (3330) NH; 2180 C⋮N	C
Alumina reaction product (S.2)	3385, 3255 (3420, 3332, 3228) NH_2; 2188 C⋮N; 1660 C:N; 1633 NH_2	K
Sodium iodide reaction product (S.1)	2212 C⋮N	K

The spectrum of S.1, which was much less complex than those of the other compounds examined, showed no indication of carbonyl, hydroxyl, or primary or secondary amino-groups. The nitrile absorption occurs at higher frequency and is less intense than in the other compounds.

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