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PYROLYSIS OF 1,1,1-TRIMETHYLAMINE-2-ARYLCARBAMOYLIMIDES[1]

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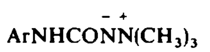
Abstract— Pyrolysis of 1,1,1-trimethylamine-2-phenylcarbamoylimide gave *sym*-diphenylurea, phenylurea, 1,1-dimethyl-4-phenylsemicarbazide, 1,1,2-trimethyl-4-phenylsemicarbazide, aniline, 1,1-dimethylhydrazine, trimethylamine, nitrogen and carbon monoxide as products. Azoformanilide, a possible intermediate, decomposed at lower temperatures and gave diphenylurea, formanilide, and phenyl isocyanate. 1,1,1-Trimethylamine-2-[1-naphthylcarbamoyl]imide behaved similarly to the phenyl derivative and gave in addition a small amount of naphthalene. Carbamoylimides involving two substituents in the 2-position behaved differently and gave indazolones.

The pyrolysis of aminimides containing the trimethylamine group has been found to produce isocyanates.[4] The corresponding reaction with aminimides with a benzyl group formed the rearranged product in which the benzyl group migrated to the negatively charged N atom.[5,6] The present study has extended the reaction to various 1,1,1-trimethylamine-2-arylcarbamoylimides(**1**, **2**) to determine whether arylamino isocyanates would be produced.



$\mathrm{ArNHCO\overset{-}{N}\overset{+}{N}(CH_3)_3}$

1a: Ar = C_6H_5

b: Ar = 1-$C_{10}H_7$

$\mathrm{C_6H_5\overset{\overset{R}{|}}{N}CO\overset{-}{N}\overset{+}{N}(CH_3)_3}$

2a: R = CH_3

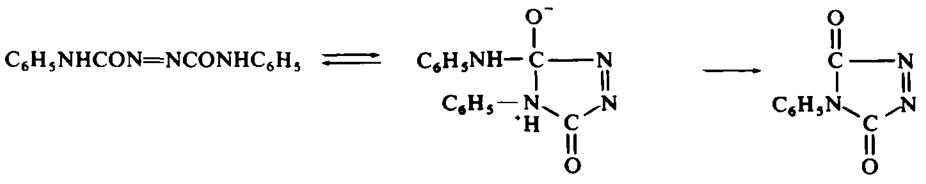
b: R = C_6H_5

Pyrolysis of 1,1,1-trimethylamine-2-phenylcarbamoylimide(**1a**) at 236–250° gave *sym*-diphenylurea (61·7%), phenylurea (2·7%), 1,1-dimethyl-4-phenylsemicarbazide (9·5%), 1,1,2-trimethyl-4-phenylsemicarbazide (trace), aniline (2·23%), 1,1-dimethylhydrazine (0·83%), trimethylamine, nitrogen, carbon monoxide and polymeric material.

The formation of phenylurea suggested the generation of a nitrene as an intermediate in this reaction. To determine whether this precursor was the source of the diphenylurea, a study was made of the pyrolysis products of azoformanilide(**3**), the dimer of the nitrene. Azoformanilide(**3**) decomposed at 176° and gave diphenylurea (64·1%) formanilide (3·37%) and phenylisocyanate (3·17%). The results suggested that the pyrolysis proceeds by two routes. The main decomposition probably occurs through the pyrazolone(**4**) which would eliminate aniline and form 4-phenyl-1,2,4-triazoline-3,5-dione(**5**); this compound is reported[7] to form phenyl isocyanate on heating. The reaction of the latter with aniline would explain the formation of diphenylurea.

The formation of formanilide suggests an elimination reaction with a concomitant formation of phenyl isocyanate. The yields obtained of these two compounds is in agreement with such a mechanism.

The absence of formanilide in decomposition products of the carbamoylimide(**1a**)



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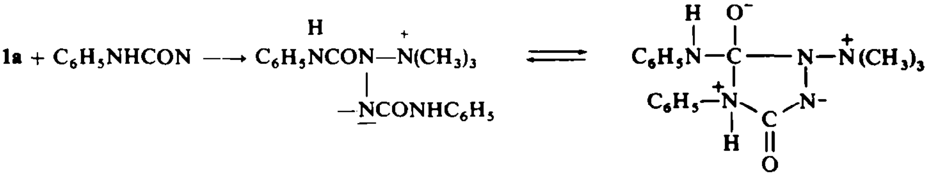
precludes the existence of azoformanilide(3) per se in the pyrolysis reaction. An intermediate(7) related to 4, however, could be formed by a reaction of the nitrene



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with the carbamoylimide(**1a**), and would lead to the formation of aniline, phenyl isocyanate and trimethylamine.

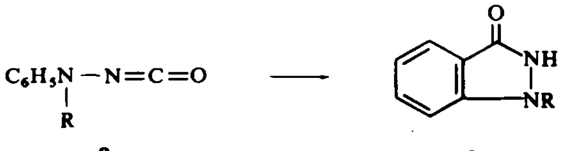
The aniline isolated may result either from this step if a portion of the phenyl isocyanate is trimerized or polymerized by the trimethylamine present, or by an elimination reaction which would form the phenylamide ion. Abstraction of a proton from the carbamoylimide(**1a**) by this species could lead to some of the 1,1-dimethyl-4-phenylsemicarbazide isolated.

The formation of 1,1,2-trimethyl-4-phenylsemicarbazide would result from a Wawzonek rearrangement of the carbamoylimide(**1a**).

No products resulting from the rearranged product, phenylamino isocyanate, were found, and eliminate this type of reaction from consideration. This result is in agreement with the behavior of the rigid azide, phenylcarbamoylazide.[8]

1,1,1-Trimethyl-2-(1-naphthylcarbamoyl)imide(**1b**) gave on pyrolysis many of the same types of products as were found with the phenyl derivative(**1a**). One exception was naphthalene; the corresponding hydrocarbon, benzene, may have been formed from **1a** but was lost in the workup of the pyrolysis mixture.

The pyrolysis of 1,1,1-trimethylamine-2-methyl-2-phenylcarbamoylimide(**2a**) and 1,1,1-trimethylamine-2,2-diphenylcarbamoylimide(**2b**) proceeded in a different manner and paralleled that observed with non-rigid azides.[8] Rearrangement of the intermediate nitrene occurred to the aminoisocyanate(**8**) which cyclized to the indazolone(**9**). This reaction for both examples was accompanied by the formation of the secondary amine and polymeric materials.



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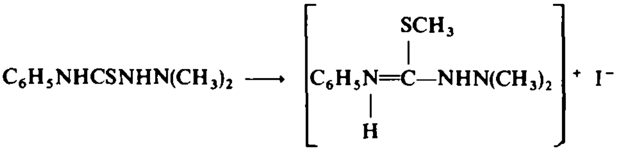
The carbamoylimides used in this investigation were prepared from the corresponding 1,1-dimethyl-4-arylsemicarbazides and 1,1-dimethyl-4-substituted-4-phenylsemicarbazides by alkylation with methyl *p*-toluenesulfonate followed by treatment with base.[9]

Extension of this investigation to phenylthiocarbamoyl derivatives failed in the alkylation step. Treatment of 1,1-dimethyl-4-phenylthiosemicarbazide with methyl iodide gave 1-methylthio-N-phenyl-N′-dimethylaminoformamidinium iodide.



$$C_6H_5NHCSNHN(CH_3)_2 \longrightarrow \left[\begin{array}{llll} & & SCH_3 & \\ & & | & \\ C_6H_5N & = & C & -NHN(CH_3)_2 \\ | & & & \\ H & & & \end{array}\right]^{+} I^{-}$$

EXPERIMENTAL*

1,1-*Dimethyl-4-phenylsemicarbazide*. This compound was prepared by the method given in the literature[9] in a 90% yield. Recrystallization from a mixture of benzene and (30–60°) light petroleum gave a sample melting at 109–110° (lit[9] mp 105–7°): IR($HCCl_3$), 3350, 1680 cm^{-1}: NMR(CCl_4): δ 7·87, 8·15(2,s,2NH): 7·20(m, 5, C_6H_5): 2·95(s, 6, CH_3).

1,1,1-*Trimethyl-4-phenylsemicarbazonium* p-*toluenesulfonate*. A soln of 1,1-dimethyl-4-phenylsemicarbazide (40·1 g) and methyl *p*-toluenesulfonate (54·4 g) in acetonitrile (100 ml) was refluxed for 18 hr. Cooling the resulting soln gave white needles (79·2 g) which on recrystallization from acetonitrile melted at 175–176°. (Found: C, 55·42: H, 6·48: N, 11·44. $C_{17}H_{23}N_3SO_4$ requires: C, 55·89: H, 6·30: N, 11·51%).

1,1,1-*Trimethylamine-2-phenylcarbamoylimide* (**1a**). A soln of 1,1,1-trimethyl-4-phenylsemicarbazonium *p*-toluenesulfonate (79·2 g) in hot water (100 ml) was treated with a soln of NaOH (40 g) in water (50 ml). The resulting soln upon cooling gave white needles (39·2 g) which upon recrystallization from water melted at 222° with decomposition (lit[9] m.p. 205 dec): IR(nujol) 3300 and 1625 cm^{-1}: NMR(DMSO-d_6) at 74°: δ 7·15(m, 5, C_6H_5): 3·23(s, 9, CH_3).

Pyrolysis of 1,1,1-*trimethylamine-2-phenylcarbamoylimide*(**1a**). The carbamoylimide **1a** (1·93 g) was heated between 236–250° for 30 min and the resulting solid was dissolved in EtOAc and chromatographed on silica gel (dry column) using EtOAc as the eluting solvent. The following compounds were eluted in the order given: *sym*-diphenylurea (0·65 g), 1,1,2-trimethyl-4-phenylsemicarbazide (trace), 1,1-dimethyl-4-phenylsemicarbazide (0·17 g), phenylurea (0·04 g) and a solid (0·12 g) which melted above 350°. The 1,1,2-trimethyl-4-phenylsemicarbazide was identified by comparing its migration time on silica gel with that of an authentic sample.

The volatile products from the pyrolysis were collected in HClaq and were trimethylamine, 1,1-dimethylhydrazine (0·83%) and aniline (2·23%). Identification was made by VPC using a 10% silicon rubber W98 column.

The presence of CO was demonstrated by IR.

1,1,2-*Trimethyl-4-phenylsemicarbazide*. Trimethylhydrazine[10] (2·0 g) was treated with phenyl isocyanate (2·0 g) at room temp and the mixture was allowed to stand for 0·5 hr. Removal of the excess trimethylhydrazine gave a white solid (2·6 g) which was recrystallized from 75% EtOH: m.p. 75–77°: IR(nujol) 3400 and 1760 cm^{-1}: NMR($DCCl_3$): δ 6·8–7·8(m, 5, C_6H_5): 2·80(s, 3, CH_3): 2·47(s, 6, $(CH_3)_2$). (Found: C, 62·11: H, 7·93: N, 21·61. $C_{10}H_{15}N_3O$ requires: C, 62·18: H, 7·83: N, 21·76%).

Pyrolysis of azoformanilide.[11] Azoformanilide (2·62 g) was decomposed at 176° and the resulting solid when dissolved in EtOAc gave using dry column chromatography on silica gel with EtOAc as the eluting solvent, formanilide (0·04 g) and *sym*-diphenylurea (1·33 g). A third component was obtained in amounts too small to identify.

The gases evolved in the pyrolysis were collected in a soln of benzene containing methylaniline. Removal of the latter with HCl gave methyldiphenylurea (0·07 g, 3·17%) m.p. 106°.

* Mg pts are corrected. Identification of the compounds formed in the pyrolyses was made by comparison with authentic samples.

1,1-*Dimethyl*-4-(1-*naphthyl*)*semicarbazide*. 1-Naphthyl isocyanate (20 g) was added dropwise to 1,1-dimethylhydrazine (7·9 g) in benzene (20 ml) at 0° and the resulting solid after standing for 30 min was filtered: yield, 25·8 g. Recrystallization from EtOH gave a sample melting at 163–5°; IR(nujol) 3400 and 1700 cm^{-1}: NMR(DMSO-d_6): δ 7·4–8·2(m, 7, $C_{10}H_7$); 2·66(s, 6, CH_3); 8·12 and 9·40(s, 2 NH). (Found: C, 67·96; H, 6·25; N, 18·60. $C_{13}H_{15}N_3O$ requires: C, 68·21; H, 6·55; N, 18·55%).

1,1,1-*Trimethyl*-4-(1-*naphthyl*)*semicarbazonium* p-*toluenesulfonate*. 1,1-Dimethyl-4-(1-naphthyl)semicarbazide (40·3 g) was refluxed with methyl *p*-toluenesulfonate (35 g) in dry MeOH (300 ml) for 12 hr. The salt (62·3 g) obtained on cooling was recrystallized from EtOH; m.p. 180·5–181°. (Found: C, 60·66; H, 6·01; N, 9·96. $C_{21}H_{25}N_3SO_4$ requires: C, 60·72; H, 6·07; N, 10·12%).

1,1,1-*Trimethylamine*-2-(1-*naphthyl*)*carbamoylimide*(**1b**). The *p*-toluenesulfonate (10 g) was neutralized in MeOH (100 ml) with NaOMe. Removal of the MeOH was followed by extraction with hot anhydrous benzene (100 ml). On cooling the carbamoylimide (3·26 g) crystallized and melted at 176–7° after further recrystallization from benzene: IR(nujol) 3500 and 1625 cm^{-1}: NMR(D_2O) δ 6·7–7·8(m, 7, $C_{10}H_7$); 2·78(s, 9, CH_3). (Found: C, 69·50; H, 7·20; N, 17·51. $C_{14}H_{17}N_3O$ requires: C, 69·23; H, 7·05; N, 17·28%).

Pyrolysis of 1,1,1-*Trimethylamine*-2-(1-*naphthyl*)*carbamoylimide*(**1b**). The carbamoylimide **1b** (3·75 g) was heated at 190–195° until all gas evolution ceased. The residue was treated with benzene and the resulting mixture of solid and liquid was decanted from the oily solid in the flask. Filtration of the benzene mixture gave 0·47 g of di-α-naphthylurea. Extraction of the benzene filtrate with dilute acid gave a mixture of α-naphthylamine (0·30 g) and 1,1-dimethyl-4-(1-naphthyl)semicarbazide (0·16 g) which were separated by acetylating the α-naphthylamine. The benzene extract when chromatographed on silica gave naphthalene (0·0045 g). The other fractions obtained were present in insufficient amounts to identify.

The oily residue from the pyrolysis when treated with EtOH gave 0·37 g of di-α-naphthylurea: the filtrate contained resinous polymeric material.

1,1,4-*Trimethyl*-4-*phenylsemicarbazide*. A soln of ethyl 2,2-dimethyl carbazate[12] (90 g) and methylaniline (72·8 g) in *p*-xylene (300 ml) was distilled slowly to remove the *p*-xylene. The residue was heated for 12 hr at 230° and then distilled at reduced pressure to remove starting materials. The resulting solid when recrystallized from hexane gave white platelets (53 g) melting at 88°: IR(nujol) 3350 and 1650 cm^{-1}: NMR($CDCl_3$): δ 7·47(m, 5, C_6H_5): 5·28(s, 1, NH): 3·25(s, 3, NCH_3): 2·51(s, 6, $N(CH_3)_2$). (Found: C, 62·01; H, 7·95; N, 22·01 $C_{10}H_{15}N_3O$ requires: C, 62·15; H, 7·82; N, 21·74%).

1,1,1,4-*Tetramethyl*-4-*phenylsemicarbazonium* p-*toluenesulfonate*. A soln of 1,1,4-trimethyl-4-phenylsemicarbazide (8·0 g) and methyl *p*-toluenesulfonate (11 g) in acetonitrile (30.ml) was refluxed for 4·5 hr. Removal of the solvent gave an oil which was crystallized from a mixture of EtOAc and diethyl ether; yield, 4·25 g; m.p. 113·5–114°; IR(nujol) 3300, 1695 and 1190 cm^{-1}; NMR(DMSO-d_6): δ 7·05–7·76(m, 9, C_6H_5, C_6H_4); 3·59(s, 9, $N(CH_3)_3$); 3·29(s, 1, NH), 3·17(s, 3, N–CH_3); 2·31(s, 3, CH_3). (Found: C, 56·91; H, 6·70; N, 10·87. $C_{18}H_{25}N_3O_4S$ requires: C, 56·98; H, 6·64; N, 11·07%).

1,1,1-*Trimethyl*-2-*methyl*-2-*phenylcarbamoylimide*(**2a**). 1,1,1,4-Tetramethyl-4-phenylsemicarbazonium *p*-toluenesulfonate (18·5 g) was treated with NaOMe (2·6 g) in MeOH (200 ml) and the resulting soln was allowed to stand for 12 hr. Removal of the MeOH followed by extraction with two 200 ml portions of hot benzene gave a pale brown oil which was recrystallized from a mixture of benzene and hexane: yield, 5·5 g; m.p. 106–7°. IR(nujol) 1570 cm^{-1}; NMR($CDCl_3$): δ 7·72(m, 5, C_6H_5); 3·38(s, 9, $N(CH_3)_3$); 3·23(s, 3, NCH_3). (Found: C, 63·95; H, 8·54; N, 20·18. $C_{11}H_{17}N_3O$ requires: C, 63·74; H, 8·27; N, 20·27%).

Pyrolysis of 1,1,1-*trimethylamine*-2-*methyl*-2-*phenylcarbamoylimide*(**2a**). The carbamoylimide **2a** (1·3 g) was heated at 190° in a sublimator until all gas evolution ceased. Sublimation of the residue under reduced pressure gave a product (0·71 g) which was dissolved in benzene and chromatographed on silica gel (dry column) using EtOAc as the eluting solvent. Products isolated were methylaniline (0·24 g), 1-methylindazolone[13] (0·17 g) and a solid (0·30 g) which melted above 350° and could not be purified sufficiently to be characterized. The residue (0·2 g) from the sublimation likewise melted above 350°.

1,1-*Dimethyl*-4,4-*diphenylsemicarbazide*. A soln of diphenylcarbamoyl chloride (57·9 g) in benzene (200 ml) was treated at 0° dropwise with 1,1-dimethylhydrazine (15 g). The resulting soln which upon reaching room temp became semisolid, was treated with dilute NaOHaq. The benzene layer upon removal of the solvent gave a solid which was recrystallized from a mixture of benzene and hexane: yield, 23 g; m.p. 133·5–134°; IR(nujol) 3325, 1680 cm^{-1}; NMR($CDCl_3$): δ 7·25(m, 10, $(C_6H_5)_2$): 5·56(s, 1, NH): 2·57(s, 6, $N(CH_3)_2$). (Found: C, 70·35; H, 6·59; N, 16·14. $C_{15}H_{17}N_3O$ requires: C, 70·58; H, 6·70; N, 16·45%).

1,1,1-*Trimethyl*-4,4-*diphenylsemicarbazonium* p-*toluenesulfonate*. A soln of 1,1-dimethyl-4,4-diphenylsemicarbazide (15·3 g) and methyl *p*-toluenesulfonate (11·5 g) in acetonitrile (250 ml) was refluxed for

12 hr. Removal of the acetonitrile gave an oil which was recrystallized from a mixture of acetonitrile and ether: yield, 19·5 g; m.p. 126–127°; IR(nujol) 3600, 1700, 1180 cm^{-1}; NMR(CD_3CN): δ 7·07–7·68(m, 14, $(C_6H_5)_2$, C_6H_4); 3·60(s, 9, $N(CH_3)_3$); 3·28(s, 1, NH); 2·32(s, 3, CH_3). (Found: C, 62·36; H, 6·38; N, 9·45. $C_{23}H_{27}N_3O_4S$ requires: C, 62·56; H, 6·16; N, 9·52%).

1,1,1-*Trimethylamine-2,2-diphenylcarbamoylimide*(**2b**). The *p*-toluenesulfonate (8·0 g) was treated with NaOMe (1·0 g) in MeOH (20·0 ml) and the soln was allowed to stand for 0·5 hr. Removal of the MeOH followed by extraction with benzene (500 ml) gave a pale brown solid which was recrystallized from a mixture of benzene and hexane: yield, 3·54 g, m.p. 182°d.; IR(nujol) 1600 cm^{-1}; NMR($CDCl_3$): δ 7·15(m, m, 10, $(C_6H_5)_2$); 3·27(s, 9, $(CH_3)_3$). (Found: C, 71·65; H, 7·45; N, 15·51. $C_{16}H_{19}N_3O$ requires: C, 71·34; H, 7·13; N, 15·59%).

Pyrolysis of 1,1,1-*trimethylamine-2,2-diphenylcarbamoylimide*(**2b**). The carbamoylimide **2b** (1·0 g) was heated at 200° until gas evolution ceased. The residue (0·85 g) was extracted with hot benzene (30 ml) and the extract was chromatographed on silica gel (dry column) using benzene as the eluting solvent. Products isolated were diphenylamine (0·26 g), 1-phenylindazolone[14] (0·15 g), and a solid (0·35 g) which melted above 350° and was difficult to purify.

Decomposition of the carbamoylimide (1·5 g) was also brought about by refluxing in *p*-xylene for 12 hr. The resulting products were diphenylamine (0·36 g), 1-phenylindazolone (0·29 g) and polymeric material (0·04 g).

1,1-*Dimethyl-4-phenylthiosemicarbazide*. 1,1-Dimethylhydrazine (15 g) was treated dropwise at 0° with phenyl isothiocyanate (27·1 g). Removal of excess dimethylhydrazine gave a solid which was recrystallized from EtOH: yield, 27·8 g; m.p. 180–182°; IR(nujol) 3300, 1220 cm^{-1}; NMR(DMSO-d_6) δ 7·10(m, 5, C_6H_5) 2·62(s, 6, CH_3). (Found: C, 55·64; H, 6·45; N, 21·54. $C_9H_{13}N_3S$ requires: C, 55·38; H, 6·72; N, 21·54%).

1-*Methylthio*-N-*phenyl*-N′-*dimethylaminoformamidinium iodide*. A soln of 1,1-dimethyl-4-phenylthiosemicarbazide (27·8 g) and MeI (20 ml) in acetonitrile (50 ml) was refluxed for 30 min. Cooling the resulting soln gave crystals (25·0 g) which were recrystallized from MeOH; m.p. 148–150°; IR(nujol) 3300 cm^{-1}; NMR($CDCl_3$) δ 7·45(5, m, C_6H_5); 2·71(s, 6, $(CH_3)_2N$) 2·53(s, 3, S–CH_3). (Found: C, 35·53; H, 4·76; N, 12·77. $C_{10}H_{16}N_3SI$ requires: C, 35·53; H, 4·76; N, 12·53%).

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