Synthesis of 3,5-Disubstituted-4,5-dihydroindeno[1,2-*c*][1,2]diazepin-6(1*H*)-ones

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3,5-Disubstituted 4,5-dihydroindeno[1,2-*c*][1,2]diazepin-6(1*H*)-ones (**3a-g**) were obtained in 29-72% yields by condensing 2-(substituted-2-acylethyl)-1,3-indandiones (**1a-n**) with hydrazine. The NH group of the indenodiazepinones **3a-g** is quite unreactive. Two methods based on the Michael reaction were used for preparing the acylethylindandiones **1a-n**: one from 1,3-indandione and chalcone-type compounds and the other from 2-benzylidene-1,3-indandione and acetophenones. The latter method was found more practical and of more general application.

In preceding papers the reaction of 2-acyl-1,3-indandiones with hydrazine was investigated (1,2). Formation of 2-acyl-1,3-indandione monohydrazones and of indeno[1,2-*c*]pyrazol-4(1*H*)-ones was observed. We now report the reaction of 2-acylethyl-1,3-indandiones (**1a-n**, Scheme I) with hydrazine to form a new indenodiazepine ring system.

Relatively little work has been done on the cyclization of 1,5-dicarbonyl compounds with hydrazine to form 1,2-diazepines and in several instances the structures of the products have not been adequately proven (3). We found that treatment of 2-(substituted 2-acylethyl)-1,2-indandiones with hydrazine in refluxing alcohol, with or without an acid catalyst, gave directly 3,5-disubstituted 4,5-dihydroindeno[1,2-*e*][1,2]diazepin-6(1*H*)-ones (**3a-g**).

2-Acylethylindandiones **1a**, **1b** and **1m** (see Table I) were prepared by reacting 1,3-indandione with the appropriate α,β-unsaturated carbonyl compound, following the procedure described by Zalukajevs (4) for the preparation of **1a**. This method requires anhydrous conditions in order to prevent side reactions, such as the condensation of 1,3-indandione with itself to form [$\Delta^{1,2}$-biindan]-1',3,3'-trione (bindone) (5). All attempts to prepare other 2-acylethylindandiones by this procedure gave only the above trione and the unreacted α,β-unsaturated ketones.

The method developed by M. V. Ionescu and O. G. Popescu (6) for preparing 2-(2-benzoyl-1,2-diphenylethyl)-1,3-indandione (**1f**) from 2-benzylidene-1,3-indandione and 2-phenylacetophenone in the presence of sodium methoxide was found more practical and was used for the preparation of the acylethylindandiones **1c-l** and **1n**. The yields varied from 12 to 67%, the highest values having been obtained when one equivalent of base catalyst was used.

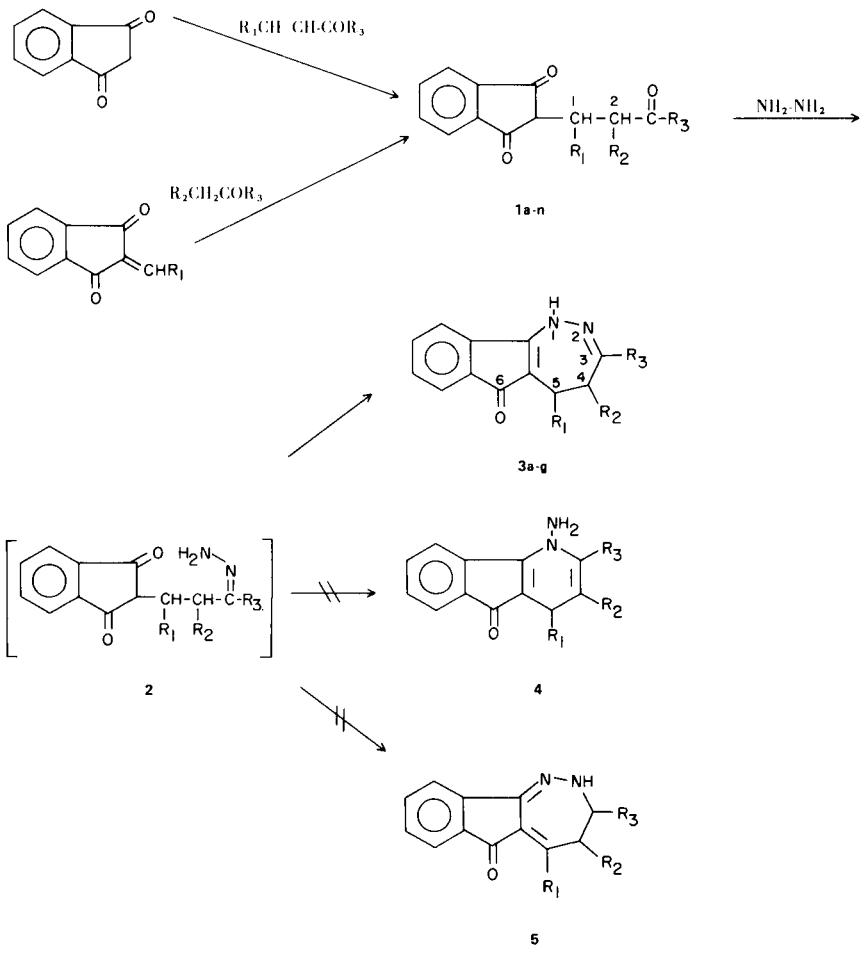
The structures of the new acylethylindandiones (**1c-e** and **1g-n**) are based upon the elemental analyses and the similarities of their uv and ir spectra with those of the known acylethylindandiones **1a**, **1b** and **1f**. The uv spectra of compounds **1a-n** show absorption bands at 227-230 mμ and at 245-291 mμ. In comparison with unsubstituted 1,3-indandione (bands at 223 and 248 mμ), the bathochromic shift to 227-230 mμ is the expected result of the presence of a 2-alkyl substituent on 1,3-indandione (7,8). The absorption band in the range 245-291 mμ is probably due to the side chain carbonyl. It is not the enhanced 248 mμ band of 1,3-indandione, as shown by the spectrum of compound **1e**, which has, in addition to the 228 and 291 mμ bands, a weak absorption at 248 mμ.

The ir spectra of the 2-acylethylindandiones **1a-n** show two carbonyl absorptions, at 5.8 and 5.9 μ, the longer wavelength one being stronger, or three carbonyl absorptions at 5.8, 5.9 and 6.0 μ, the middle one being the strongest. The first two bands are typical for the symmetric and asymmetric stretches of the indandione carbonyls. The third absorption, when not masked by the indandione carbonyls, is due to the side chain carbonyl.

Condensation of equimolar quantities of the acylethylindandiones **1** with hydrazine in refluxing ethanol gave the indenodiazepinones **3a-g** (Table II) in 29-72% yields. In some cases 2-propanol was used as the solvent and acetic acid was added as a catalyst. In this reaction, as in that between hydrazine and 2-acetyl-1,3-indandione (1), the hydrazine presumably adds to the side chain carbonyl forming the intermediate monohydrazones **2**, which then ring-close to yield compounds **3a-g**. No attempts were made to isolate the intermediate monohydrazones **2** or to determine their structures.

Several of the acylethylindandiones listed in Table I, particularly those having three aromatic rings in the side chain, did not give indenodiazepinones or any other characterizable compound. This may be due to the increased

SCHEME I



steric hindrance to the hydrazine attack on the side chain carbonyl.

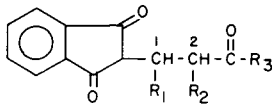
Supporting evidence for the structures of compounds **3** is provided by the elemental analyses and spectral data. The alternative structure **4** was ruled out because the ir spectra of compounds **3a-g** show a single absorption at 3.05-3.08 μ and lack the two absorption bands of a primary amino group. Further support for structure **3** instead of **4** is given by the nmr spectra of **3a** and **3b**. Both show the pattern of an AB_2 system due to the interaction of the three protons in the structure $>CH-CH_2-$.

The nmr spectra also ruled out the tautomeric structures of **3**, with the exception of structure **5**, which was discounted on the basis of the uv spectra. In fact no changes in the uv were observed when different substituents were present in R_1 (Table III), indicating that R_1 is not conjugated with any of the chromophores. If structure **5** were present, some changes would have been seen. On the other hand, changes in the uv spectra were observed, as expected, with changes in R_3. These changes would not have been observed if structure **5** were present.

Treatment of the indenodiazepinone **3b** with refluxing aqueous ethanolic sodium hydroxide solution showed no reaction. With stronger bases, such as sodium hydride, in benzene and a trace of methanol, compound **3b** gave a red solid, which by treatment with benzoyl chloride or *p*-nitrobenzoyl chloride yielded sodium chloride and the starting indenodiazepinone **3b**. Compounds **3a** and **3b** were unchanged on refluxing in 6 *N* hydrochloric acid and ethanol. All attempts to alkylate or acylate the indenodiazepinones **3a** and **3b** under varying conditions were unsuccessful. The starting materials were recovered. When alcoholic solutions of **3b** and **3e** were refluxed with excess hydrazine in the presence of acetic acid, the corresponding monohydrazones were obtained.

TABLE I

2-(Substituted-2-acylethyl)-1,3-indandiones (1a-n)

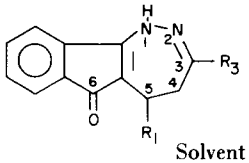


Compound	R_1	R_2	R_3	Refluxing Time, hr.	Molecular Formulas	Analyses Calcd., % C	H	N	Found, % C	H	N
1a	C_6H_5	H	CH_3	0.25	$C_{19}H_{16}O_3$	78.06	5.52	—	77.67	5.25	—
1b	C_6H_5	H	C_6H_5	(a)	$C_{24}H_{18}O_3$	81.34	5.12	—	80.95	4.87	—
1c	C_6H_5	H	p-$NO_2C_6H_4$	2	$C_{24}H_{17}NO_5$	72.17	4.29	3.51	71.74	4.04	3.72
1d	C_6H_5	H	p-$NH_2C_6H_4$	96	$C_{24}H_{19}NO_3$	78.03	5.18	3.79	78.31	5.47	3.86
1e	C_6H_5	H	p-$AcNHC_6H_4$	48	$C_{26}H_{21}NO_4$	75.89	5.15	3.40	75.47	5.20	3.45
1f	C_6H_5	C_6H_5	C_6H_5	0.5	$C_{30}H_{22}O_3$	83.70	5.15	—	83.84	5.12	—
1g	p-$NO_2C_6H_4$	C_6H_5	C_6H_5	3	$C_{30}H_{21}NO_5$	75.73	4.45	2.95	75.32	4.67	3.11
1h (b)	p-ClC_6H_4	H	C_6H_5	90	$C_{24}H_{17}ClO_3$	74.13	4.41	—	73.92	4.55	—
1i (c)	p-ClC_6H_4	H	p-$NO_2C_6H_4$	2	$C_{24}H_{16}ClNO_5$	66.44	3.72	3.23	66.07	3.74	3.16
1j (d)	p-ClC_6H_4	C_6H_5	C_6H_5	16	$C_{30}H_{21}ClO_3$	77.49	4.55	—	77.19	4.46	—
1k	p-HOC_6H_4	H	p-$NO_2C_6H_4$	5	$C_{24}H_{17}NO_6$	69.32	4.23	3.37	69.61	4.18	3.58
1l	p-$Me_2NC_6H_4$	H	p-$NO_2C_6H_4$	2	$C_{26}H_{22}N_2O_5$	70.57	5.01	6.33	70.81	5.16	6.26
1m	3-C_5H_4N	H	C_6H_5	6	$C_{23}H_{17}NO_3$	77.73	4.82	3.94	77.76	4.78	4.26
1n	C_6H_5	H	2-C_5H_4N	2.5	$C_{23}H_{17}NO_3$	77.73	4.82	3.94	77.71	4.97	4.28

(a) Kept at room temperature for 24 hours. (b) % Chlorine: Calcd., 9.12. Found, 9.13. (c) % Chlorine: Calcd., 8.17. Found, 7.89. (d) % Chlorine: Calcd., 7.63. Found, 7.67.

TABLE II

3,5-Disubstituted-4,5-dihydroindeno[1,2-*c*][1,2]diazepin-6(1*H*)-ones (**3a-g**)

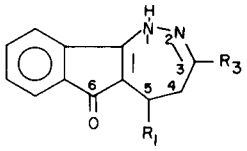


Compound	R_1	R_3	Method	Acylethyl-indandione	Refluxing Time, hr.	Solvent distilled off, ml.	Yield %	M.p. °C	Molecular Formulas		Analyses C	H	N
3a	C_6H_5	CH_3	B	**1a**	1	100	43	229-230	$C_{19}H_{16}N_2O$	Calcd.,	79.14	5.59	9.72
										Found,	79.13	5.57	9.73
3b	C_6H_5	C_6H_5	B	**1b**	1	150	66	224-225	$C_{24}H_{18}N_2O$	Calcd.,	82.26	5.18	7.99
										Found,	82.40	5.22	8.13
3c	C_6H_5	*p*-$NO_2C_6H_4$	B	**1c**	1.5	50	73	242 dec.	$C_{24}H_{17}N_3O_3$	Calcd.,	73.15	4.33	10.63
										Found,	72.97	4.53	10.54
3d	C_6H_5	*p*-$AcNHC_6H_4$	A	**1e**	5	25	57	261-262 dec.	$C_{26}H_{21}N_3O_2$	Calcd.,	76.64	5.20	10.31
										Found,	76.71	5.08	10.41
3e (a)	*p*-ClC_6H_4	C_6H_5	A	**1h**	2	15	29	228	$C_{24}H_{17}ClN_2O$	Calcd.,	74.89	4.45	7.28
										Found,	74.94	4.65	7.38
3f (b)	*p*-ClC_6H_4	*p*-$NO_2C_6H_4$	A	**1i**	5	25	72	245 dec.	$C_{24}H_{16}ClN_3O_3$	Calcd.,	67.06	3.75	9.78
										Found,	67.04	3.84	9.62
3g	C_6H_5	2-C_5H_4N	A	**1n**	2	---	43	212-214	$C_{23}H_{17}N_3O$	Calcd.,	78.61	4.88	11.96
										Found,	78.43	4.75	11.83

(a) % Chlorine: Calcd., 9.22. Found, 9.34. (b) % Chlorine: Calcd., 8.25. Found, 8.16.

TABLE III

3,5-Disubstituted-4,5-dihydroindeno[1,2-c][1,2]diazepin-6(1H)-ones (3a-g)



Compound	R_1	R_3	Absorption Maxima mμ (ε x 10^{-3})	mμ (ε x 10^{-3})	mμ (ε x 10^{-3})	mμ (ε x 10^{-3})
3b	C_6H_5	C_6H_5	229 (21.4)	265 (20.8)	305 (12.5)	330 sh (3.7)
3e	p-ClC_6H_4	C_6H_5	225 (31.5)	265 (25.8)	305 (13.8)	330 sh (10.0)
3a	C_6H_5	CH_3	229 (16.6)	264 (24.2)	286 (12.1)	320 sh (3.6)
3b	C_6H_5	C_6H_5	229 (21.4)	265 (20.8)	305 (12.5)	330 sh (3.7)
3c	C_6H_5	p-$NO_2C_6H_4$	223 (20.4)	263 (24.7)	298 (13.0)	345 (11.4)
3g	C_6H_5	2-C_5H_4N	228 (22.8)	264 (18.9)	305 (10.2)	335 sh (6.0)

EXPERIMENTAL (9)

2-(Substituted-2-acylethyl)-1,3-indandiones (**1a-n**).

Method A. (4)

A mixture of equimolar quantities of 1,3-indandione, the appropriate α,β-unsaturated ketone and sodium methoxide (as a solution containing 0.05 mole of sodium in 100 ml. of methanol) was refluxed (except for compound **1b**) for the time indicated in Table I. The reaction mixture was diluted with about an equal volume of ice-water and acidified with dilute hydrochloric acid. The solid was collected by filtration and recrystallized from methanol.

2-(2-Acetyl-1-phenylethyl)-1,3-indandione (**1a**).

This compound was obtained in 55% yield, as large yellow crystals, m.p. 115-116° (Lit. (4) 113-114°); uv max mμ (ε) 229 (36,600), 249 (15,800); ir 5.78, 5.90, 12.89, 13.22, 13,48, 14.12 and 14.32 μ.

2-(2-Benzoyl-1-phenylethyl)-1,3-indandione (**1b**).

This compound was obtained in 77% yield, as colorless plates, m.p. 128-129° (Lit. (4) 128-129°); uv max mμ (ε) 228 (40,200), 245 (22,800); ir 5.81, 5.92, 6.00 (sh), 12.85, 13.30, 14.20, 14.39, 14.52 μ.

Compound **1b** was also prepared from 2-benzylidene-1,3-indandione and acetophenone according to Method B. The refluxing time was 24 hours. A 32% yield was obtained.

2-[2-Benzoyl-1-(3-pyridyl)ethyl]-1,3-indandione (**1m**).

From 1,3-indandione (0.73 g.), 3-(3-pyridyl)acrylophenone (19) (1.05 g.), sodium methoxide solution (10 ml.) and absolute methanol (30 ml.), there was obtained a 62% yield of **1m**, as colorless crystals, m.p. 151-153°; ir spectrum similar to that of compound **1b**.

Method B. (6)

A mixture of the appropriate 2-benzylidene-1,3-indandione (0.005 mole), the appropriate acetophenone (0.005 mole), sodium methoxide solution (10 ml. of a stock solution containing 0.05 g.-atom of sodium in 100 ml. of methanol) and absolute methanol (30 ml.), except where otherwise noted, was refluxed for the time indicated in Table I. The reaction mixture was then worked-up as described under the preceding method.

2-[2-(*p*-Nitrobenzoyl)-1-phenylethyl]1,3-indandione (**1c**).

From 2-benzylidene-1,3-indandione (11) (3.51 g.), 4'-nitroacetophenone (2.49 g.), sodium methoxide solution (30 ml.) and absolute methanol (90 ml.), there was obtained a 67% yield of **1c** as light yellow crystals, m.p. 152-153°; uv max mμ (ε) 229 (39,900), 258 (24,700); ir 5.80, 5.90, 5.95 (sh), 6.67, 7.52, 11.82, 11.93, 12.96, 13.52 and 14.30 μ.

2-[2-(*p*-Aminobenzoyl)-1-phenylethyl]-1,3-indandione (**1d**).

The crude product obtained from the reaction of 2-benzylidene-1,3-indandione (11) and 4'-aminoacetophenone gave after crystallization from methanol a first crop of red-brown crystals (0.41 g.), m.p. 150-152° (starting indandione). The filtrate was concentrated to 40 ml. by distillation and allowed to stand three days. A 29% yield of **1d** was obtained, m.p. 188-193°. A second crystallization from methanol gave light orange crystals, m.p. 198-200°.

Compound **1d** was also obtained by reduction of **1c** with iron filings in refluxing dilute acetic acid.

2-[2-(*p*-Acetamidobenzoyl)-1-phenylethyl]-1,3-indandione (**1e**).

From 2-benzylidene-1,3-indandione (11) and 4'-acetamidoacetophenone there was obtained a 36% yield of **1e**, as light orange crystals, m.p. 217-219°; uv max mμ (ε) 228 (25,700) 248 sh (10,000) and 291 (22,400).

Compound **1e** was also obtained by acetylation of **1d** with acetic anhydride.

2-(2-Benzoyl-1,2-diphenylethyl)-1,3-indandione (**1f**).

From 2-benzylidene-1,3-indandione (11) and 2-phenylacetophenone there was obtained a 36% yield of **1f** as colorless crystals, m.p. 203-204° (Lit. (6) 188-190°); ir 5.77, 5.88, 5.97, 12.87, 13.18, 13.34, 13.97 and 14.20 μ.

2-[2-Benzoyl-1-(*p*-nitrophenyl)-2-phenylethyl]-1,3-indandione (**1g**).

A mixture of 2-(*p*-nitrobenzylidene)-1,3-indandione (11) (1.40 g.), 2-phenylacetophenone (1.0 g.), sodium methoxide solution (10 ml.) and absolute methanol (30 ml.) was refluxed for 3 hours.

The reaction mixture was filtered to remove a very small amount of starting material before diluting and acidifying as in Method B. Recrystallization gave a first crop of colorless needles (unidentified). The second and third crops gave **1g** in 33% yield as yellow crystals, m.p. 185-192°. A second recrystallization of **1g** from methanol gave light yellow prisms, m.p. 195-198°; ir 5.79, 5.92, 6.00, 6.64, 7.52, 11.72, 12.68, 13.34 and 14.37 μ.

2-[2-Benzoyl-1-(*p*-chlorophenyl)ethyl]-1,3-indandione (**1h**).

This compound was obtained in 51% yield as colorless crystals, m.p. 118-119°, from 2-(*p*-chlorobenzylidene)-1,3-indandione (11) and acetophenone; uv max mμ (ε) 227 (52,600), 258 (30,400).

2-[2-(*p*-Nitrobenzoyl)-1-(*p*-chlorophenyl)ethyl]-1,3-indandione (**1i**).

This compound was obtained in 50% yield from 2-(*p*-chlorobenzylidene)-1,3-indandione (11) and 4′-nitroacetophenone, as light yellow crystals, m.p. 154-155°; uv max mμ (ε) 230 (60,800), 258 (52,200); ir spectrum similar to that of compound **1c**.

2-[2-Benzoyl-1-(*p*-chlorophenyl)-2-phenylethyl-1,3-indandione (**1j**).

A mixture of 2-(*p*-chlorobenzylidene)-1,3-indandione (11) (2.70 g.), 2-phenylacetophenone (2.0 g.), sodium methoxide solution (20 ml.) and absolute methanol (50 ml.) was refluxed for 16 hours. Recrystallization yielded 2.76 g. of colorless needles and yellow crystals. Treatment with hot petroleum ether (b.p. 75-90°) dissolved the colorless needles and gave **1j** in 22% yield as light yellow prisms, m.p. 180-182.

2-[2-(*p*-Nitrobenzoyl)-1-(*p*-hydroxyphenyl)ethyl]-1,3-indandione (**1k**).

From 2-(*p*-hydroxybenzylidene)-1,3-indandione (11) and 4′-nitroacetophenone there was obtained a 12% yield of **1k**, as yellow crystals, m.p. 203-204°; ir 2.91, 5.81, 5.96, 6.62, 7.54, 11.73, 11.91, 12.12, 1313, 13.42, 13.60 μ.

2-[2-(*p*-Nitrobenzoyl)-1-(*p*-dimethylaminophenyl)ethyl]-1,3-indandione (**1l**).

This compound was obtained in 50% yield, from 2-(*p*-dimethylaminobenzylidene)-1,3-indandione (11) and 4′-nitroacetophenone. The reaction mixture after refluxing was cooled and filtered to remove 0.59 g. of dark red needles, m.p. 218-219°. The filtrate when treated as described in Method B gave **1l** as dark red crystals, m.p. 168-169°, ir 5.70, 5.93, 5.99, 6.64, 7.52, 11.72, 12.00, 12.21, 12.49, 13.25, 13.44 μ.

2-(2-Pyridylcarbonyl-1-phenylethyl)-1,3-indandione (**1n**).

This compound was obtained as almost colorless crystals, m.p. 156-157°, from 2-benzylidene-1,3-indandione (11) and 2-acetylpyridine. The ir spectrum showed peaks at 5.77, 5.90, 5.97, 12.88, 13.36 and 14.20 μ.

3,5-Disubstituted 4,5-Dihydroindeno[1,2-*c*][1,2]diazepin-6(1*H*)-ones (**3a-g**).

Method A.

A mixture of the appropriate 2-acylethylindandione (0.001 mole), 95% hydrazine (0.001 mole) and ethanol (50 ml.) was refluxed for the time indicated in Table II. Part of the solvent was removed by distillation and the precipitate was crystallized from methanol to give orange crystals.

Method B.

Acetic acid (2 ml., 5 ml. in the case of compound **3b**) was added to a solution of the appropriate 2-acylethylindandione (0.01 mole) and 95% hydrazine (0.011 mole) in 2-propanol (200 ml., 400 ml. in the case of compound **3c**) and the solution refluxed for the time indicated in Table II. The reaction mixture was worked-up as in Method A. Orange crystals were obtained.

The ir absorption spectra of compounds **3a-g** showed bands in the region 3.05-3.08 (N–H), 6.01-6.04 (C=O), 6.21-6.28 (C–N) and 6.60-6.70 μ (NH def). Other bands in common were at 3.30, 6.35, 7.25, 7.50, 8.35, 9.20 and 10.95 μ. In addition, compounds **3c** and **3f** showed bands at 6.61, 7.52 μ and 6.67, 7.51 μ (NO_2), respectively. The nmr of compound **3a** showed peaks at 1.58 (3 methyl protons), 2.84 (multiplet, 2 protons), 4.53 (multiplet, 1 proton) and 7.17 ppm (9 aromatic protons). The nmr of compound **3b** showed multiplets at 3.27 (2 protons), 4.63 (1 proton) and at 7.12 ppm (14 aromatic protons).

Reaction of Compound **3b** with Sodium Hydride.

Methanol (10 drops) was added to a mixture of **3b** (0.70 g.), 51% sodium hydride in mineral oil (0.10 g.) and benzene (30 ml.). The suspended orange compound **3b** immediately turned deep red. The mixture was heated to reflux, then cooled and filtered to give red crystals (0.72 g.) of m.p. above 300°. The ir showed no NH band, a weak carbonyl band and two new strong bands at 6.8 and 6.9 μ. A mixture of this red compound (0.40 g.), benzene (10 ml.) and benzoyl chloride (1.0 ml.) was refluxed for a few minutes, then filtered hot to give 0.06 g. of sodium chloride. Evaporation of the filtrate to dryness and crystallization of the residue from methanol gave 0.3 g. of **3b**, m.m.p. 224-225°.

Reaction with Hydrazine.

The hydrazone of **3b** was prepared by reacting **1b** with hydrazine as described under Method B, with the modification that at the end of the refluxing time additional 95% hydrazine (5.0 g.) and acetic acid (2 ml.) were added and the mixture refluxed for 4 hours. There was obtained 2.92 g. (80%) of orange crystals, m.p. 248-249°.

Anal. Calcd. for $C_{24}H_{20}N_4$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.03; H, 5.51; N, 15.19.

Hydrazone of **3c**.

This compound was prepared by carrying out the reaction of **1h** with hydrazine as described under Method A, with the modification that at the end of the refluxing time, 20 ml. of the solvent was distilled off, 95% hydrazine (1.0 g.) and acetic acid (0.05 ml.) were added and the mixture refluxed for 18 hours. There was obtained 0.22 g. (55%) of yellow crystals, m.p. 227° dec.

Anal. Calcd. for $C_{24}H_{19}ClN_4$: C, 72.26; H, 4.80; Cl, 8.89; N, 14.05. Found: C, 71.90; H, 4.90; Cl, 9.02; N, 14.22.

Acknowledgment.

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