Investigation of Routes to Indeno[2,1-*f*]-2*H*-1,2,4-triazepinediones

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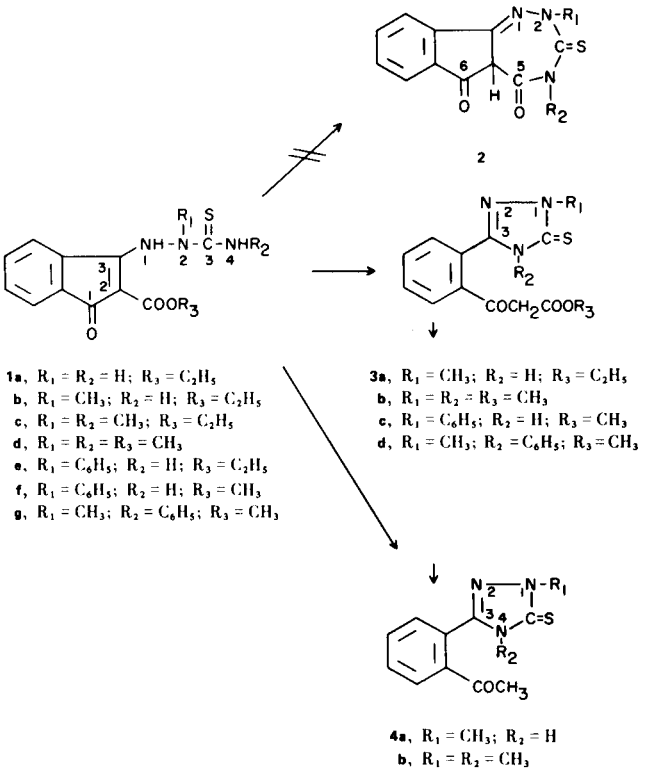
The synthesis of a number of 3-(substituted thiosemicarbazido)-2-(alkoxycarbonyl)indones (**1**) from 2-alkoxycarbonyl-1,3-indandiones and substituted thiosemicarbazides is described. Cyclization of compounds **1** in the presence of a variety of catalysts gave substituted Δ^2-1,2,4-triazoline-5-thiones (**3**) and (**4**), instead of the expected substituted 3(4*H*)-thioxoindeno[2,1-*f*]-2*H*-1,2,4-triazepine-5(5a*H*),6-diones (**2**). The preparation of 4-(2-methyl-1,3-dioxo-2-indanylmethyl)semicarbazide (**9**) is reported. Cyclization of **9** gave 5,5a-dihydro-5a-methylindeno[2,1-*f*]-2*H*-1,2,4-triazepine-3(4*H*),6-dione (**10**). Structure assignments of these compounds are discussed.

As part of our interest in the chemistry of ring fused 1,3-indandione systems (1-3), we studied the preparation of compounds containing the 1,2,4-triazepine moiety fused to the indane ring, namely the indeno[2,1-*f*]-2*H*-1,2,4-triazepinediones. Two routes have been investigated: (a) cyclization of 3-(substituted thiosemicarbazido)-2-(alkoxycarbonyl)indones (**1**) and (b) cyclization of 4-(2-methyl-1,3-dioxo-2-indanylmethyl) semicarbazide (**9**).

SCHEME I



(a) Cyclization of indones **1**.

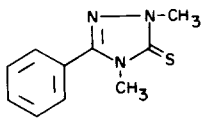
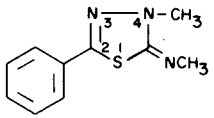
Following the route developed by Loss, Hessler and Barth (4) for the preparation of substituted 2,6-dihydro-5*H*-1,2,4-triazepin-5-ones, we attempted the preparation of substituted 3(4*H*)-thioxoindeno[2,1-*f*]-2*H*-1,2,4-triazepine-5(5a*H*),6-diones (**2**) as outlined in Scheme I.

3-(Substituted thiosemicarbazido)-2-(alkoxycarbonyl)-indones (**1a-g**) were prepared in yields varying from 23 to 63% by reacting the sodium salts of 2-alkoxycarbonyl-1,3-indandiones with the appropriate thiosemicarbazide in cold aqueous alcoholic solutions or in dimethylformamide in the presence of hydrochloric acid. The product of this reaction may exist as a mixture of compound **1** and its tautomer, the substituted thiosemicarbazone of 2-alkoxycarbonyl-1,3-indandione. Spectral and chemical evidence favor structure **1** as being predominant if not exclusive.

The indones **1b-g** when refluxed in alcoholic solution under a variety of acidic, basic and neutral conditions gave substituted Δ^2-1,2,4-triazoline-5-thiones (**3**), instead of the expected 3(4*H*)-thioxoindeno[2,1-*f*]-2*H*-1,2,4-triazepine-5(5a*H*),6-diones (**2**). The catalyst generally used was sodium methoxide and the yields varied from 46 to 86%. Compound **1a** did not form an isolable product. The triazolinethiones **3** when refluxed for 7 hours in aqueous alcoholic solutions in the presence of potassium carbonate or when refluxed for 0.5 hour in aqueous methanolic hydrochloric acid solutions gave substituted 3-(*o*-acetylphenyl)-Δ^2-1,2,4-triazoline-5-thiones (**4**). These compounds were also obtained directly from the indones **1** by refluxing in aqueous ethanolic solutions in the presence of potassium carbonate. The structures assigned to compounds **3** and **4** are supported by elemental analyses and by the infrared, ultraviolet, and nuclear magnetic resonance spectra (Table

TABLE I

Spectral Data of Triazolinethiones and Related Compounds

Compound	Infrared Spectrum (cm^{-1}) (a) NH	C=O	C=S I	C=S II	C=S III	Ultraviolet Spectrum λ max mμ	Ultraviolet Spectrum $\epsilon \times 10^{-3}$	Nuclear Magnetic Resonance Field Positions 1-NCH_3 (b)	Nuclear Magnetic Resonance Field Positions 4-NCH_3 (b)
1d	3350 3250	1725 1690 1660	1490	1300 1355	1155	259	30.8	3.78 (c)	3.38 (c)
3a	3160	1760 1725	1480	1330	1160	255	22.0	3.73 3.78	
3b		1745 1700	1480	1330	1165	251	22.0	3.74 3.78	3.34 3.37
4a	3300	1670	1490	1368	1130	253.5	21.0	3.80	
4b		1690	1490	1360	1155	250	29.0	3.82	3.31
5 			1475	1360	1150	255 220	16.0 11.0	3.86	3.65
6 			1440 (d)	1340 (d)		323 233	12.0 14.0	3.55	3.07 (e)

(a) Thiol absorption at 2500-2600 cm^{-1} is absent in all spectra. (b) Position in the heterocyclic ring, except in compound **6**. (c) Dimethylformamide was used as solvent. Groups - NCH_3 are in positions 2 and 4 of the thiosemicarbazido radical. (d) Appropriate bands included for comparison. (e) Band of the 5-methylimino group.

1). For comparison, the spectral data of the model compounds: 1,4-dimethyl-3-phenyl-Δ^2-1,2,4-triazoline-5-thione (**5**) and the known 4-methyl-5-methylimino-2-phenyl-Δ^2-1,3,4-thiadiazoline (5) (**6**), are also listed in Table I.

The occurrence in the infrared spectrum of strong bands in all three coupled vibrational regions attributed to the -N-C=S grouping (6) and of bands in the regions attributed to ester and keto carbonyl groupings agrees with the assigned structures **3** and **4**. The infrared and ultraviolet spectral similarities of compounds **3** and **4** to triazolinethione **5** and the spectral dissimilarities to thiadiazoline **6** substantiates that the ring system formed is a triazoline rather than a thiadiazoline.

The nuclear magnetic resonance spectra show that the chemical shift of the two N-CH_3 groups in compounds **1d**, **3b** and **4b** is essentially constant. This indicates constant shielding of these methyl protons and points to a continuity of the grouping -N(CH_3)-N(=S)-C(=N-)-. The presence of the grouping -N(CH_3)-N(=NCH_3)-C(-)-S- would presumably lead to different shielding. The chemical shift of the 1-NCH_3 group is relatively constant in compounds **4** and in model triazolinethione **5**. Apparently there is an interaction between the *ortho* acetyl group and the 4-NCH_3 group in compound **4b**, since its signal is at lower field position than that of the same group in triazolinethione **5**. The presence of the ketoester group, arising from indane ring opening, in triazolinethiones **3** is confirmed by comparison of their nmr spectra with that of ethyl benzoylacetate as the model compound.

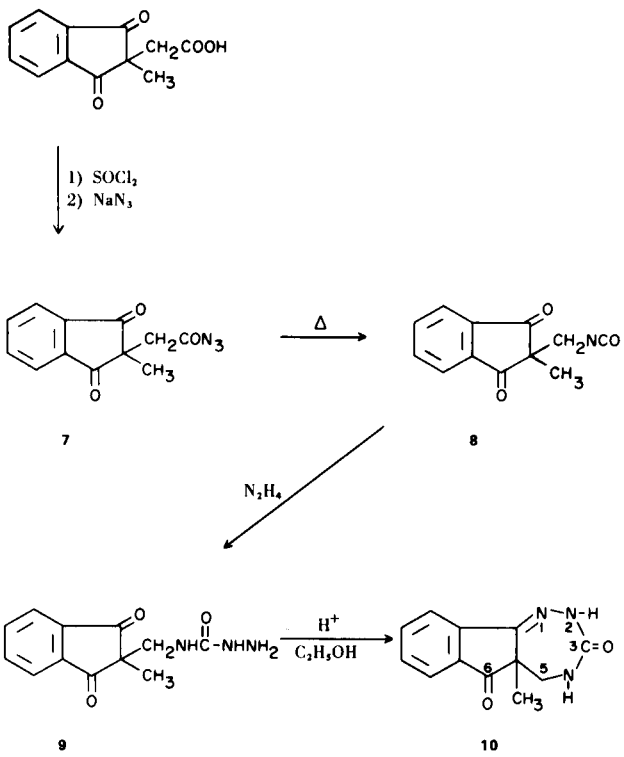
(b) Cyclization of 4-(2-Methyl-1,3-dioxo-2-indanylmethyl)-semicarbazide (**9**).

This route to compounds containing the 1,2,4-triazepine moiety fused to the indane ring is outlined in Scheme II. The azide **7** was obtained by adding a solution of 2-methyl-1,3-dioxo-2-indanacetyl chloride, prepared from the corresponding known acid (7), to a chilled aqueous acetone solution of sodium azide. The corresponding isocyanate **8** was formed by refluxing the azide **7** in toluene. Application of the technique used by Van Gelderen (8) for preparing 4-(4-biphenyl) semicarbazide, allowed us to obtain the carbazide **9**, which by acid catalyzed cyclization gave 5,5a-dihydro-5a-methylindeno[2,1-*f*]-2*H*-1,2,4-triazepine-3(4*H*),6-dione (**10**) in over 60% yield.

Evidence for the structure assigned to **10** is provided by elemental analyses and by infrared and ultraviolet spectra. The infrared spectrum of **10** shows the presence of two NH functions in different environments. The absence of a doublet in the NH region precludes the possibility of a structure with an $-NH_2$ function. In the carbonyl region there is a strong band at 1725 cm^{-1} and two less intense bands at 1690 and 1670 cm^{-1}. The absence of a band at 1750 cm^{-1}, present as part of the doublet in almost all non-enolizing 1,3-indandiones (9), as well as cyclic anhydrides, cyclic imides and cyclopentene-3,5-dione (10), suggests that the 1,3-diketo structure is no longer present.

The bands in the ultraviolet spectra of α,β-unsaturated ketones, normally in the 220-260 mμ range, are shifted to longer wave lengths (*ca.* 265 mμ) upon semicarbazone formation (11). Comparison of the absorption bands of semicarbazide **9** with those of triazepinedione **10** suggests that semicarbazone formation occurred since the bands in the spectrum of compound **9** have been displaced to longer wave lengths in the spectrum of compound **10**.

SCHEME II



EXPERIMENTAL (12)

3-Thiosemicarbazido-2-(ethoxycarbonyl)indone (**1a**).

A solution of thiosemicarbazide (1.82 g., 0.02 mole) in water (40 ml.), ethanol (40 ml.) and 5% hydrochloric acid (14.2 ml., 0.02 mole), cooled to 0°, was added to a solution of 4.8 g. (0.02 mole) of sodium 2-ethoxycarbonyl-1,3-indandione (13) (the sodium salt was used in all the preparations of compounds **1a-g**, because the free ester is stable only in cold solution and cannot be stored in the solid state) in water (40 ml.) and ethanol (50 ml.), cooled to 0°. After 1 hour the formed yellow needles were collected by filtration to give 3.61 g. (62%) of **1a**, which after purification by dissolving it in dimethylformamide and precipitating with ethanol,

melted at 187°; ir 3550, 3400, 3350, 3200 and 1685 cm^{-1}.

Anal. Calcd. for $C_{13}H_{13}N_3O_3S$: C, 53.59; H, 4.50. Found: C, 52.78; H, 4.61.

3-(2-Methylthiosemicarbazido)-2-(ethoxycarbonyl)indone (**1b**).

A solution of 2-methylthiosemicarbazide (14) (7.83 g., 0.0746 mole) in ethanol (100 ml.), water (100 ml.) and 5% hydrochloric acid (53 ml., 0.0746 mole), cooled to 0° was added to a solution of sodium 2-ethoxy-carbonyl-1,3-indandione (13) (17.9 g., 0.0746 mole) in water (130 ml.) and ethanol (130 ml.), cooled to 0°. After standing in a refrigerator for 6 days, the yellow needles were collected by filtration to give 14.29 g. (63%) of crude **1b**, m.p. 202-203°. Addition of ethanol to a solution of this crude product in dimethylformamide gave **1b**, m.p. 209.5-210.5°; ir 3400, 3220 (NH); 1730, 1690, 1660 (C=O); 1480, 1355, 1300 and 1153 cm^{-1} (C=S); uv λ max mμ 262, (ε, 27,000).

Anal. Calcd. for $C_{14}H_{15}N_3O_3S$: C, 55.06; H, 4.95; N, 13.76; S, 10.50. Found: C, 55.11; H, 4.68; N, 13.97; S, 10.90.

3-(2,4-Dimethylthiosemicarbazido)-2-(ethoxycarbonyl)indone (**1c**).

By using the above procedure, from sodium 2-ethoxycarbonyl-1,3-indandione (13) (2.4 g., 0.01 mole) and 2,4-dimethylthiosemicarbazide (15) (1.19 g., 0.01 mole) there was obtained a 63% yield of **1c**, as small yellow needles m.p. 167.5-168.5°; ir 3350, 3250 (2 NH bands indicative of 2 NH groups (16)), 1725, 1690, 1660 (C=O), 1490, 1355, 1300, 1155 cm^{-1} (C=S); nmr (dimethylformamide as solvent) at δ 4.36 (2 NH protons), 3.87 (OCH_3), 3.78 and 3.38 ppm ($-NCH_3$) and complete absence of methine proton. The ferric chloride enol test was negative.

Anal. Calcd. for $C_{15}H_{17}N_3O_3S$: C, 56.42; H, 5.06; N, 13.16; S, 10.03. Found: C, 56.08; H, 5.06; N, 13.66; S, 10.30.

3-(2,4-Dimethylthiosemicarbazido)-2-(methoxycarbonyl)indone (**1d**).

Following the above procedure, from sodium 2-methoxycarbonyl-1,3-indandione (13) (4.46 g., 0.02 mole) and 2,4-dimethylthiosemicarbazide (15) (2.38 g., 0.02 mole) there was obtained a 56% yield of **1d**, as small yellow needles, m.p. 170-171°; ir and nmr spectra were identical with those of **1c**.

3-(2-Phenylthiosemicarbazido)-2-(ethoxycarbonyl)indone (**1e**).

To a solution of sodium 2-ethoxycarbonyl-1,3-indandione (13) (2.4 g., 0.01 mole) in dimethylformamide (10 ml.) was added a solution of 2-phenylthiosemicarbazide (17) (1.67 g., 0.01 mole) in dimethylformamide (10 ml.). The mixture was cooled to 0° diluted with cold 5% hydrochloric acid (7.1 ml., 0.01 mole) and kept in a refrigerator for 5 days to give 1.35 g. (38%) of crude **1e**, m.p. 185°. Purification by diluting a dimethylformamide solution of this crude product with methanol gave **1e** as yellow needles m.p. 190.5-191°; ir 3380, 3220 (NH), 1730, 1690, 1650 (C=O), 1490, 1350, 1310, 1155 cm^{-1} (C=S).

Anal. Calcd. for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44; S, 8.73. Found: C, 62.11; H, 4.52; N, 11.63; S, 8.55.

3-(2-Phenylthiosemicarbazido)-2-(methoxycarbonyl)indone (**1f**).

Following the above procedure, from 0.01 mole of sodium 2-methoxycarbonyl-1,3-indandione (13) and 0.01 mole of 2-phenylthiosemicarbazide (17) there was obtained a 23% yield of **1f** as orange needles, m.p. 186-188°; ir spectrum identical with that of the above ethyl ester **1e**.

3-(2-Methyl-4-phenylthiosemicarbazido)-2-(methoxycarbonyl)-indone (**1g**).

To a solution of sodium 2-methoxycarbonyl-1,3-indandione (13) (2.26 g., 0.01 mole) in dimethylformamide (20 ml.) and water (3 ml.), chilled to -4°, was added a solution of 2-methyl-4-phenylthiosemicarbazide (15) (1.81 g., 0.01 mole) in a mixture of methanol (5 ml.), dimethylformamide (4 ml.) and concentrated hydrochloric acid (0.82 g., 0.01 mole), also chilled to -4°. After 8 days in a refrigerator, the precipitate was collected by filtration to give 0.936 g. (25%) of **1g** of crude product, m.p. 167-169°. Purification by diluting with methanol a dimethylformamide solution of the crude product gave **1g** as yellow needles m.p. 168.5°.

Anal. Calcd. for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44; S, 8.73. Found: C, 62.02; H, 4.60; N, 11.32; S, 8.68.

3-[(*o*-Ethoxycarbonylacetyl)phenyl]-4-methyl-Δ^2-1,2,4-triazoline-5-thione (**3a**).

To a solution of sodium (0.53 g., 0.023 g.-atom) in absolute methanol (70 ml.) was added **1b** (1.382 g., 0.00453 mole). After 5 days at room temperature acetic acid (1.4 ml., 0.0245 mole) was added. The reaction mixture was concentrated under reduced pressure and the residue mixed with ether containing methanol. After separation of an insoluble yellow powder by filtration, the filtrate was diluted with water and extracted three times with ether. The extracts were shaken with brine, dried over magnesium sulfate, concentrated and the residue crystallized from benzene ("Darco") to give 0.646 g. (46%) of **3a** as colorless crystals. Elution in benzene from an alumina column and recrystallization from benzene gave 0.526 g. (38%) of **3a**, m.p. 150.5-151°; nmr shows peaks at δ 5.43 and 3.97 ppm, beside the peaks listed in Table I. Ethyl benzoylacetate shows peaks at δ 5.65 and 3.97 ppm (CH_2 group between the carbonyl and the ester groups). In the presence of deuterium oxide the CH_2 signals of compound **3a** and of ethyl benzoylacetate (for this compound an equivalent of pyridine was present) diminish slowly and disappear completely after 2 hours.

Anal. Calcd. for $C_{14}H_{15}N_3O_3S$: C, 55.06; H, 4.95; N, 13.76; S, 10.50. Found: C, 55.10; H, 4.78; N, 14.01; S, 10.64.

Compound **3a** was obtained also (yield 29%) by stirring for 12 hours at 100° a mixture of **1b** (0.5 g., 0.00164 mole), acetic acid (10 ml.) and ethanol (5 ml.), evaporating the solvents under reduced pressure and crystallizing the residue from 2-propanol. The ir spectrum was almost identical to that of **3a** prepared by the above method.

3-[(*o*-Methoxycarbonylacetyl)phenyl]-1,4-dimethyl-Δ^2-1,2,4-triazoline-5-thione (**3b**).

To a solution, obtained by refluxing for 18 hours a mixture of calcium hydride (1.26 g., 0.03 g.-atom) in anhydrous 2-propanol (50 ml.), was added at room temperature **1d** (1 g., 0.00328 mole) and the mixture stirred for 6 hours with exclusion of moisture. Filtration, acidification of the filtrate with 5% hydrochloric acid (42.6 ml., 0.06 mole), extraction with ether, evaporation of the ether and treatment of the oily residue with cold, dilute acetic acid gave 0.8413 g. (67%) of **3b** as yellow powder, m.p. 115.5-116.5°.

Anal. Calcd. for $C_{14}H_{15}N_3O_3S$: C, 55.06; H, 4.95; N, 13.76; S, 10.50. Found: C, 54.99; H, 4.80; N, 13.66; S, 10.58.

Compound **3b** was obtained also (yield 86%) by refluxing for 22 hours a solution of **1d** (2.17 g., 0.00712 mole) in methanol (50 ml.), concentrating under reduced pressure and recrystallizing the residue from 2-propanol, m.p. 115.5-116.5°.

Compound **3b** was recovered unchanged after standing 1 hour at room temperature in 10% sodium hydroxide solution or after refluxing in acetic anhydride. Treatment of **3b** with sodium hydride and then with methyl iodide gave back the starting material.

3-[(*o*-Methoxycarbonylacetyl)phenyl]-4-phenyl-Δ^2-1,2,4-triazoline-5-thione (**3c**).

Following the method described above for **3a**, from **1f** (0.4 g.,

0.0011 mole) and a solution of sodium (0.017 g.-atom) in methanol (43 ml.) there was obtained 0.335 g. (84%) of **3c** as pale yellow needles, m.p. 150-151°. Recrystallization from benzene gave 0.2319 g. (58%) of **3c**, m.p. 161.5-162.5°; ir 3110, 1750, 1715, 1470, 1450, 1330, 1160 cm^{-1}; uv λ max mμ 289, (ε, 16,000).

Anal. Calcd. for $C_{18}H_{15}N_3O_3S$: C, 61.12; H, 4.28; N, 11.89; S, 9.07. Found: C, 60.97; H, 4.56; N, 12.22; S, 8.96.

3-[(*o*-Methoxycarbonylacetyl)phenyl]-1-methyl-4-phenyl-Δ^2-1,2,4-triazoline-5-thione (**3d**).

A solution of **1g** (0.5 g., 0.00136 mole) in methanol (50 ml.) was refluxed 22 hours, concentrated under reduced pressure and crystallized from benzene-petroleum ether (b.p. 75-90°) to give 0.413 g. (83%) of **3d** as white prisms m.p. 133-133.5°; ir 1740, 1690, 1440, 1340, 1160 cm^{-1}; uv λ max mμ 230-245, (ε, 17,000).

Anal. Calcd. for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44; S, 8.73. Found: C, 62.31; H, 4.72; N, 11.56; S, 8.83.

3-(*o*-Acetylphenyl)-1-methyl-Δ^2-1,2,4-triazoline-5-thione (**4a**) from Indone **1b**.

A mixture of **1b** (2.87 g., 0.0094 mole), potassium carbonate hydrate ($K_2CO_3 \cdot 1.5H_2O$; 15.5 g., 0.094 mole), ethanol (140 ml.) and water (140 ml.) was refluxed for 15 hours. After removal of the alcohol under reduced pressure, the mixture was neutralized slowly with a solution of concentrated hydrochloric acid (15.6 ml., 0.188 mole) in water (50 ml.). Addition of ether gave 0.75 g. (34%) of **4a** as pink plates, m.p. 169-170.5°. Extraction of the filtrate with ether, evaporation of the solvent and crystallization from benzene gave an additional 0.783 g. (36%) of **4a** m.p. 171-172°.

Anal. Calcd. for $C_{11}H_{11}N_3OS$: C, 56.63; H, 4.75; N, 18.01; S, 13.75. Found: C, 56.67; H, 4.87; N, 17.99; S, 13.76.

Compound **4a** was recovered unchanged after refluxing for 0.5 hour in alcoholic hydrochloric acid solution or for 12 hours in sodium methoxide methanolic solution. Treatment of **4a** with methyl iodide in ethyl acetate or in potassium carbonate gave starting material or dark oil, respectively. Treatment of a solution of **4a** (0.466 g., 0.002 mole) in ethanol (50 ml.) with 85% hydrazine hydrate (0.115 ml., 0.002 mole) at reflux for 3 hours gave 0.256 g. (52%) of the corresponding hydrazone, as light tan prisms, m.p. 254° (benzene-petroleum ether); ir 3400, 3260 (NH) and 1620 (C=N) cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}N_5S$: C, 53.42; H, 5.30; N, 28.32; S, 12.91. Found: C, 54.04; H, 5.45; N, 27.62; S, 12.61.

From Triazoline **3a**.

A mixture of **3a** (0.305 g., 0.001 mole), ethanol (20 ml.), water (20 ml.) and potassium carbonate hydrate ($K_2CO_3 \cdot 1.5H_2O$; 1.65 g., 0.01 mole) was refluxed for 7.5 hours. After concentration under reduced pressure and neutralization in the cold with 14.2 ml. (0.02 mole) 5% hydrochloric acid, the mixture was extracted with ether. The combined ether extracts were washed with water and brine, dried over anhydrous magnesium sulfate, concentrated, and the residue crystallized from benzene-petroleum ether (b.p. 75-90°) to give 0.1754 g. (75%) of **4a**, as slightly pink plates, m.p. 169.5-170.5°. The infrared spectrum was identical to that of **4a** prepared from compound **1b** as described above.

3-(*o*-Acetylphenyl)-1,4-dimethyl-Δ^2-1,2,4-triazoline-5-thione (**4b**) from Indone **1d**.

A mixture of **1d** (0.73 g., 0.0024 mole), methanol (40 ml.), water (40 ml.) and potassium carbonate hydrate ($K_2CO_3 \cdot 1.5H_2O$; 3.96 g., 0.024 mole) was refluxed for 5.5 hours. Distillation of the methanol under reduced pressure, neutralization of the residue with 5% hydrochloric acid (34.1 ml., 0.048 mole) and cooling yielded 0.5 g. (85%) of **4b**, as gray crystalline powder. Recrystallization from benzene petroleum ether (b.p. 75-90°) gave 0.376 g. (64%) of **4b** as colorless prisms, m.p. 152-153°.

Anal. Calcd. for $C_{12}H_{13}N_3OS$: C, 58.27; H, 5.30; N, 16.99; S, 12.96. Found: C, 58.45; H, 5.26; N, 16.95; S, 12.92.

From Triazoline **3b**.

A mixture of **3b** (0.84 g., 0.00275 mole), methanol (20 ml.), concentrated hydrochloric acid (5 ml.) and water (5 ml.) was refluxed for 0.5 hour, then cooled and neutralized with a dilute aqueous sodium hydroxide solution. After cooling in a refrigerator, the formed precipitate was collected by filtration to give 0.318 g. (47%) of **4b**. The infrared spectrum was identical to that of **4b**, obtained from indone **1d**, as described above.

1,4-Dimethyl-3-phenyl-Δ^2-1,2,4-triazoline-5-thione (**5**).

A solution of 1-benzoyl-2,4-dimethylthiosemicarbazide (5) (1.0 g., 0.0048 mole) in ethanol (30 ml.) containing sodium ethoxide (0.015 mole) was refluxed for 3.75 hours. Filtration of the solid which separated on cooling yielded 0.86 g. (94%) of **5** as fine white needles, m.p. 134.5°.

Anal. Calcd. for $C_{10}H_{11}N_3S$: C, 58.51; H, 5.40; N, 20.47; S, 15.62. Found: C, 58.44; H, 5.25; N, 20.39; S, 15.61.

2-Methyl-1,3-dioxo-2-indanacetyl Azide (**7**).

A mixture of 2-methyl-1,3-dioxo-2-indanacetic acid (7) (1.5 g., 0.0063 mole) and thionyl chloride (15 ml., 0.204 mole) was stirred at room temperature for 17 hour period. The excess of thionyl chloride was removed under reduced pressure, the residue was dissolved in dry acetone (3 ml.) and the solution obtained added over a 20 minute period to a chilled (ice-water bath) solution of sodium azide (0.6 g., 0.009 mole) in acetone (2 ml.) and water (4 ml.). The mixture was stirred for an additional 50 minutes, then poured into water (100 ml.), stirred for 30 minutes and the precipitate collected by filtration to give 1.494 g. (97%) of **7**, m.p. 73-75° dec. Recrystallization from benzene-petroleum ether (b.p. 75-90°) yielded 0.975 g. (62%) of **7**, ir shows a band at 2150 cm^{-1} (azide) and two bands at 1750 and 1710 cm^{-1} (carbonyl).

Anal. Calcd. for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.40; H, 3.80; N, 17.15.

4-(2-Methyl-1,3-dioxo-2-indanylmethyl)semicarbazide (**9**).

A solution of **7** (0.672 g., 0.0027 mole) in dry toluene (10 ml.) was refluxed 20 minutes to form the isocyanate **8** *in situ*, then added over a 45 minute period to a cold (ice-salt bath) solution of 100% hydrazine hydrate (1.34 ml., 0.0275 mole) in ethanol (5 ml.). Solvent and excess hydrazine were removed under vacuum with continued chilling and the oily residue was poured onto a porous plate and allowed to solidify. Digestion with hot benzene gave 0.537 g. (79%) of **9**, m.p. 171.5° (2-propanol); ir 3420, 3280, 3100, 1750, 1705, 1660 cm^{-1}; uv λ max mμ (ε) 224.5 (24,000), 244 (10,000), 290 (1,400).

Anal. Calcd. for $C_{12}H_{13}N_3O_3$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.19; H, 5.21; N, 16.80.

5,5a-Dihydro-5a-methylindeno[2,1-*f*]-2*H*-1,2,4-triazepine-3(4*H*),6-dione (**10**).

To a solution of **9** (100 mg., 0.405 mmole) in absolute ethanol (160 ml.) was added concentrated hydrochloric acid (0.5 ml.) and the mixture refluxed for 1 hour. The residue, obtained by directing a stream of air on the surface of the reaction mixture, was mixed with water and the precipitate collected by filtration, washed and dried to give 59.3 mg. (64%) of a light tan powder, m.p. 255-260°. Two recrystallizations from methanol gave **10** as small white prisms,

m.p. 283-285°; ir 3320, 3200, (NH), 1725, 1690, 1670 (C=O) and 1635 cm^{-1} (C=N); uv λ max mμ (ε) 241 (20,000), 297 (13,000), 348 (2,000) and 365 (1,100). Neither the nmr spectrum nor the molecular weight could be obtained because of the very low solubility of compound **10** in dimethylformamide, dimethylsulfoxide-d, chloroform and camphor.

Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.88; H, 4.84; N, 18.33. Found: C, 62.72; H, 4.92; N, 18.11.

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