

Studies of Polarized Ethylenes

Part II.* Preparation of 1,1-Bis-dimethylaminoethylenes and 1,3-Dimethyl-2-methylene-imidazolidines

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Ten 1,1-bis-dimethylaminoethylenes (1A-10A) with electron-attracting substituents on C², and eleven analogous 1,3-dimethyl-2-(substituted methylene)-imidazolidines (1B-11B) have been prepared by one of the two following methods. 1) By reaction of the corresponding 1,1-bis-methylthioethylenes with dimethylamine or *N,N'*-dimethyl-ethylenediamine, or 2) by reaction of carbanions from active methylene compounds with *N,N,N',N'*-tetramethyl-methylthioformamidinium iodide or 1,3-dimethyl-2-methylthioimidazolidinium iodide.

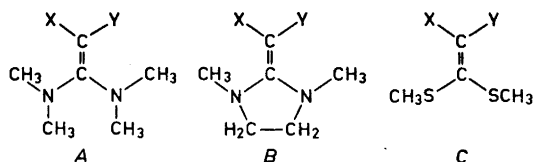
A number of ethylenes with two dimethylamino groups on C¹ and two electron-attracting groups on C² (1A-10A) have been prepared for a study of barriers to internal rotation around the C¹-C² and C¹-N bonds. (See Ref. 1 for a preliminary account.) However, studies of molecular models indicate that the dimethylamino nitrogen atoms, like the corresponding groups in tetramethylurea² and -thiourea cannot be trigonal-coplanar for steric reasons, and therefore they cannot exert their full electron-donating capacity. For comparison, a series of analogs (1B-11B) has therefore been prepared, in which planarity of the N₂C¹=C² system is enforced by cyclization. (For a preliminary account see Ref. 3.)

Simple 1,1-bis-dimethylaminoethylenes (A, X = Y = H and X = H, Y = Ph) have been known for some time,⁴⁻⁶ and diaminoethylenes similar to those described here have been prepared by Gompper and Töpfl⁷ by reaction between amines and 1,1-bis-methylthioethylenes with electron-attracting groups on C². Hartke and Salamon^{8,9} have recently prepared 6,6-bis-dimethylaminofulvenes by reaction of the corresponding cyclopentadienes with *N,N,N',N'*-tetramethyl-chloroformamidinium chloride, using triethylamine or sodium hydride as base. Kessler¹⁰ used the same method to prepare a series of 1,1-bis-dimethyl-

* Part I. *Acta Chem. Scand.* 24 (1970) 1191.

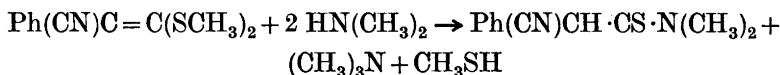
amino-2-aryl-2-cyanoethylenes, two of which (4*A* and 5*A*) are the same as the compounds described here.

The compounds prepared in the present work are numbered 1*A*–10*A* (bis-dimethylaminoethylenes) and 1*B*–11*B* (1,3-dimethyl-2-methyleneimidazolidines). Since the corresponding 1,1-bis-(methylthio)ethylenes 1*C*–11*C* were available (see Part I), attempts were made to prepare compounds *A* by reaction between compounds *C* and two equivalents of dimethylamine, and compounds *B* from *C* and one equivalent of *N,N'*-dimethylethylenediamine, analogous to the reactions described in Ref. 7.



| X | Y | X | Y |
|--|-------------------|------------------------|---|
| 1 CH ₃ OCO | CN | 7 PhCO | COCH ₃ |
| 2 PhCO | CN | 8 CH ₃ CO | COCH ₃ |
| 3 CN | CN | 9 CH ₃ OCO | COCH ₃ |
| 4 <i>p</i> -O ₂ N-C ₆ H ₄ | CN | 10 CH ₃ OCO | CO ₂ CH ₃ |
| 5 Ph | CN | 11 PhCO | CO ₂ C ₂ H ₅ |
| 6 Ph | COCH ₃ | | |

It was observed that the reactivity of compounds *C* towards amines depends on the substituents X and Y, and also on the amine component, the reaction with dimethylethylenediamine generally proceeding more smoothly than the reaction with dimethylamine. Compounds 8*C* and 9*C* reacted rapidly with dimethylamine in benzene at room temperature, and 2*C* and 11*C* in refluxing benzene solution. 1*C*, 6*C*, and 7*C* required heating with dimethylamine in benzene in sealed tubes at 120–150°. Of these, 6*C* required the highest temperature. Under these conditions 4*C* did not react at all, whereas 5*C* on prolonged reaction at 160° gave *N,N*-dimethyl- α -cyano- α -phenylthioacetamide:



The structure of this compound was demonstrated by elemental analysis and spectroscopic evidence. The NMR spectrum shows one singlet at δ 7.40 (C₆H₅), one at δ 5.66 (CH), and one doublet at δ 3.43 and δ 3.18 (N(CH₃)₂). The mass spectrum shows a prominent molecular ion and the base peak at *m/e* 88. This ion is also displayed by all members of a series of simple *N,N*-dimethylthioamides on electron impact, having 75 % intensity in tetramethylthiourea and forming the base peak of methyl *N,N*-dimethyldithiocarbamate. Evidently, it is due to the fragment (CH₃)₂N–C⁺=S. The ultraviolet spectrum shows maxima at 371 nm (ϵ 56) and 277 nm (ϵ 7000) corresponding to the *n* → π^* and first π → π^* transitions of an unconjugated thioamide.

Table 1.

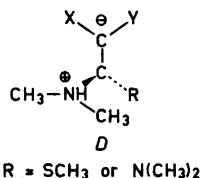
| Compound | Yield % | Solvent of recryst. | M.p. | Found % | | | Required % | | | |
|--|------------|----------------------------|------------|---------|------|------|------------|------|------|------|
| | | | | C | H | N | C | H | N | O |
| 1A. C ₉ H ₁₅ N ₃ O ₂ | 36 | toluene:lignoïn 1:3 | 80—82° | 54.1 | 7.47 | 21.2 | 54.8 | 7.67 | 21.3 | 16.2 |
| 2A. C ₁₄ H ₁₇ N ₃ O | 55 | toluene:lignoïn 3:2 | 123—125° | 68.8 | 7.06 | 17.2 | 69.1 | 7.04 | 17.3 | 6.58 |
| 3A. C ₆ H ₁₃ N ₄ | 83 | toluene | 133—135° | | | | | | | |
| 4A. C ₁₃ H ₁₆ N ₄ O ₂ | 19 | methanol | 145—146.5° | 60.3 | 6.14 | 21.3 | 60.0 | 6.15 | 21.5 | 12.3 |
| 5A. C ₁₃ H ₁₇ N ₃ | 47 | toluene:lignoïn 1:3 | 80—81° | 72.6 | 7.92 | 19.3 | 72.5 | 7.96 | 19.5 | — |
| 6A. C ₁₄ H ₂₀ N ₂ O | 68 | cyclohexane | 103—104° | 72.1 | 8.71 | 12.1 | 72.4 | 8.68 | 12.1 | 6.89 |
| 7A. C ₁₅ H ₂₀ N ₂ O ₂ | 89 | toluene:cyclohexane 5:7 | 119—121° | 69.3 | 7.98 | 10.9 | 69.2 | 7.74 | 10.8 | 12.3 |
| 8A. C ₁₀ H ₁₈ N ₂ O ₂ ·1/2H ₂ O | 100 | toluene | 126—127° | 58.2 | 9.26 | 13.3 | 57.9 | 9.24 | 13.5 | 19.3 |
| 9A. C ₁₀ H ₁₈ N ₂ O ₃ ·3H ₂ O | 40 | acetone (—50°C) | 63—64° | 45.3 | 9.23 | 10.3 | 44.8 | 9.02 | 10.4 | 35.8 |
| 10A. C ₁₀ H ₁₈ N ₂ O ₄ | 13 | toluene:lignoïn 2:1 | 106—109° | 52.2 | 7.90 | 12.3 | 52.2 | 7.88 | 12.2 | 27.8 |

Table 2.

| Compound | Yield % | Solvent of recryst. | M.p. | Found % | | | Required % | | | | |
|--------------------------------------|------------|-----------------------------|----------|---------|------|------|------------|------|------|------|------|
| | | | | C | H | N | O | C | H | N | O |
| 1B. $C_9H_{18}N_3O_2$ | 82 | butanol:lignoïn | 138—139° | 55.1 | 6.77 | 21.3 | 16.4 | 55.4 | 6.71 | 21.5 | 16.4 |
| 2B. $C_{14}H_{15}N_3O$ | 66 | toluene | 163—164 | 69.8 | 6.11 | 17.5 | 6.75 | 69.7 | 6.27 | 17.4 | 6.63 |
| 3B. $C_8H_{10}N_4$ | 49 | toluene | 97—99° | 59.0 | 6.10 | 34.6 | | 59.3 | 6.17 | 34.6 | |
| 4B. $C_{13}H_{14}N_4O_2$ | 31 | methanol | 158—159° | 60.8 | 5.66 | 21.7 | 12.5 | 60.5 | 5.46 | 21.7 | 12.4 |
| 5B. $C_{13}H_{15}N_3$ | 81 | toluene:lignoïn 3:5 | 96—98° | 73.1 | 6.98 | 19.6 | | 73.2 | 7.09 | 19.7 | |
| 6B. $C_{14}H_{18}N_2O$ | 25 | toluene | 155—157° | 73.0 | 7.90 | 12.2 | 7.20 | 73.0 | 7.88 | 12.2 | 6.95 |
| 7B. $C_{15}H_{18}N_2O_2$ | 48 | acetone | 149—152° | 69.3 | 7.21 | 10.7 | 12.5 | 69.8 | 6.98 | 10.9 | 12.4 |
| 8B. $C_{10}H_{16}N_2O_2 \cdot 3H_2O$ | 95 | acetone (—50°) | 54—57° | 47.8 | 8.86 | 11.3 | 31.7 | 48.0 | 8.81 | 11.2 | 32.0 |
| 9B. $C_{10}H_{16}N_2O_3$ | 42 | toluene | 161—166° | 56.1 | 7.69 | 13.1 | 22.7 | 56.6 | 7.60 | 13.2 | 22.6 |
| 10B. $C_{10}H_{16}N_2O_4$ | 24 | CH_2Cl_2 :xylylene 1:1 | 187—189° | 52.3 | 6.94 | 12.3 | 27.6 | 52.6 | 7.07 | 12.3 | 28.0 |
| 11B. $C_{16}H_{20}N_2O_3$ | 72 | CCl_4 | 129—130° | 66.6 | 7.04 | 9.68 | 16.9 | 66.7 | 6.94 | 9.72 | 16.7 |

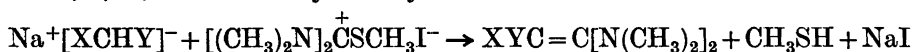
On reaction of *3C* and *10C* with dimethylamine no definite products were obtained, which may be due to secondary reactions.

A crude correlation seems to exist between the ease of reaction of compounds *C* with dimethylamine and the barrier to rotation around the C¹–C² bond. *4C*, *5C*, and *6C* have barriers higher than 25 kcal/mole, whereas *2C*

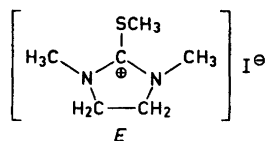


has a barrier of 20.6 kcal/mole and *7C* 18.0 kcal/mole (see Part I). The barriers in *8C* and *10C* do not affect the NMR spectrum, but in *8A* the C¹–C² barrier is too low to be measured,¹ and in *10A* it is around 8 kcal/mole,¹¹ compared to 15 kcal/mole in *4A* and 21 kcal/mole in *5A*.¹⁰ This order is reasonable, if the rate-determining step involves a dipolar tetrahedral intermediate of type *D*. In this case both the rate of addition of dimethylamine and the rate of rotation around the C¹–C² bond are governed by the difference in π -electron energy between the initial state and the system [X–C–Y][–]. In all systems except *6* the first dimethylamino group is introduced considerably more rapidly than the second one, which allows the isolation of the intermediate 1-dimethylamino-1-methylthioethylenes.

The systems that could not be prepared by direct reaction of compounds *C* with dimethylamine, were obtained by reaction of the carbanions [XCHY][–] with *N,N,N',N'*-tetramethyl-methylthioformamidinium iodide.¹²



Compounds *1B*, *2B*, and *7B* to *11B* were prepared by reaction of the corresponding compounds *C* with *N,N'*-dimethylethylenediamine in refluxing benzene, but *4C* required heating with this reagent to 120°C in a sealed tube.



The remaining compounds *B* could not be obtained by this reaction but were prepared by reaction of the appropriate carbanions with 1,3-dimethyl-2-methylthioimidazolidinium iodide (*E*).

EXPERIMENTAL

Yields, solvents for recrystallization, melting points, and analytical data are collected in Tables 1 and 2.

1,1-Bis-dimethylaminoethylenes (A)

1,1-Bis-dimethylamino-2-carbomethoxy-2-cyanoethylene (1A). 1,1-Bis-(methylthio)-2-carbomethoxy-2-cyanoethylene (1C, 10.2 g) and 2.7 M dimethylamine in benzene (50 ml) were cooled to -78° in a Pyrex tube, which was then sealed and heated in a steel tube at 120° for 3 days. The solution was then evaporated, and the oily-crystalline residue was dried on a porous tile and finally recrystallized.

1,1-Bis-dimethylamino-2-benzoyl-2-cyanoethylene (2A) was prepared in an analogous way, but it required only heating at 50° for 24 h.

1,1-Bis-dimethylamino-2,2-dicyanoethylene (3A). Malonodinitrile (5.8 g) was added to a suspension of sodium hydride (5.0 g) in benzene (100 ml), and dimethylformamide (10 ml) was added, followed by a solution of *N,N,N',N'*-tetramethyl-methylthioformamidium iodide¹² (23.9 g) in dimethylformamide (70 ml) at such a rate as to maintain a gentle reaction. The mixture was then heated at 50° for 1 h, cooled, and poured into water (500 ml). The benzene layer was separated, and the water phase was extracted with chloroform. The combined organic phases were evaporated, and recrystallization of the residue gave colourless prisms, m.p. $133-135^{\circ}$ (lit.¹³ $129-130^{\circ}$).

1,1-Bis-dimethylamino-2-cyano-2-p-nitrophenylethylene (4A) and *1,1-bis-dimethylamino-2-cyano-2-phenylethylene (5A)* were prepared in the same way as 3A, using *p*-nitrophenyl-acetonitrile and phenylacetonitrile, respectively, as methylene components. The melting points of both compounds are in good agreement with those reported by Kessler.¹⁰

1,1-Bis-dimethylamino-2-acetyl-2-phenylethylene (6A) was obtained by reaction of 6C with dimethylamine in benzene at 146° for 24 h, and *1,1-bis-dimethylamino-2-acetyl-2-benzoylethylene (7A)* in the same way from 7C by reaction at 120° for 24 h.

1,1-Bis-dimethylamino-2,2-diacetylethylene (8A). This compound is formed in a slow reaction between 8C and dimethylamine in benzene at room temperature, but it is more conveniently prepared by reaction in a sealed tube at 50° for 24 h.

1,1-Bis-dimethylamino-2-acetyl-2-methoxycarbonylethylene (9A) was obtained when 9C and two equivalents of dimethylamine in benzene were left at room temperature for one week.

1,1-Bis-dimethylamino-2,2-bis-methoxycarbonylethylene (10A). Dimethyl malonate (26.4 g) in dioxan (100 ml) was added dropwise with stirring to a suspension of sodium hydride (5.0 g) in dioxan (350 ml). To the resulting suspension of dimethyl sodiomalonate was added a solution of *N,N,N',N'*-tetramethyl-methylthioformamidinium iodide in dichloromethane (100 ml). After 0.5 h at room temperature the mixture was kept at 50° for 1 h. The filtered solution was evaporated, and the oily residue was subjected to chromatography on alumina. After elution of by-products with benzene and benzene-ether, 10A was eluted with a mixture of ether and acetone.

Judging from the resulting NMR spectrum, compound 11A was formed in the reaction between 11C and dimethylamine in refluxing benzene, but it could not be induced to crystallize.

1,3-Dimethyl-2-(substituted methylene)-imidazolidines

1,3-Dimethyl-2-(carbomethoxy-cyanomethylene)-imidazolidine (1B) and the analogs 2B, 7B, 8B, 9B, and 11B were prepared by reaction of the corresponding compounds C with *N,N'*-dimethylethylenediamine in refluxing benzene, followed by evaporation and recrystallization from the solvents given in Table 2.

*1,3-Dimethyl-2-(α -cyano-*p*-nitrobenzyliden)-imidazolidine (4B)* was prepared by reaction between 4C and one equivalent of *N,N'*-dimethylethylenediamine in benzene in a sealed tube at 120° for 16 h. After evaporation, the dark green reaction mixture was subjected to chromatography on alumina. Acetone eluted by-products, and 4B appeared on elution with acetone-ethanol and was obtained as brick red prisms after recrystallization.

1,3-Dimethylimidazolidine-2-thione. Carbon disulphide (38 g) was added dropwise with stirring and cooling to a solution of *N,N'*-dimethylethylenediamine (33 g) in pyridine (200 ml). The mixture was refluxed for 2 h, and evaporation gave the desired product in nearly quantitative yield, m.p. $111-112^{\circ}$ (lit.¹⁴ $110-112^{\circ}$) after recrystallization from toluene-ligroin.

1,3-Dimethyl-2-methylthioimidazolidinium iodide (E). Methyl iodide (29 g) was added to a solution of the thione described above (20 g) in dry acetone (150 ml). The salt started to precipitate within a few minutes, and on the following day colourless prisms were collected (74 % yield), m.p. 132–135° (decomp.), and used without further purification. (Found: C 26.6; H 4.90; I 46.8; N 10.2; S 12.5. $C_6H_{13}IN_2S$ (272.15) requires C 26.5; H 4.81; I 46.6; N 10.3; S 11.8.)

1,3-Dimethyl-2(dicyanomethylene)-imidazolidine (3B). Malonodinitrile (4.6 g) in dry dimethylformamide (50 ml) was added dropwise with stirring to a suspension of sodium hydride (3.5 g) in dry benzene (100 ml). After 1 h a solution of *E* (19.0 g) in dimethylformamide (100 ml) was added to the ice-cooled reaction mixture. The resulting slurry was left at room temperature for 1 h, then heated at 50° for 40 min, and on the following day it was extracted with several portions of water. The water phase was extracted with chloroform, and the combined organic layers were evaporated. The remaining oil, which could not be induced to crystallize, was subjected to chromatography on alumina. Benzene-ether eluted *3B* as colourless prisms.

The 2-(α -cyanobenzylidene) analog *5B* was prepared in a similar way, whereas the 2-(1-phenylpropan-2-on-1-ylidene) compound *6B* and the 2-(bis-methoxycarbonylmethylene) compound *10B* were more conveniently prepared with dioxan as solvent. Compound *5B* crystallized spontaneously on work-up, whereas *6B* was isolated from the reaction mixture as a crystalline picrate, m.p. 140°, which was then decomposed by N NaOH to give *6B* as colourless prisms. The crude *10B* was obtained as an oil, which was subjected to chromatography on alumina. By-products were eluted with ether, and pure *10B* was obtained on elution with acetone.

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