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HYDANTOINS, THIOHYDANTOINS, GLYCOCYAMIDINES—36[a]

1,5,5- AND 3,5,5-TRIPHENYL DERIVATIVES

GY. SIMIG and K. LEMPERT*
Research Group for Alkaloid Chemistry of the Hungarian Academy of Sciences, 1111 Budapest XI, Gellért tér 4

and

J. TAMÁS
Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest

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Abstract—In contrast to the α-chloroamides **1a–c** which, when reacted with potassium N-cyanoanilide, furnish anomalous substitution products (**2a–c**), the related nitrile and ester yields normal substitution products (**3a** and **b**) under the same conditions. 1,5,5-Triphenylhydantoin (**4a**) and a series (**5a–8a**, **13** and **14**) of its derivatives have been prepared starting with **3a** and **b**. Acid hydrolysis of **3a** yields, in addition to the normal products (**4a** and **5a**) considerable quantities of the rearranged product **4b**. An authentic sample of the latter, as well as a series of its derivatives (**5b–8b** and **11**) have been prepared starting with α,α-diphenylglycinonitrile and 2-methylthio-1,4,4-triphenyl-2-imidazolin-5-one (**9**). When reacted with ammonia and ammonium iodide, **9** gave, in addition to the normal ammonolysis product **7b**, the Dimroth rearrangement product **16**, as well as 5,5-diphenylglycocyamidine, by apparent dephenylation of **16**. The mass spectra of the imidazole derivatives **4–8**, **a** and **b**, **9**, **11**, **13** and **14** are discussed.

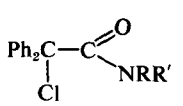
α-Chloro-α,α-diphenylacetamides (**1a–c**) have been recently found to yield, when reacted upon with potassium N-cyanoanilide in DMSO, the *p*-substituted derivatives **2a–c** as the anomalous products of substitution.[2] In order to explore the scope and limitations of this new reaction, α-bromo-α-cyanodiphenylmethane[3] and ethyl α-chlorodiphenylacetate[4] were reacted under the same conditions as **1a–c** with potassium N-cyanoanilide, and in both cases the *normal* substitution products: N-cyano-N-(α-cyanobenzhydryl)-aniline (**3a**) and ethyl α-(N-cyanoanilino)-diphenylacetate (**3b**) were obtained in 61 and 32% yield, respectively. The structure assignments of these products rested mainly on the NMR and IR spectra. Thus, the NMR spectrum of **3a** contained only aromatic proton signals and that of **3b** only signals of the OEt group as well as of aromatic protons while the anomalous substitution products corresponding to **2** (with —C≡N and —COOEt, respectively, instead of —CONRR') would, in accordance with compounds **2**, exhibit also benzhydryl proton signals in their NMR spectra. The IR spectra of **3a** and **b**, on the other hand, clearly demonstrated the presence of cyanoamino groups in both compounds, excluding thereby the isomeric carbodiimide structures for the products which might have resulted by nucleophilic attack of the *terminal* N atom of the cyanoanilide anion at the tetrahedral C atoms of their reaction partners.†

In order to corroborate their structure assignments, **3a** and **b** were subjected to hydrolysis. Alkaline hydrolysis of **3b** furnished 1,5,5-triphenylhydantoin (**4a**) while that of **3a** gave 4-imino-1,5,5-triphenyl-2-imidazolidinone (**5a**) in excellent yields. **4a** has previously been prepared in low yield by thermolysis of N-(α-anilinodiphenylacetyl)-N'-methylurea.[6] Our attempts to reproduce this synthesis failed but the m.p. (198–199°) of the product obtained by alkaline (or acid) hydrolysis of **3b** was practically identical with the lit.[6] m.p. (197–198°) of **4a**. Proof of the structure of our product rests on its mass spectrum (see below) and its alternative mode of synthesis through **13** (see below).

The gross structure of **5a** follows from its non-identity with **7a** (see below), the other conceivable product of the alkaline hydrolysis of **3a**, from its alternative synthesis through **14** (see below), its acid hydrolysis to **4a**, as well as from its mass spectrum (see below). **5a** is potentially tautomeric and

[a]For Part 35 see Ref 1.

†For the formation of carbodiimides by alkylation of cyanoamide anions *cf* Ref 5.



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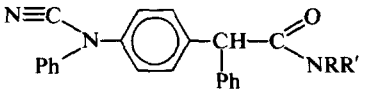

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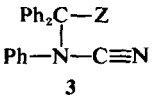
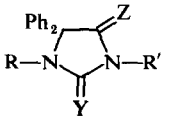


3

a: Z = C≡N
b: Z = COOEt

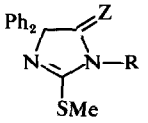
a: R = R′ = H
b: R = t-Bu, R′ = H
c: R = R′ = Me



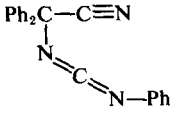
4–8

	Y	Z
4	O	O
5	O	NH
6	S	O
7	NH	O
8	S	NH

a: R = Ph, R′ = H
b: R = H, R′ = Ph



9: R=Ph, Z=O
10· R=H, Z=O*
11: R = Ph, Z = NH



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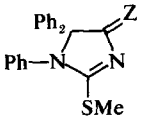
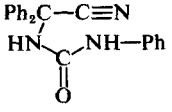


13. Z=O
14: Z = NH



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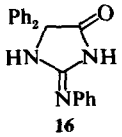


16

*For the tautomerism of this compound see Ref 1.

might exist also as the corresponding 4-amino tautomer. That, at least in the crystalline state, this is actually not the case, follows from the IR spectrum which does not exhibit νNH_2 bands and in which the $\nu C{=}O$ and $\nu C{=}N$ bands appear at 1720 and 1650 cm^{-1}, respectively, proving thereby that the corresponding groups are *not* conjugated.

The result of the acid hydrolysis of **3a** was striking. Treatment of **3a** with 20% hydrochloric acid furnished, in addition to 19% of **4a** and 13% of **5a**, an isomer of the former as the main product (25% yield). This main product was identified as 3,5,5-triphenylhydantoin (**4b**) by comparison with an authentic sample prepared by acid hydrolysis of 2-methylthio-1,4,4-triphenyl-2-imidazolin-5-one (**9**).[7] A reasonable pathway for the formation of the anomalous product **4b** consists in the acid catalysed isomerization of **3a** to the carbodiimide **12**—for similar isomerizations *cf* Refs 8 and 9—and subsequent hydrolysis and ring closure of the latter. Support for this hypothesis comes from the observation that in the IR spectrum of **3a** an intensive carbodiimide band gradually develops on heating the potassium bromide pellet to 110°.[10] (Similar rearrangements did not occur either during acid hydrolysis, or on thermal treatment of **3b**.)

Hydrogen sulfide treatment of **3a** and **b** furnished compounds **8a** and **6a**, respectively, in excellent yields; methylation of the latter led to compounds **14** and **13**, respectively. The structure of **13** follows from its non-identity with **9**[7] and its transformation into **7a**. The structure of **14**, on the other hand, follows partly from its transformation into **4a** and **5a** (establishing its structural relation to **13** whose acid hydrolysis also led to **4a**) and partly from its mass spectrum (see below). Thus, during hydrogen sulfide treatment of **3a** and **b** no rearrangements analogous to that experienced during acid hydrolysis of **3a** occurred.

Compound **8a** is potentially tautomeric and might exist, similarly as the oxo analogue **5a**, as the 4-amino tautomer. That, at least in the crystalline state, this is actually not the case, is shown by the comparatively high wave number (1640 cm^{-1}) of the $\nu C{=}N$ band (which proves that the C=N group is not conjugated) and by the absence of νNH_2 bands from the IR spectrum.

In addition, some experiments were performed with the purpose of obtaining the 3,5,5-triphenyl isomers of the 1,5,5-triphenylhydantoin derivatives discussed above and of establishing possible differences between the reactivities of the isomers.

When α,α-diphenylglycinonitrile[12] was reacted with phenyl isocyanate in pyridine, a 57% yield of α-(3-phenylureido)-diphenylacetonitrile (**15**) was obtained; the latter could be cyclized by alkaline treatment to **5b**. Treatment of α,α-diphenylglycinonitrile with phenyl isothiocyanate

under the conditions used with phenyl isocyanate, on the other hand, directly furnished the cyclized product **8b**. Acid hydrolysis and methylation of **8b** furnished **6b**[7] and **11**, respectively, and acid hydrolysis of the latter gave **4b**.

The imino group in position 4 seems to be less reactive if the N-phenyl group is attached to N-1 than if it is attached to N-3. Thus, in contrast to **8b**, **8a** could not be hydrolysed to **6a** even under more vigorous conditions and at least part of **5a** was found to be stable under the conditions of the acid hydrolysis of **3a**. Similarly, **4b** was obtained in somewhat better yield by hydrochloric acid hydrolysis of **11** even under less vigorous conditions than **4a** by hydrolysis of **14**, and refluxing of **11** with aqueous acetic acid furnished **4b** whereas, on similar treatment of **14**, the reaction stopped at the intermediate stage **5a**.

Ammonolysis of **9** could be achieved only in the presence of ammonium ions, *cf* Ref 13, and furnished, in addition to the normal product **7b**, the isomer **16** of the latter which was also obtained by anilinolysis* of **10**.[14] Similar Dimroth rearrangements in the glycocyamidine series have already been observed earlier.[15] When prolonged reaction times were applied in the ammonolysis reaction of **9**, 5,5-diphenylglycocyamidine was also formed by apparent dephenylation of **16**, *cf* Ref 15.

The glycocyamidines **7a**, **7b** and **16** are potentially tautomeric compounds. Although they have been depicted as the tautomers containing exocyclic double bonds, they might as well exist as one or the other tautomer with an endocyclic double bond. Some studies concerning the tautomeric structure of glycocyamidines have been performed, the results based on the IR spectra[16] and on the stabilities towards alkaline hydrolysis[17] are, however, somewhat conflicting. We therefore abstain at present from discussing the tautomeric structures of compounds **7a**, **7b** and **16**.

MASS SPECTROMETRY

The mass spectra of the isomeric compounds **4–8**, **a** and **b** are presented in Figs 1–5, those of the isomeric pairs **9** and **13**, and **11** and **14** in Figs 6 and 7, respectively. The structures of all compounds could unequivocally be deduced from their mass spectra and were, in all cases, in full agreement with the structure assignments based on their chemistry. The structures of the isomers, in particular, could unequivocally be assigned on the basis of their mass spectra.

The spectra of all compounds display abundant molecular ion peaks permitting to check the elemental compositions of these ions by high resolution mass measurements. The spectra were, in general, highly reminiscent of those of the 1- and 3-Me

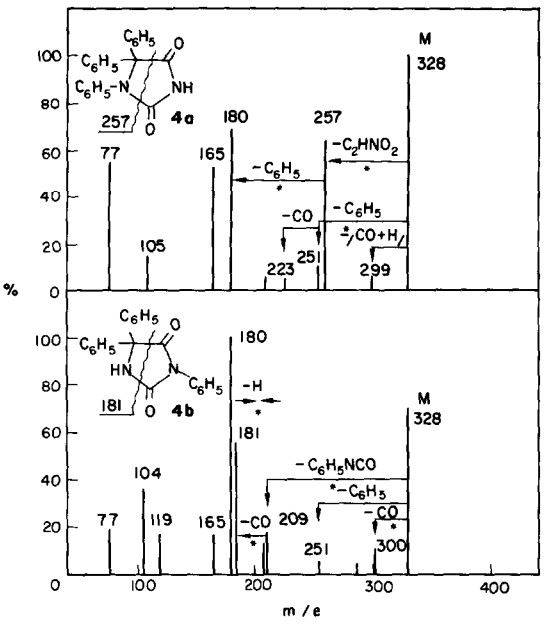


Fig 1.

derivatives of 5,5-diphenylhydantoin,[18] as well as of the different Me derivatives of 5,5-diphenyldithiohydantoin:[19] several peaks were observed at identical mass numbers, and a substantial part of the ions is formed by analogous processes. M–Ph ions as well as ions at *m/e* 180, 165 and 77 were present in all spectra.

In the spectra of all 1,5,5-triphenyl derivatives

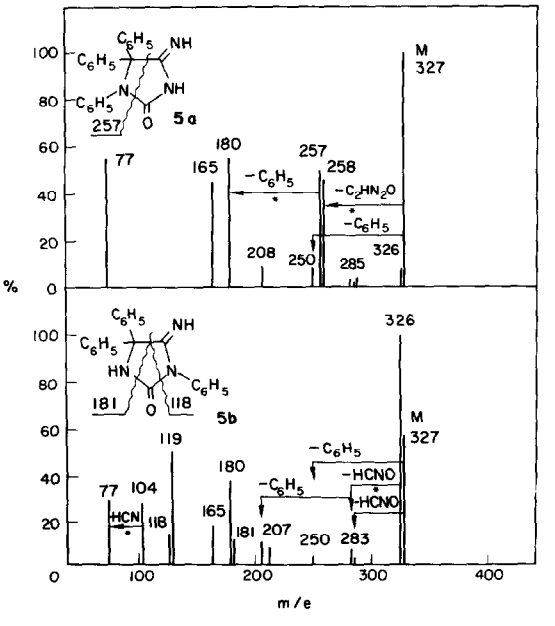


Fig 2.

*Experiment by the late J. Puskás

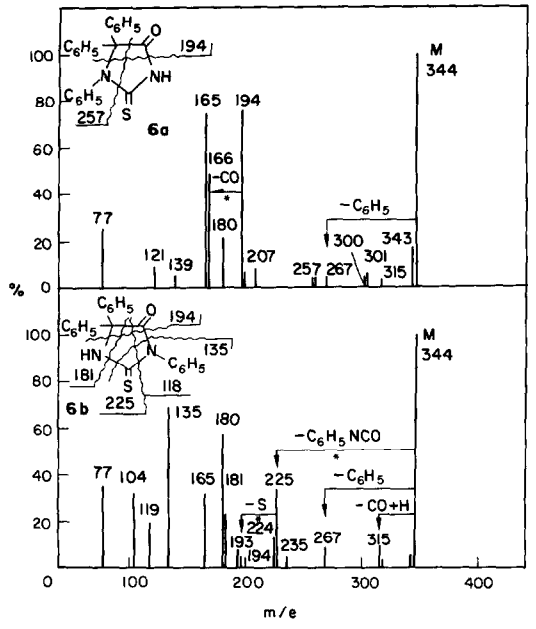
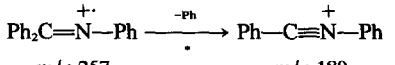


Fig 3.

ion peaks at *m/e* 257 and/or 258 could be recognized, their intensity being significant in all but the cases of compounds **6a**, **8a** and **13**. (In the latter cases different fragmentation processes become more prominent.) The *m/e* 257 ions are formed by cleavage of the N(1)–C(2) and C(4)–C(5) bonds of the imidazolidine and 2-imidazoline rings, respectively, (this process being analogous to the formation of the *m/e* 195 ion from 1-methyl-5,5-diphenylhydantoin[18]) and are likewise capable of losing subsequently a phenyl radical:



An abundant *m/e* 258 peak is found only in the spectra of those 1,5,5-triphenyl derivatives containing an imino group, *i.e.* where hydrogen rearrangements and losses are else more frequent. (*e.g.* the M − 1 ions are abundant in these cases.)

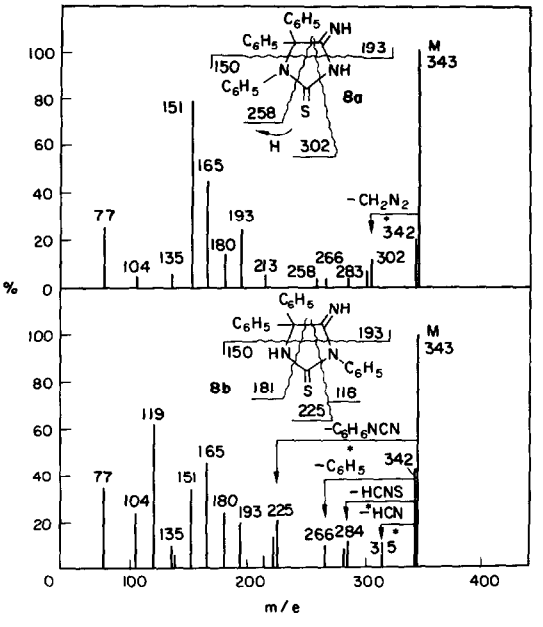


Fig 5.

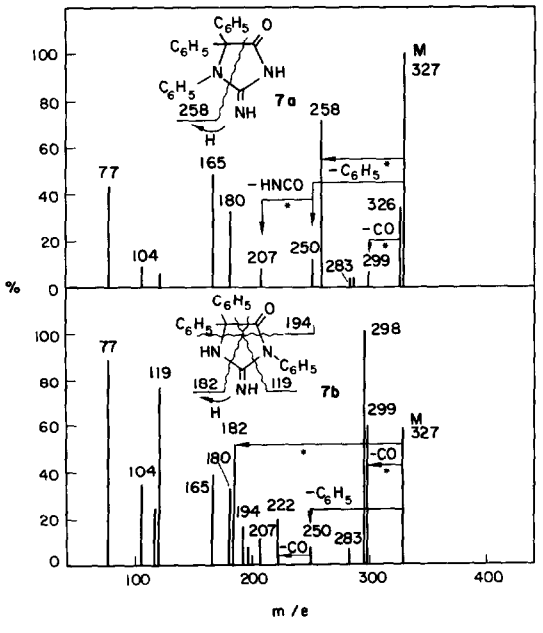
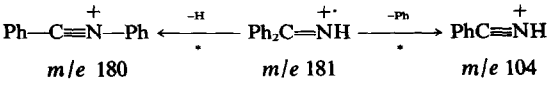


Fig 4.

The formation of the *m/e* 181 ion in the spectra of the 3,5,5- and 1,4,4-triphenyl derivatives is analogous to the process leading to the *m/e* 257 ion in the 1,5,5-triphenyl series. The intensity of this ion, however, is generally low, the ion being rapidly converted into *m/e* 180 and 104 ions, respectively:



While the *m/e* 180 ion has been observed in all spectra, the intensity of the *m/e* 104 ion is significant only in the 3,5,5- and 1,4,4-triphenyl series.

The points of attachment of the S atom and the imino group may as well be established on the basis of the mass spectra. Both isomeric pairs **6a** and **b**, and **8a** and **b** display *inter alia* the fragmentation pattern experienced earlier in the case of the two

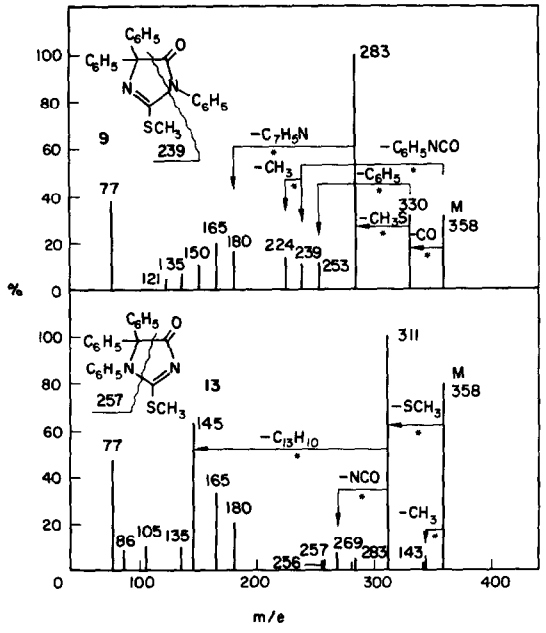


Fig 6.

isomeric N-methyl-5,5-diphenyldithiohydantoins, and this permits to establish unambiguously the point of attachment of the S atom: the formation of the *m/e* 194 and 193 ions from **6a** and **8a**, respectively, is completely analogous to that

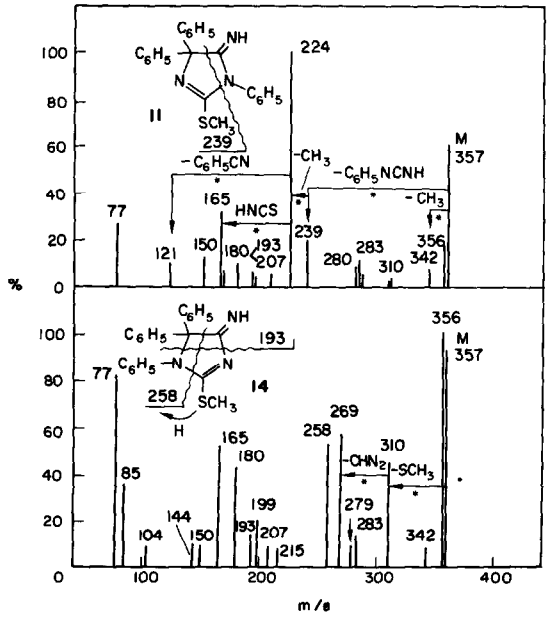


Fig 7.

*For the notation see Ref 19.

†*cf loc. cit.* with the mass spectra of V, VI and X.

of the *m/e* 210 ion from 1-methyl-5,5-diphenyldithiohydantoin,[19] while the *m/e* 225 ion is a common fragment of **6b**, **8b** and 3-methyl-5,5-diphenyldithiohydantoin.

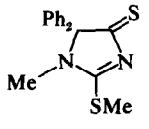
An analogous fragmentation process was observed among compounds **5** and **7** only in the case of **7b** and, on the basis of the appearance of the *m/e* 194 ion, permitted the unambiguous assignment of the position of the imino group. When, however, the observation[18] that, in general, only the CO group in position 4 is eliminated from the hydantoin ring is taken into account, the position of the imino and CO groups may, by considering the frequencies of the CO and CO+H losses, respectively, be ascertained in the other cases as well: while practically no CO eliminations occur from the molecular ions of **5a** and **b**, abundant peaks are formed by such processes in the case of **7a** and, especially, of **7b**. The position of the CO group in **9** may similarly be established on the basis of the abundant M-28 peak.

The main fragmentation pattern of **11** is identical with those of the group B derivatives of 5,5-diphenyldithiohydantoin,*† *viz*

$$M^+ \rightarrow 239 \rightarrow 224 \rightarrow 121,$$

and this fact establishes the point of attachment of the methylthio group unambiguously. The same process was observed with **9** as well, its frequency, however being inferior in this case since consecutive loss of CO and MeS here furnishes the exceedingly stable $Ph_2C{=}N{-}C{\equiv}\overset{+}{N}{-}Ph$ ion (*m/e* 283).

A certain similarity exists also between the fragmentations of **13** and **14**, on the one hand, and of 1-methyl-2-methylthio-5,5-diphenyl-2-imidazoline-4-thione (**17**) (compound VII of Ref 19): ready loss of Me and methylthio groups from the molecular ions occurs in all three cases. The further fragmentation patterns are, however,



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completely different. Thus, the *m/e* 311 ion, formed from the molecular ion of **13** by loss of MeS, furnishes by elimination of $C_{13}H_{10}$ an ion of mass number 145 whose structure may be represented most probably by $Ph{-}\overset{+}{N}{\equiv}C{-}N{=}C{=}O$. The point of attachment of the methylthio group in **14** is corroborated by the appearance of an ion of the composition $C_{14}H_{11}N$ (*m/e* 193) whose structure is probably $Ph_2C{=}C{=}\overset{+}{N}H$.

EXPERIMENTAL

NMR spectra were obtained at 60 MHz with the aid of a Perkin-Elmer spectrometer (Type R 12) with TMS as internal reference; the δ scale was used. Mass spectra were

obtained with the aid of an AEI MS-902 mass spectrometer, equipped with a direct sample insertion system, at an electron energy of 70 eV and an ion source temperature of 120–150°. The exact mass measurements were carried out with an accuracy of 2 ppm.

N-Cyano-N-(α-cyanobenzhydryl)aniline (**3a**)

A mixture of α-bromo-α-cyanodiphenylmethane[3] (27·2 g; 0·1 mole), potassium N-cyanoanilide (46·9 g; 0·3 moles) and anhyd DMSO (150 ml) was allowed to stand for 4 days at rt to yield 8·3 g of crystalline **3a**, m.p. 127–128° (EtOH), which was filtered off by suction, washed with *cold* EtOH and a large amount of water. A further crop of 10·5 g of **3a**, m.p. 127–128° (EtOH), was obtained by pouring the mother liquor of the first crop into water (600 ml), separating the oily product thereby formed from the aqueous soln, triturating it with ether (100 ml) whereby it turned crystalline, and by collecting the crystals after the mixture had been allowed to stand overnight in a refrigerator. The total yield amounted to 61%. (Found for **3a**: C, 81·49; H, 5·01; N, 13·64. $C_{21}H_{15}N_3$ (309·37) requires: C, 81·53; H, 4·89; N, 13·58%); IR (KBr): 2218 (C≡N), 1590, 1485, 1400, 760, 750, 700 (phenyl); NMR ($CDCl_3$): 465–430 Hz (m).

Ethyl α-(N-cyanoanilino)-diphenylacetate (**3b**)

A mixture of ethyl α-chlorodiphenylacetate[4] (12·4 g; 45 mmoles), potassium N-cyanoanilide (21 g; 135 mmoles) and anhyd DMSO (100 ml) was allowed to stand 5 weeks at rt to yield 3·5 g of crystalline **3b**, m.p. 148–149° (MeOH), which was filtered off, washed with cold MeOH and a large amount of water. The mother liquor of the crude first crop was poured into water (600 ml) and the crystalline (or, from time to time, oily) ppt was triturated with ether to yield a second crop of 1·7 g of **3b**, m.p. 148–149° (MeOH). The total yield was 32·5%. (Found for **3b**: C, 77·75; H, 5·83; N, 7·64. $C_{23}H_{20}N_2O_2$ (356·43) requires: C, 77·51; H, 5·66; N, 7·86%); IR (KBr): 2220 (C≡N); 1730, 1225, 1012 (ester), 1590, 1490, 1445, 765 (d), 745, 700 (phenyl); NMR ($CDCl_3$): 460–415 Hz, m, 15H; δ 4·25, qu, 2H and δ 1·08, tr, 3H, J = 7·5 Hz.

1,5,5-*Triphenylhydantoin* (**4a**)

(a) A mixture of **3b** (0·33 g; 0 9 mmoles), N/1 NaOH and EtOH (10 ml, each) was refluxed for 4 hr, the EtOH was distilled off and the residue acidified with conc HCl to yield 0·28 g (92%) of **4a**, colourless crystals, m.p. 198–199°C (aqueous EtOH), lit.[6] 197–198°. (Found for **4a**: C, 76·65; H, 4·92; N, 8·22. $C_{22}H_{16}N_2O_2$ (328·37) requires C, 76·82; H, 4·91; N, 8·53%); IR (KBr): 3250–3000 with local maximum at 3150 and shoulder at 3050 (NH); 1770+1750* and 1730+1710* (O=C—N—C=O); 1600, 1500 and 1460 (skeletal vibrations).

(b) A mixture of **3b** (0·5 g; 1·4 mmoles) and 20% HCl (20 ml) was refluxed for 7 hr. The mixture remained heterogeneous throughout and the oily insoluble material solidified on cooling This product was thoroughly washed with water and recrystallized from aqueous EtOH to yield 0·25 g (54%) of **4a** identical, according to its IR spectrum, with the product obtained as described under (a).

TLC examination of the mother liquors of both the crude and recrystallized **4a** disproved the presence even of traces of the rearranged product **4b**.

*The reason of the dublet splitting of these bands is not known.

(c) A mixture of **5a** (see below; 0·5 g; 1·5 mmoles), conc HCl and EtOH (10 ml, each) was refluxed for 8 hr and, after being allowed to cool, diluted with water. The crystalline product was recrystallized from aqueous EtOH to yield 0·15 g (30%) of **4a**, m.p. 198–199°C, identical with the product prepared according to (a).

(d) A mixture of **13** (see below; 0·30 g; 0·8 mmoles), conc HCl and EtOH (5 ml, each) was refluxed for 5 hr to yield a crystalline ppt of 0·20 g (73%) of **4a**, m.p. 197–198°C (aqueous EtOH), identical with the product obtained according to (a).

(e) A mixture of **14** (see below; 0·30 g; 0·8 mmoles), conc HCl and EtOH (5 ml, each) was refluxed for 5 hr and, after being allowed to cool, diluted with water to yield 0·15 g (55%) of **4a**, m.p. 198–199° (aqueous EtOH), identical with the product obtained according to (a).

4-*Imino-1,5,5-triphenyl-2-imidazolidinone* (**5a**)

(a) A mixture of **3a** (2·0 g; 6·5 mmoles), N/1 NaOH and EtOH (20 ml, each) was refluxed for 8 hr and the EtOH was distilled off. The colourless crystalline product which separated on cooling was recrystallized from EtOH to yield 2·0 g (85%) of colourless **5a**+EtOH, m.p. 286–287°. The solvent of crystallization was removed by keeping the product *in vacuo* (15 Torr) at 110°. The m.p. of **5a** is 287°. (Found for **5a**+EtOH: C, 74·10; H, 6·27; N, 11·29. $C_{21}H_{17}N_3O$+EtOH (373·46) requires: C, 73·97; H, 6·21; N, 11·25%); (Found for **5a**: C, 76·82; H, 5·24; N, 13·00. $C_{21}H_{17}N_3O$ (327·39) requires: C, 77·04; H, 5·23; N, 12·84%); IR (KBr): 3600–2800 with local maxima at 3350 and 3050 (NH), 1720 (C=O), 1650 (C=N).

The same product was obtained by treating **3a** with alkaline H_2O_2.

(b) A mixture of **14** (see below; 0·20 g; 0·56 mmoles), 10% NaOH aq (2 ml) and DMSO (10 ml) was stirred for 16 hr and subsequently poured into water (80 ml). The crystalline product was worked up as described under (a) to yield 0·12 g (66%) of **5a**, m.p. 280–281° (EtOH), identical according to the IR spectra with the product obtained according to (a).

Attempted hydrolysis of **14** with aqueous AcOH (1:1) furnished a considerably less pure product from which pure **5a** could be isolated only in low yield by repeated recrystallizations.

4-*Imino-1,5,5-triphenyl-2-imidazolidinethione* (**8a**)

A stream of H_2S was introduced at rt into a mixture of **3a** (2·0 g; 6·5 mmoles), anhyd pyridine (10 ml) and anhyd triethylamine (3 ml). After about 15 min the precipitation of colourless crystals started. The introduction of H_2S was continued for a further hr and the crystalline product, 2·15 g (97%), m.p. 305–306° (EtOH) was filtered by suction and washed with *cold* EtOH. (Found for **8a**: N, 11·96; S, 9·04. $C_{21}H_{17}N_3S$ (343·45) requires: N, 12·23; S, 9·34%); IR (KBr): 3500–2600 with local maxima at 3350 and 2900 (NH); 1640 (C=N); 1590, 1500, 1450, 760, 750, 700 (phenyl); UV (EtOH): 280 (4·40); 350 (2·50), sh.

4-*Imino-2-methylthio-1,5,5-triphenyl-2-imidazoline* (**14**)

A mixture of **8a** (2·0 g; 5·8 mmoles), anhyd MeOH (20 ml) and MeI (0·5 ml; 8·1 mmoles) was gently refluxed for 15 min and, after being allowed to cool, treated with N/1 NaOH until alkaline. The crystalline product was precipitated by dilution with water and recrystallized from gasoline to yield 1·4 g (67%) of the colourless crystals of **14**, m.p. 183–184°. (Found for **14**: N, 12·19; S, 8·99. $C_{22}H_{19}N_3S$ (357·48) requires: N, 11·77; S, 8·97%); IR

(KBr): 3250 (NH); 1640 and 1470 (C=N); 1500, 780, 760, 700 (phenyl); UV (EtOH): 240 (4·33), 280 (4·21).

1,5,5-Triphenyl-2-thiohydantoin (**6a**)

A stream of H_2S was introduced into a refluxing mixture of **3b** (3·0 g; 8·4 mmoles), anhyd pyridine (30 ml) and anhyd triethylamine (10 ml) until (after about 9 hr), according to TLC (adsorbent: Kieselgel $PF_{254+366}$, Merck, development: benzene, detection: iodine vapour), no more unchanged starting substance was present. The hot soln was subsequently poured into water (70 ml) and the crystals of **6a** (2·4 g; 83%), m.p. 220–221° (EtOH), which separated on cooling were filtered by suction and washed with *cold* EtOH. (Found for **6a**: C, 73·14; H, 4·82; N, 8·15. $C_{22}H_{16}N_2OS$ (344·44) requires: C, 73·23; H, 4·68; N, 8·13%); IR (KBr): 3250–2850 with local maxima at 3100 and 2900 (NH); 1730 (C=O); 1590, 1500, 1450, 750, 700 (phenyl); UV (EtOH)· 234 (4·39); 279 (4·38); 328 (2·60), sh.

2-Methylthio-1,5,5-triphenyl-2-imidazolin-4-one (**13**)

A soln of **6a** (0·8 g; 2·3 mmoles) in a mixture of MeOH (15 ml) and 10% NaOH aq (2 ml) was treated with MeI (1·0 ml; 16 mmoles). After the mixture had been thoroughly shaken for a few min at rt, the precipitation of the colourless crystals of **13** (0·6 g; 72%), m.p. 185–187° (EtOH), started. The product was separated after the mixture had been allowed to stand overnight. (Found for **13**: N, 8·02; S, 9·22. $C_{22}H_{18}N_2OS$ (358·46) requires: N, 8·09; S, 9·25%); IR (KBr): 1740 (C=O), 1530 (C=N); 1500, 1450 (skeletal vibrations); UV (EtOH): 250 (4·25).

1,5,5-Triphenylglycocyamidine (**7a**)

A mixture of **13** (0·15 g; 0·4 mmoles) and 10% (w/v) ethanolic ammonia soln (10 ml) was heated in a sealed tube for 6 hr at 100°. The resulting soln was allowed to cool and poured into water to yield 0·11 g (81%) of the colourless crystals of **7a**, m.p. 289–290° from aqueous EtOH. (Found for **7a**: C, 77·28; H, 5·39; N, 12·69. $C_{21}H_{17}N_3O$ (327·39) requires: C, 77·04; H, 5·23; N, 12·84%); IR (KBr): 3450 and 3250–2500 with local maxima at 2900 and 2700 (NH), 1730 (C=O), 1660 (C=N), 1500, 1450, 780, 760, 710 (phenyl).

α-(3-Phenylureido)-diphenylacetonitrile (**15**)

Phenyl isocyanate (0·65 ml; 6 mmoles) was added to a solution of α,α-diphenylglycinonitrile[12] (1·0 g; 4·8 mmoles) in pyridine (10 ml). Heat was evolved and the precipitation of colourless crystals started soon. The mixture was allowed to stand overnight and the first crop of **15** (0·65 g), m.p. 206–207° (EtOH) was filtered off by suction and washed with EtOH. The mother liquor was diluted with EtOH (10 ml), and water was added by drops until the precipitation of the second crop of **15** (0·25 g), m.p. as above, started. The total yield was 57%. (Found for **15**: C, 76·83; H, 5·53; N, 13·06. $C_{21}H_{17}N_3O$ (327·39) requires: C, 77·04; H, 5·23; N, 12·84%); IR (KBr): 3400, 3300 and 1560 (NH); 1650 (C=O); 1610, 1510, 1460 (skeletal vibrations).

5-Imino-1,4,4-triphenyl-2-imidazolidinone (**5b**)

A mixture of **15** (0·4 g; 1·2 mmoles), N/1 NaOH and MeOH (20 ml, each) was refluxed for 4 hr. When the MeOH was distilled off, the colourless crystalline product, 0·27 g (67·5%) of **5b**, m.p. 216–217° (EtOH), separated. (Found for **5b**· C, 76·83; H, 5·39; N, 12·77 $C_{21}H_{17}N_3O$ (327·39) requires: C, 77·04, H, 5·23; N, 12·84%); IR (KBr): 3300–2800 with local maxima at 3100 and 2850 (NH), 1760 (C=O), 1670 (C=N); 1600, 1500, 1440, 770, 760, 710 (phenyl).

5-Imino-1,4,4-triphenyl-2-imidazolinethione (**8b**)

A mixture of α,α-diphenylglycinonitrile[12] (10 g; 48 mmoles), pyridine (30 ml) and phenyl isothiocyanate (7·0 ml; 58 mmoles) was allowed to stand for a week at rt. The product, 8·5 g (52%), m.p. 218–219° (EtOH), was precipitated by the addition of EtOH. (Found for **8b**: C, 73·19; H, 5·08; N, 12·26; S, 9·33. $C_{21}H_{17}N_3S$ (343·45) requires: C, 73·44; H, 4·99; N, 12·23; S, 9·34%); IR (KBr): 3250–2800 with local maxima at 3100 and 2900 (NH); 1670 (C=N), 1520 (βNH); 1600, 1500, 1450, 750, 710, 700 (phenyl); UV (EtOH) 268 (4·48); 304 (2·54), sh.

3,5,5-Triphenyl-2-thiohydantoin (**6b**)

A soln of **8b** (0·5 g; 1·5 mmoles) in a mixture of water (20 ml), MeOH (30 ml) and conc HCl (5 ml) was allowed to stand for 2 weeks at rt, whereby 0·4 g (80%) of the product, m.p. 254–255° (EtOH), lit.[7] m.p. 254° (EtOH), separated in crystalline form. IR (KBr): 3290 and 1480 (NH), 1735 (C=O), 1230 (thiourea); 1500, 750, 690 (phenyl); UV (EtOH): 274 (4·33), 322 (2·27).

Under similar conditions, and even after refluxing an aqueous methanolic hydrochloric acid solution for 7 hr **8a** remained unchanged.

2-Methylthio-1,4,4-triphenyl-2-imidazolin-5-one (**9**)

This was obtained as described in the literature;[7] IR (KBr): 1735 (C=O), 1565 (C=N); 1580, 1490, 1445, 750, 695 (phenyl); UV (EtOH): only end absorption.

5-Imino-2-methylthio-1,4,4-triphenyl-2-imidazoline (**11**)

MeI (0·2 ml; 3·2 mmoles) was added to a soln of **8b** (0·5 g; 1·5 mmoles) and NaOH (0·1 g; 2·5 mmoles) in 80% (v/v) aqueous MeOH (10 ml) and, after being thoroughly shaken, the mixture was allowed to stand at rt for 1 day. During this time 0·4 g (77%) of the colourless crystalline product, m.p. 140–141° (gasoline), separated. (Found for **11**. C, 74·04; H, 5·30; N, 11·92; S, 8·67. $C_{22}H_{19}N_3S$ (357·48) requires: C, 73·92; H, 5·36; N, 11·77; S, 8·97%); IR (KBr): 3250 (vw., NH); 1660, 1560 (C=N); 1500, 1450, 760, 740, 710 (phenyl); UV (EtOH): only end absorption.

3,5,5-Triphenylhydantoin (**4b**)

(a) A mixture of **11** (0·17 g; 0·5 mmoles), conc HCl and MeOH (5 ml, each) was refluxed for 3 hr, whereby the precipitation of the crystalline product started. The yield was 0·10 g (64%), m.p. 207–208° (EtOH), lit.[7] m.p.: 203·5°. The product was, according to its IR spectrum, identical with an authentic sample prepared as described in the literature.[7] IR (KBr): 3300–3050 with local maxima at 3220 and 3100 (NH); 1770, 1715 (O=C—N—C=O); 1600, 1490, 1445 (skeletal vibrations), 1400 (βNH).

(b) A mixture of **11** (0·5 g; 1·4 mmoles), water and AcOH (5 ml each) was refluxed for 6 hr and subsequently evaporated to dryness *in vacuo*. The residue was triturated with N/1 NaOH (10 ml) and the colourless crystals of 0·32 g (70%) of **4b**, m.p. 194–196°C (aqueous EtOH) thereby obtained were filtered by suction

According to its IR spectrum this product was identical with the product prepared according to (a).

Ammonolysis of **9**

(a) A mixture of **9**[7] (2·0 g, 5·6 mmoles), 10% (w/v) ethanolic ammonia soln (20 ml) and NH_4I (2·0 g) was heated in a sealed tube for 3·5 hr at 148°. When the soln

was chilled in ice-water, 0·84 g of a mixture (fraction A) consisting of **7b**, **16** and unchanged **9** was obtained. By addition of water to the mother liquor of A another fraction (B; 0·81 g), consisting of **7b** and unchanged **9** was obtained.

When fraction A was boiled with EtOH (20 ml), 0·27 g (15%) of **16**, m.p. 325–326° (pyridine-EtOH), identical according to its IR spectrum with an authentic sample (see below), was obtained as the insoluble residue. By adding water to the mother liquor of **16**, a mixture (0·46 g) of **7b** and **9** separated. This was boiled up with gasoline, and **7b** (0·15 g), m.p. 237–238°, was obtained as the insoluble residue, whereas unchanged **9** (0·3 g), m.p. 141–142°, crystallized from the gasoline soln on cooling.

Fraction B was boiled up with toluene (20 ml), and **7b** (0·3 g), m.p. 240–242°, was obtained as the insoluble residue. The toluene soln was allowed to cool and light petroleum was added to precipitate a mixture (0·3 g) of **7b** (0·04 g, m.p. 237–238°) and unchanged **9** (0·2 g, m.p. 141–142°) which were separated by boiling up with gasoline as described above. By evaporation of the toluene-light petroleum soln an additional amount of **9** (0·1 g) was obtained. The total yield was 0·6 g (30%) of recovered **9**, m.p. 141–142° (gasoline), 0·54 g (30%) of **7b**, m.p. 242–243° (aqueous MeOH) and 0·27 g (15%) of **16**, m.p. 325–326° from pyridine-EtOH. (Found for **7b**: C, 76·98; H, 5·39; N, 12·50. $C_{21}H_{17}N_3O$ (327·39) requires: C, 77·04; H, 5·23; N, 12·84%); IR (KBr): 3450 and 3050 (broad) (NH); 1740 (C=O); 1690 (C=N); 1600, 1500, 1460, 760, 700 (phenyl).

An *authentic sample* of **16** was obtained* in 80% yield by refluxing **10**[14] with aniline in ethanolic soln, m.p. 331–333° from DMF. (Found for **16**: C, 76·73; H, 5·33; N, 12·73. $C_{21}H_{17}N_3O$ (327·39) requires: C, 77·04; H, 5·23; N, 12·84%); IR (KBr): 3600–2800 with a shoulder at 3350 and a local maximum at 3060 (broad) (NH); 1695 (C=O); 1640 (C=N); 760 and 700 (phenyl).

(b) A mixture of **9** (0·3 g; 0·84 mmoles), 5% (w/v) ethanolic ammonia soln (10 ml) and NH_4I (0·3 g) was heated for 7 hr at 145°. 0·05 g (18%) of crystalline **16** separated on cooling. The filtrate was evaporated to dryness *in vacuo* and the residue was triturated with 20 ml warm water to yield 0·14 g (67%) of 5,5-diphenylglycocyamidine, identical by IR spectrum with an authentic sample,[15b] as the insoluble residue.

Hydrochloric acid hydrolysis of **3a**

Compound **3a** (0·5 g; 1·6 mmoles) was refluxed with 20% HCl (40 ml) for 7 hr. The crystalline ppt (0·48 g) was filtered off by suction after the mixture had been chilled in ice-water; it was worked up by preparative TLC (4 plates, 20×20 cm, each, adsorbent: Kieselgel $PF_{254+366}$, Merck, thickness of layer 1·5 mm; development: benzene-MeOH, 9:1; detection. UV light or I_2 vapour).

The three main components were separately eluted with MeOH, and by evaporation of the solvent 0·13 g (24·5%) of **4b**, m.p 203–204° (EtOH), lit.[7] m.p. 203·5°, IR spectrum identical with that of an authentic sample,[7] and 0·10 g (19%) of **4a**, m.p. and mixed m.p. with an authentic sample (see above) 198–199° (aqueous MeOH), IR spectrum identical with that of an authentic sample, and the *hydrochloride* of **5a** were obtained. The latter was recrystallized from EtOH containing some NaOH to yield, after drying *in vacuo* at 110°, 0·07 g (13%) of **5a**, m.p. and mixed m.p. with an authentic sample (see above) 286–287°. The IR spectra of this product and that of an authentic sample were identical.

For the acid hydrolysis of the related **3b**, see above.

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