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Reactions of the iminoesters **3a-c** with hydrazine or 1,2-dimethylhydrazine gave 4,5-dihydro-**4a-c** or 2,5-dihydro-1,2,4-triazin-6(1H)ones **7a-c**, respectively. When methylhydrazine was employed, 1-methyl-4,5-dihydro- **5a-c** and 2-methyl-2,5-dihydro-1,2,4-triazin-6(1H)ones **6a-c** were obtained. Compounds **6a-c** exist as zwitterions in the solid state and in polar aprotic solvents.

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In connection with our studies on the thermally induced isomerisation of isoxazol-5-ylhydrazines (2) we became interested in the preparation and structural assignment of the rearrangement products, especially 2,5- and 4,5-dihydro-1,2,4-triazin-6(1H)ones.

Kjaer (3) reported that reaction between the iminoesters **1a-c** and hydrazine afforded 2,5-dihydro-1,2,4-triazin-6(1H)ones **2a-c**, on the basis of the analytical data and colourimetric reactions.

The present work was intended to verify the structure assignment employing different iminoesters and also to extend the study further to mono or dimethylated hydrazines.

The iminoesters **3a-c** reacted with 1,2-dimethylhydrazine to afford 1,2-dimethyl-2,5-dihydro-1,2,4-triazin-6(1H)ones **7a-c**, whose structures were assigned on the basis of their spectral properties (Table I). The ir spectra in the neat state and in chloroform solution show stretching vibrations of a CO group; coupling between the CH and methyl group is present only in the nmr spectrum of **7b**; the ultraviolet spectra of compounds **7a** and **7b** show very closely related patterns as a consequence of the presence of an identical chromophoric system.

When the iminoesters **3a-c** reacted with hydrazine hydrate, 4,5-dihydro-1,2,4-triazin-6(1H)ones **4a-c** were produced in almost quantitative yield. The triazinone **4a** was identified by comparison with an authentic sample (4), whereas the structures of compounds **4b,c** were based on their spectral properties (Table I). The ir spectra always show bands attributable to a CO group; in the nmr spectra CH couples with the NH and methyl group for **4b**, whereas with NH only for **4c**.

Reaction of the iminoesters **3a-c** with methylhydrazine gave two isomeric products, 1-methyl-4,5-dihydro-1,2,4-

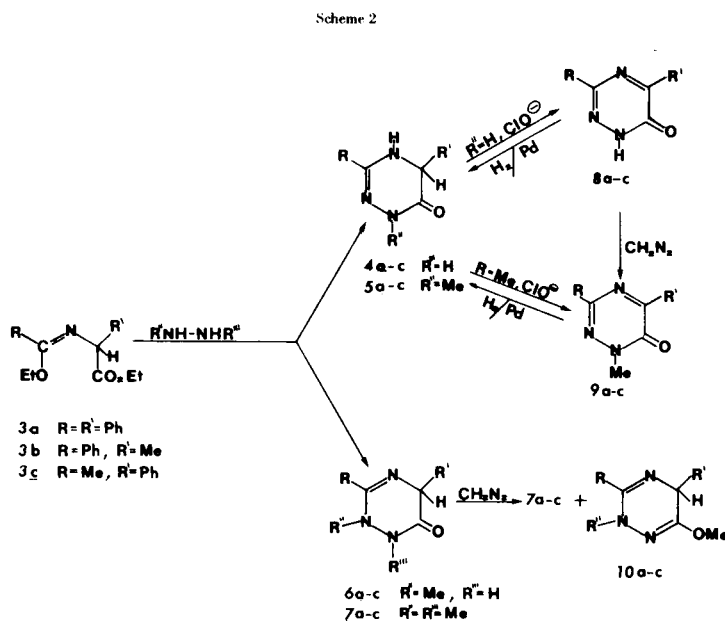
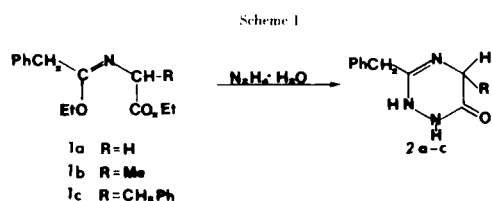


Table I
 Ir, Uv and Nmr Spectral Data of Compounds 4, 5, 6, 7 and 10

| Compound | Phase | ν max/cm ⁻¹ | λ max (log ϵ) nm | Solvent | δ Values | Proton Assignment |
|----------|-------------------|----------------------------|--|--------------------|--|---|
| 4b | potassium bromide | 3230 br, 1645 | 225 (4.12) | DMSO | 1.26 (d, J = 6.5) 3.92 (qd, J = 6.5, J' = 1.5) (a) 7.26, 10.28 (br) (b) 7.30-7.80 (m) | CH ₃ (3H) CH (1H) NH (2H) C ₆ H ₅ (5H) |
| | chloroform | 3420, 1675 | 298 (3.87) | | | |
| 4c | potassium bromide | 3240 sh, 3180, 1670 | 277 (3.56) | DMSO | 1.90 (s) 4.88 (d, J = 2.0) (c) 7.33 (s) 7.48, 10.10 (br) (b) | CH ₃ (3H) CH (1H) C ₆ H ₅ (5H) NH (2H) |
| | chloroform | 3420, 1675 | | | | |
| 5a | potassium bromide | 3330, 1640 | 227 (4.18) | deuteriochloroform | 3.32 (s) 5.00 (d, J = 2.0) (c) 5.90 (br) (b) 7.20-7.80 (m) | NCH ₃ (3H) CH (1H) NH (1H) C ₆ H ₅ (10H) |
| | chloroform | 3440, 1660 | 307 (3.79) | | | |
| 5b | potassium bromide | 3300, 1640 | 225 (4.21) | DMSO | 1.31 (d, J = 7.0) 3.22 (s) 7.30-7.86 (m) | CH ₃ (3H) NCH ₃ (3H) CH (1H) |
| | chloroform | 3440, 1655 | 301 (3.89) | | 4.01 (qd, J = 7.0, J' = 2.0) (a) | C ₆ H ₅ , NH (6H) |
| 5c | potassium bromide | 3290, 1660 | 277 (3.44) | DMSO | 1.91, 3.11 (s) 4.94 (d, J = 2.0) (c) 7.32 (s) 7.70 (br) (b) | CH ₃ , NCH ₃ (6H) CH (1H) C ₆ H ₅ (5H) NH (1H) |
| | chloroform | 3420, 1665 | | | | |
| 6a | potassium bromide | 3100-2200 br | 225 (4.18) 311 (3.76) | DMSO | 3.15 (s) 4.88 (s) | NCH ₃ (3H) CH (1H) |
| | chloroform | 1680 w | 230 (4.10) (d) 278 (3.71) (d) | | 5.30 (br) (b) 7.27, 7.50 (s) | NH/OH (1H) C ₆ H ₅ (10H) |
| 6b | potassium bromide | 3100-2100 br | 223 (4.03) 308 (3.75) | DMSO (e) | 1.28 (d, J = 6.5) 3.08 (s) | CH ₃ (3H) NCH ₃ (3H) |
| | chloroform | 1675 w | 230 (4.00) (d) 277 (3.73) (d) | | 3.78 (q, J = 6.5) 7.51 (s) | CH (1H) C ₆ H ₅ (5H) |
| 6c | potassium bromide | 3100-2000 br | 290 (3.71) | DMSO (e) | 2.23 (s) 3.23 (s) 4.61 (s) 7.21 (s) | CH ₃ (3H) NCH ₃ (3H) CH (1H) C ₆ H ₅ (5H) |
| | chloroform | 1630 | 265 (3.58) (d) | | | |
| 7a | potassium bromide | 1665 | 234 (4.32) 265 sh (3.59) 241 (4.17) (d) 275 sh (3.77) (d) | deuteriochloroform | 2.77, 3.22 (s) 5.58 (s) 7.20-7.60, 7.69-8.00 (m) | NCH ₃ (6H) CH (1H) C ₆ H ₅ (10H) |
| | chloroform | 1660 | | | | |

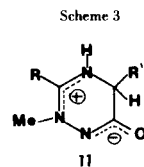
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|------------|------------|------|---|--------------------|--|---|
| 7b | neat | 1670 | 232 (4.20) 269 sh (3.42) 237 (4.07) (d) 278 (3.67) (d) | deuteriochloroform | 1.46 (d, J = 6.5) 2.93, 3.20 (s) 4.14 (q, J = 6.5) 7.20-7.47, 7.54-7.82 (m) | CH ₃ (3H) NCH ₃ (6H) CH (1H) C ₆ H ₅ (5H) |
| | chloroform | 1660 | 225 sh (3.84) 250 sh (3.49) 264 (3.52) (d) | deuteriochloroform | 2.14 (s) 2.90, 3.08 (s) 5.15 (s) 7.25 (s) | CH ₃ (3H) NCH ₃ (6H) CH (1H) C ₆ H ₅ (5H) |
| | neat | 1645 | 220 sh (4.20) 283 (3.41) | deuteriochloroform | 3.13, 3.72 (s) 5.23 (s) 7.19, 7.53 (s) | NCH ₃ , OCH ₃ (6H) CH (1H) C ₆ H ₅ (10H) |
| 7c | neat | 1660 | 220 (4.02) 276 (3.49) | deuteriochloroform | 1.33 (d, J = 7.0) 3.09, 3.72 (s) 4.02 (q, J = 7.0) 7.32 (s) | CH ₃ (3H) NCH ₃ , OCH ₃ (6H) CH (1H) C ₆ H ₅ (5H) |
| 10a | neat | 1650 | 265 (3.34) 273 (3.34) | deuteriochloroform | 2.08, 3.21, 3.66 (s) 5.02 (s) 7.28 (s) | CH ₃ , NCH ₃ , OCH ₃ (9H) CH (1H) C ₆ H ₅ (5H) |
| 10b | neat | 1645 | | | | |
| 10c | neat | 1650 | | | | |

(a) Signal collapsed to a quartet upon addition of deuterium oxide. (b) Signal disappears on deuteration. (c) Signal collapsed to a singlet upon addition of deuterium oxide. (d) Methanol + 0.1N sulfuric acid. (e) At 70°.

triazin-6(1H)ones **5a-c** and 2-methyl-2,5-dihydro-1,2,4-triazin-6(1H)ones **6a-c**, whose structures were established by their spectroscopic properties and chemical behavior. Compounds **5a-c**, which exhibit ir, uv and nmr spectra very closely related to the corresponding triazinones **4a-c**, were readily oxidized to 1-methyl-1,2,4-triazin-6(1H)ones **9a-c**. The latter compounds were also obtained by oxidation of 4,5-dihydro-1,2,4-triazin-6(1H)ones **4a-c** to 1,2,4-triazin-6(1H)ones **8a-c** followed by treatment with diazomethane. Catalytic hydrogenation of 1,2,4-triazin-6(1H)ones **8a-c** and **9a-c** yielded the corresponding 4,5-dihydro-1,2,4-triazin-6(1H)ones **4a-c** and **5a-c**.

As expected, compounds **6a-c** reacted with diazomethane to give a mixture of the triazinones **7a-c** and 6-methoxy-2-methyl-2,5-dihydro-1,2,4-triazines **10a-c**.

The ultraviolet spectra of the triazinones **6a-c** in methanol (Table I) show a different absorption pattern from that of the corresponding *N*-methyl **7a-c** and *O*-methyl derivatives **10a-c**, whereas in acidified methanolic solution the spectra of **6a-c** and **7a-c** are very similar. In Table II are reported the ultraviolet absorption maxima of compounds **6a-c** in different solvents, showing that in chloroform and in acetonitrile a bathochromic shift is present and also that the uv spectra of aqueous neutral and alkaline solutions of **6a-c** are very similar. This behavior suggests that triazinones **6a-c** in polar aprotic solvents mainly exist as zwitterions **11**, whose chromophoric system can be modified by protonation with acids, by deprotonation



with alkali and by interaction with hydroxylic solvents.

High melting points with decomposition, water solubility and ir spectra (lack of CO stretching vibrations, presence of a broad band between 3100 and 2000 cm⁻¹) of the triazinones **6a-c** indicated that also at the solid state a dipolar form is present.

EXPERIMENTAL

All melting and boiling points are uncorrected. The infrared spectra were measured with a Perkin Elmer 357 spectrometer and the ultraviolet spectra were taken in methanol, unless otherwise stated, with a Perkin Elmer 124 spectrophotometer. ¹H nmr spectra were recorded with a Perkin Elmer R20 B instrument (60 MHz); chemical shift (J in Hz) are reported in ppm downfield from internal TMS.

General Procedure for the Iminoesters **3a-c**.

The iminoesters **3a-c** were prepared, following the procedure of Kjaer (3), from the corresponding iminoethers and amino acid ethyl ester hydrochlorides. In all cases, spectral and analytical data were in agreement with the structures.

Table II

 λ max (Log ϵ) of Compounds **6a-c** in Different Solvents

| Compound | Chloroform | Acetonitrile | Acetonitrile + 0.1N Sulfuric Acid | Water | 0.01N Sodium Hydroxide |
|-----------|------------|--------------|--------------------------------------|------------|------------------------|
| 6a | 241 (4.02) | 224 (4.23) | 231 (4.14) | 227 (4.26) | 226 sh (4.31) |
| | 331 (3.49) | 327 (3.63) | 276 (3.77) | 303 (3.81) | 303 (3.62) |
| 6b | 328 (3.48) | 224 (4.09) | 231 (4.04) | 227 (4.07) | 227 sh (4.10) |
| | | 327 (3.58) | 275 (3.76) | 300 (3.76) | 300 (3.64) |
| 6c | 304 (3.66) | 246 (3.56) | 262 (3.60) | 283 (3.67) | 283 (3.57) |
| | | 303 (3.68) | | | |

Table III

1,2- and 1,4-Dihydro-1,2,4-triazin-6(1H)ones (**4**, **5** and **6**)

| Compound | M.p. or B.p. (°C) | Yield (%) | Formula | Analysis Calcd. (Found) |
|-----------|--------------------------|-----------|--|---|
| 4a | 205 (a) | 95 | ---- | ---- |
| 4b | 166-168 (b) | 90 | C ₁₀ H ₁₁ N ₃ O | C 63.48 (63.31) H 5.86 (6.05) N 22.21 (22.30) |
| 4c | 204 (b) | 90 | C ₁₀ H ₁₁ N ₃ O | C 63.48 (63.67) H 5.86 (5.91) N 22.21 (22.40) |
| 5a | 112-113 (c) | 35 | C ₁₆ H ₁₅ N ₃ O | C 72.43 (72.41) H 5.70 (5.78) N 15.84 (15.61) |
| 5b | 108-110 (d) | 20 | C ₁₁ H ₁₃ N ₃ O | C 65.01 (65.00) H 6.45 (6.35) N 20.67 (20.43) |
| 5c | 140-141 (b) | 48 | C ₁₁ H ₁₃ N ₃ O | C 65.01 (64.97) H 6.45 (6.26) N 20.67 (20.63) |
| 6a | 168-171 (e) dec. | 53 | C ₁₆ H ₁₅ N ₃ O | C 72.43 (72.45) H 5.70 (5.76) N 15.84 (15.66) |
| 6b | 198-200 (f) dec. | 40 | C ₁₁ H ₁₃ N ₃ O | C 65.01 (64.92) H 6.45 (6.45) N 20.67 (21.00) |
| 6c | 196-199 (f) dec. | 39 | C ₁₁ H ₁₃ N ₃ O ·½H ₂ O | C 62.24 (61.96) H 6.65 (6.49) N 19.80 (19.76) |
| 7a | 104-107 (d) | 60 | C ₁₇ H ₁₇ N ₃ O | C 73.10 (73.05) H 6.13 (6.19) N 15.04 (14.80) |
| 7b | 118-121 at 0.04 mm Hg | 55 | C ₁₂ H ₁₅ N ₃ O | C 66.34 (66.61) H 6.96 (7.09) N 19.34 (19.04) |
| 7c | 153-155 at 0.05 mm Hg | 50 | C ₁₂ H ₁₅ N ₃ O ·½H ₂ O | C 63.69 (63.72) H 7.13 (6.99) N 18.57 (18.61) |

(a) From benzene; lit. (4) 203-204. (b) From benzene. (c) From benzene/light petroleum. (d) From cyclohexane. (e) From ethyl acetate/ethanol 3:1 (v/v). (f) From ethanol/ether.

Table IV

1,2,4-Triazin-6(1H)ones **8** and **9**

| Compound | M.p. (°C) | Yield (%) | Formula | Analysis Calcd. (Found) | Ir (Potassium Bromide) ν max cm^{-1} | Nmr (δ in Deuteriochloroform) | Uv λ max (log ϵ) nm |
|-----------|------------------------------|-----------|--|---|--|---|--|
| 8a | 218-220 lit. (5), 223 | 80 | ----- | ----- | ----- | ----- | ----- |
| 8b | 225-227 (a) | 57 | $\text{C}_{10}\text{H}_9\text{N}_3\text{O}$ | C 64.16 (64.31) H 4.85 (4.87) N 22.45 (22.48) | 3200-2500 br 1660 | 2.45 (3H, s, CH_3) 7.40-7.60, 7.97-8.17 (5H, m, C_6H_5) 13.20-13.60 (1H, br, NH (b)) | 315 (3.35) 263 (4.32) |
| 8c | 171-172 (a) lit. (6), 253 | 53 | $\text{C}_{10}\text{H}_9\text{N}_3\text{O}$ | C 64.16 (64.01) H 4.85 (4.85) N 22.45 (22.30) | 3300-2300 br 1650 | 2.53 (3H, s, CH_3) 7.35-7.66, 8.50-8.72 (5H, m, C_6H_5) 12.70-13.00 (1H, br, NH (b)) | 333 (3.98) 277 (3.75) 226 (3.78) |
| 9a | 114-116 | 79 | $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}$ | C 72.99 (72.70) H 4.98 (4.88) N 15.96 (15.92) | 1660 | 3.83 (3H, s, NCH_3) 7.32-7.60, 8.09-8.32 and 8.55-8.75 (10H, m, C_6H_5) | 360 (3.89) 275 (4.44) 238 (4.10) 233 (4.10) |
| 9b | 94-96 (a) | 56 | $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$ | C 65.66 (65.35) H 5.51 (5.45) N 20.88 (20.87) | 1660 | 2.54 (3H, s, CH_3) 3.70 (3H, s, NCH_3) ⁻ 7.24-7.45, 7.95-8.15 (5H, m, C_6H_5) | 320 (3.48) 265 (4.33) |
| 9c | 84-86 | 74 | $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$ | C 65.66 (65.39) H 5.51 (5.68) N 20.88 (21.13) | 1645 | 2.44 (3H, s, CH_3) 3.69 (3H, s, NCH_3) 7.25-7.55, 8.35-8.62 (5H, m, C_6H_5) | 337 (4.13) 278 (3.87) 225 (3.92) |

(a) In a sealed tube. (b) Signal disappears on deuteration.

Ethyl α -[(Ethoxyphenylmethylene)amino]benzeneacetate (**3a**).

This compound had b.p. 136-138° at 0.06 mm Hg, yield 53% based on the unrecovered starting material.

Ethyl α -[(Ethoxyphenylmethylene)amino]propionate (**3b**).

This compound had b.p. 98-100° at 0.06 mm Hg, yield 80% based on the unrecovered starting material.

Ethyl α -[(Ethoxyethylidene)amino]benzeneacetate (**3c**).

This compound had b.p. 120-122° at 0.15 mm Hg, yield 30%.

Reaction of the Iminoesters **3a-c** with Hydrazine.

A solution of the iminoester (0.01 mole) in propanol (6 ml.) and 98% hydrazine hydrate (0.01 mole) was refluxed for 90 minutes. Water (4 ml.) was added to precipitate 1,2,4-triazin-6(1H)-ones **4a-c** which were crystallized as reported in Table III.

Reaction of the Iminoesters **3a-c** with Methylhydrazine.

A solution of the iminoester (0.01 mole) and methylhydrazine (0.01 mole) in propanol (6 ml.) was refluxed for two hours. The solvent was evaporated *in vacuo* and the oily residue chromatographed on silica gel. Elution of the column with chloroform-methanol (95:5 v/v) gave 1-methyl-1,2,4-triazin-6(1H)-ones **5a-c**; further elution with methanol gave 2-methyl-1,2,4-triazin-6(1H)-ones **6a-c**. Yields, solvents of crystallization, melting points and analytical data are reported in Table III.

Reaction of the Iminoesters **3a-c** with 1,2-Dimethylhydrazine.

A mixture of the iminoester (0.01 mole) and 1,2-dimethylhydrazine (0.02 mole) was heated at 120° in a sealed tube for one hour. The solution was kept *in vacuo* on concentrated sulphuric acid and the residue chromatographed on silica gel. Elution of the column with ether gave a small amount of material which was discarded. Further elution with ethanol afforded 1,2-dimethyl-1,2,4-triazin-6(1H)-ones **7a-c** which were purified as reported in Table III.

Treatment of 2-Methyl-1,2,4-triazin-6-ones **6a-c** with Diazomethane.

To the triazinones **6a-c** (0.005 moles) in methanol (50 ml.), ethereal diazomethane (0.015 mole) was added. After 12 hours the solvents were removed *in vacuo* and the oily residue resolved into two components by preparative layer chromatography (aluminum oxide F-254 Merck) with ether as developer. The fastest running band afforded 6-methoxy-1,2,4-triazines **10a-c** as oils which were purified by sublimation or distillation *in vacuo*.

3,5-Diphenyl-6-methoxy-2-methyl-2,5-dihydro-1,2,4-triazine (**10a**).

This compound had m.p. 65-69° (40% yield) after sublimation at 50° and 0.05 mm Hg.

Anal. Calcd. for C₁₇H₁₇N₃O: C, 73.10; H, 6.13; N, 15.04. Found: C, 73.55; H, 6.19; N, 14.79.

2,5-Dimethyl-6-methoxy-3-phenyl-2,5-dihydro-1,2,4-triazine (**10b**).

This compound had b.p. 92-93° (30% yield) at 0.05 mm Hg.

Anal. Calcd. for C₁₂H₁₅N₃O: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.34; H, 6.98; N, 19.24.

2,3-Dimethyl-6-methoxy-5-phenyl-2,5-dihydro-1,2,4-triazine (**10c**).

This compound had b.p. 98-99° (35% yield) at 0.06 mm Hg.

Anal. Calcd. for C₁₂H₁₅N₃O: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.05; H, 7.11; N, 19.17.

The second band yielded 1,2-dimethyl-1,2,4-triazin-6(1H)-ones **7a-c** (**7a**: 35%; **7b**: 30%; **7c**: 16%) which were purified as reported in Table III.

Oxidation of 4,5-Dihydro-1,2,4-triazin-6(1H)-ones **4a-c** and **5a-c**.

The triazinone (0.001 mole) dissolved or suspended in *N* sodium hydroxide (10-15 ml.) was treated with an excess of sodium hypochlorite 1.05% v/v and the reaction mixture was stirred at room temperature for 12 hours. Whereas the triazinones **9a-c** were directly collected by filtration or by extraction with chloroform the triazinones **8a-c** crystallized from the reaction mixture by acidification to pH 4. All compounds obtained were purified by sublimation *in vacuo*. Melting points, yields, analytical and spectroscopic data are reported in Table IV.

Reaction of the 1,2,4-Triazin-6(1H)-ones **8a-c** with Diazomethane.

To a solution of the triazinone (0.001 mole) in ether (10 ml.) and methanol (5 ml.), ethereal diazomethane (0.002 mole) was added. After 12 hours the solvents were removed *in vacuo* and the residue gave the 1-methyl-1,2,4-triazin-6(1H)-ones **9a-c** in almost quantitative yield.

Catalytic Hydrogenation of the 1,2,4-Triazin-6(1H)-ones **8a-c** and **9a-c**.

A mixture of the triazinones **8a-c** and **9a-c** (0.001 mole), 10% palladium on charcoal (100 mg.) and ethanol (15 ml.) were shaken under hydrogen at room temperature and atmospheric pressure. After the absorption of the calculated amount of hydrogen, the catalyst was filtered off and the solvent evaporated *in vacuo* to give in almost quantitative yield 4,5-dihydro-1,2,4-triazin-6(1H)-ones **4a-c** and **5a-c**, which were purified as reported as above.

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