MESOIONIC 2-ACYLIMINO-1,3,4-THIA- AND -OXADIAZOLES

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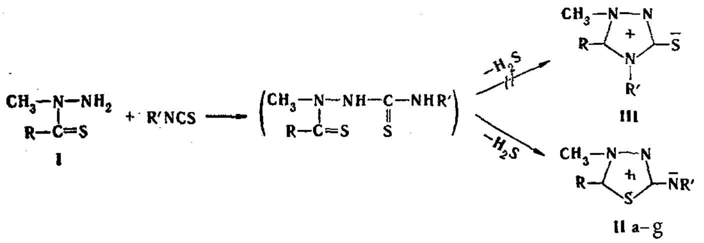
2-Acylimino-1,3,4-thiadiazoles were obtained from 1-methyl-1-thioacylhydrazines and the appropriate acyl isothiocyanates, while 2-benzoylimino-1,3,4-oxadiazole was obtained from 1-phenyl-1-benzoylhydrazine and benzoyliminocarbonic acid dichloride. The mesoionic structure of the compounds obtained was proved by their IR and mass spectra. Reduction, hydrolysis, and salt-formation reactions of them were studied.

The compound obtained by reaction of 1-thiobenzoyl-1-methylhydrazine (I, R = C_6H_5) with benzoyl isothiocyanate [1] corresponds in composition to the product of stripping of hydrogen sulfide from the intermediate thiosemicarbazide, but its IR spectrum differs substantially from the expected spectrum of the mesoionic 1,2,4-triazole-3-thione (III) [2].

For a more detailed study, we obtained a number of derivatives from I and benzoyl, acetyl, and benzenesulfonyl isothiocyanates (Table 1). In addition to the molecular ion, there is an intense peak of an $RC\equiv\overset{+}{S}$ ion (R = C_6H_5, p-$CH_3C_6H_4$, and p-$CH_3OC_6H_4$) in the mass spectra of the synthesized compounds (Table 2); this is an argument in favor of 1,3,4-thiadiazole structure II [3-5]. In almost all of the spectra one observes an intense $CH_3-\overset{+}{N}\equiv C-R$ ion, which, along with the $RC\equiv\overset{+}{S}$ ion, confirms the ring structure.

Thus, judging from the mass spectra, the mesoionic acylimino-1,3,4-thiadiazole structure can be assigned to II.



II a R=C_6H_5, R'=C_6H_5CO; b R=p-$CH_3C_6H_4$, R'=C_6H_5CO; c R=p-$CH_3OC_6H_4$, R'=C_6H_5CO; d R=C_6H_5, R'=$C_6H_5SO_2$; e R=p-$CH_3C_6H_4$, R'=$C_6H_5SO_2$; f R=p-$CH_3OC_6H_4$, R'=$C_6H_5SO_2$; g R=C_6H_5, R'=CH_3CO.

Similar mesoionic compounds, which were obtained by reaction of thioacylhydrazines with phenyliminophosgene, were described in [5]. By replacing phenyliminophosgene with benzoyliminocarbonic acid dichloride, we obtained IIa, which is identical to the compound obtained from 1-thiobenzoyl-1-methylhydrazine and benzoyl isothiocyanate. It can therefore be considered to be proved that the products of the reaction of 1-thioacylhydrazines and acyl isothiocyanates are mesoionic iminothiadiazoles. The mesoionic 2-benzoylimino-1,3,4-oxadiazole (IV) was obtained by this same method.*

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*When this work was already in press, there appeared a communication [10] in which the reaction of 1-acyl- and 1-thioacylhydrazines with acyliminocarbonic acid dichlorides was used to obtain mesoionic 1,3,4-oxa- and -thiadiazoles.

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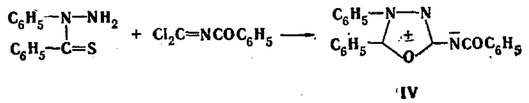
TABLE 1. Mesoionic 2-Acyliminothiadiazoles (II)

Comp.	R	R′	mp, °C	Empirical formula	Found, %				Calculated, %				λ_{max}, nm (lg ε)[a]	IR spectrum, cm⁻¹	Yield, %
					C	H	N	S	C	H	N	S			
IIa	C_6H_5	C_6H_5CO	272—272,5[b]										330(4,24), 264(4,07), 238(4,30)	1368, 1458, 1556	97
IIb	p-$CH_3C_6H_4$	C_6H_5CO	248—249,5[c]	$C_{17}H_{15}N_3OS$	65,1	4,9	14,0	10,3	65,0	4,9	13,6	10,4	331(4,22), 268(4,05), 236(4,20)	1358, 1458, 1551	60
IIc	p-$CH_3OC_6H_4$	C_6H_5CO	216—217,5[d]	$C_{17}H_{15}N_3O_2S$	62,8	4,9	13,3	9,9	62,8	4,6	12,9	9,8	335(4,30), 274(4,08)	1363, 1458, 1546	77
IId	C_6H_5	$SO_2C_6H_5$	167—168[e]	$C_{15}H_{13}N_3O_2S_2$	54,5	4,1	12,4	19,4	54,4	4,0	12,7	19,4	324(3,97), 249(4,09)	1083, 1133, 1478	~100
IIe	p-$CH_3C_6H_4$	$SO_2C_6H_5$	168—169[e]	$C_{16}H_{15}N_3O_2S_2$	55,1	4,4	12,1	18,5	55,6	4,4	12,2	18,6	313(3,92)	1085, 1143, 1283, 1303, 1483	84
IIf	p-$CH_3OC_6H_4$	$SO_2C_6H_5$	187—188,5[e]	$C_{16}H_{15}N_3O_3S_2$	53,2	4,3	11,8	17,7	53,2	4,2	11,6	17,7	330(4,18), 274(3,87)	1083, 1138, 1187, 1378, 1478	54
IIg	C_6H_5	CH_3CO	161,5—162,5[f]	$C_{11}H_{11}N_3OS$			18,0				18,0		318(4,25), 254(4,02)	1378, 1470, 1570	17

[a] In methanol. [b] Previously obtained [1]. [c] From dimethylformamide (DMF)–acetonitrile. [d] From DMF–acetone. [e] From chlorobenzene. [f] From alcohol.

TABLE 2. Principal Fragments and Their Relative Intensities in the Mass Spectra of Mesoionic 1,3,4-Thiadiazoles

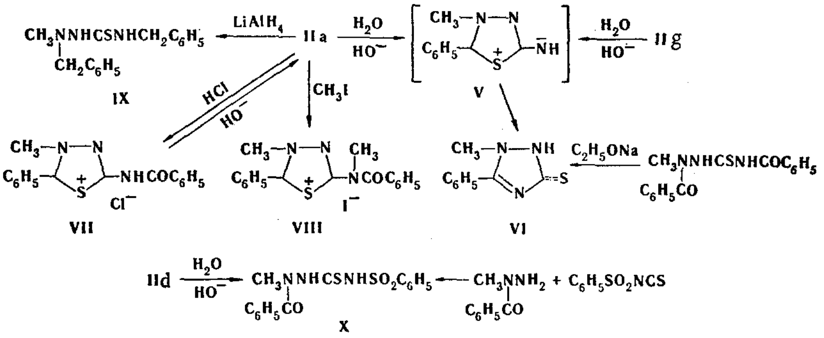
Compound	m/e	Relative intensity, %	Ion structure
IIa	295	33	$M^{\dot{+}}$
	218	95	$(M - C_6H_5)^+$
	121	48	$C_6H_5C{\equiv}S^+$
	118	25	$C_6H_5C{\equiv}\overset{+}{N}{-}CH_3$
	105	100	$C_6H_5C{\equiv}O^+$
	77	97	$C_6H_5^+$
IIb	309	27	$M^{\dot{+}}$
	232	95	$(M - C_6H_5)^+$
	135	67	$CH_3C_6H_4C{\equiv}S^+$
	132	32	$CH_3C_6H_4C{\equiv}\overset{+}{N}{-}CH_3$
	105	89	$C_6H_5C{\equiv}O^+$
	91	35	$CH_3C_6H_4^+$
	77	100	$C_6H_5^+$
IIc	325	32	$M^{\dot{+}}$
	248	100	$(M - C_6H_5)^+$
	151	63	$CH_3OC_6H_4C{\equiv}S^+$
	148	25	$CH_3OC_6H_4C{\equiv}\overset{+}{N}{-}CH_3$
	108	20	$CH_3OC_6H_5^+$
	105	80	$C_6H_5C{\equiv}O^+$
	77	80	$C_6H_5^+$
IId	331	33	$M^{\dot{+}}$
	267	17	$(M - SO_2)^+$
	132	34	$(CH_3N{-}N{=}C{-}C_6H_5)^{\dot{+}}$
	131	30	
	121	100	$C_6H_5C{\equiv}S^+$
	77	84	$C_6H_5^+$
IIe	345	33	$M^{\dot{+}}$
	281	38	$(M - SO_2)^{\dot{+}}$
	157	16	?
	145	16	?
	141	17	?
	135	94	$CH_3C_6H_5C{\equiv}S^+$
	134	35	?
	132	22	$CH_3C_6H_4C{\equiv}\overset{+}{N}{-}CH_3$
	93	20	?
	91	36	$CH_3C_6H_4^+$; $(C_6H_5N)^+$
	77	100	$C_6H_5^+$
IIf	361	69	$M^{\dot{+}}$
	162	54	$(CH_3N{-}N{=}C{-}\dot{C_6H_4}OCH_3)^+$
	161	36	?
	151	100	$CH_3OC_6H_4C{\equiv}S^+$
	133	40	$CH_3OC_6H_4C{\equiv}N^{\dot{+}}$
	108	25	$CH_3OC_6H_5^+$
	77	71	$C_6H_5^+$
IIg	233	14	$M^{\dot{+}}$
	218	100	$(M - CH_3)^+$
	121	65	$C_6H_5C{\equiv}S^+$
	118	12	$C_6H_5C{\equiv}\overset{+}{N}{-}CH_3$
	77	44	$C_6H_5^+$
	73	60	$CH_3COCN^{\dot{+}}$



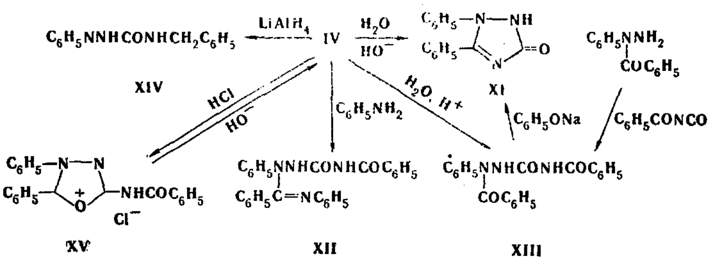
2-Benzoyl- and 2-acetylimino-1,3,4-thiadiazoles have three intense characteristic absorption bands in the IR spectra at 1358-1378, 1458-1470, and 1546-1570 cm^{-1}, while the sulfo derivatives have only one characteristic absorption band at 1478-1483 cm^{-1}. In addition to the absorption at 1627 cm^{-1}, IV also absorbs intensely at 1535 cm^{-1} and less intensely at 1300 and 1350 cm^{-1}. The nitrogen atom of the exocyclic groupings of II and IV passes from the p^2 to the sp^2 state on salt formation, the conjugation is disrupted, and the frequency of the carbonyl group increases, as is observed in acylsydnonimines [6] and mesoionic 1,3-disubstituted 4-acetylimino-1,2,3-triazole [7]. Absorption at 1670 cm^{-1} appears in the spectra of the hydrochloride and methiodide of IIa (VII and VIII), while the hydrochloride of IV absorbs at 1725 cm^{-1}, and no absorption is observed at 1627 cm^{-1}. Consequently, the absorption at 1627 cm^{-1} in the spectrum of IV can be ascribed to an exocyclic carbonyl group. A band at 1550 cm^{-1} is also present in the spectra of VII and VIII, and it is therefore hardly possible to unambiguously consider the absorption band at 1546-1570 cm^{-1} in the spectra of II to be due purely to a carbonyl group. Thus the presence of carbonyl groups in the bases can be confirmed from the spectra of the salts.

4-Methyl-5-phenyl-2-benzoylimino-1,3,4-thiadiazole (IIa) reacts with hydrogen chloride in anhydrous media to give the hydrochloride and with methyl iodide to give the methiodide. The ring is not destroyed by refluxing in alcohol-concentrated hydrochloric acid, heating with ammonia, or refluxing with aniline. Judging from the UV spectrum, IIa exists as a salt even in weak hydrochloric acid solution. It is not reduced by sodium borohydride in water. Reduction with lithium aluminum hydride leads to ring opening and the formation of 1,4-dibenzyl-1-methylthiosemicarbazide (IX). Saponification with alkali gives benzoic acid and VI. Judging from the mass spectrum, this is not 4-methyl-5-phenyl-1,3,4-thiadiazole-2-imine (V), as might have been expected, but rather 1,2,4-triazole-3-thione, the structure of which is confirmed by alternative synthesis [8]. The same compound (VI) is obtained by saponification of mesoionic 2-acetylimino-4-methyl-5-phenyl-1,3,4-thiadiazole (IIg).

In contrast to the benzoyl derivative, 2-phenylsulfonyl-4-methyl-5-phenyl-1,3,4-thiadiazole (IId) forms 1-benzoyl-4-phenylsulfonyl-1-methylthiosemicarbazide (X) on saponification with alkali; the structure of X was proved by alternative synthesis.



The oxadiazole system of IV undergoes reaction considerably more readily than the thiadiazole ring, as seen from the scheme presented below:



Judging from the mass spectrum, structure XII should be proposed for the product of reaction of IV with aniline; this is confirmed by the presence of $C_6H_5C\equiv\overset{+}{N}C_6H_5$ and $C_6H_5CONCO^+$ ions.

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 mass spectrometer with a system for direct introduction of the samples into the ion source. The IR spectra of KBr pellets were recorded with a UR-20 spectrophotometer. The UV spectra were recorded with an SF-4 spectrophotometer. The melting points were determined with a heating stage. Thin-layer chromatography (TLC) was carried out in a fixed layer of HF_{254} Al_2O_3 (Merck, West Germany) with elution with chloroform.

Mesoionic 2-Acylimino-4-methyl-5-aryl-1,3,4-thiadiazoles (IIa-IIf, Table 1). A mixture of 5 mmole of acyl isothiocyanate and 5 mmole of 1-thioacyl-1-methylhydrazine in 10 ml of absolute toluene was refluxed for 8 h. The following day the precipitated thiadiazole was separated; IIa-IIc R_f 0.59, IId and IIe R_f 0.22, and IIf R_f 0.27.

Mesoionic 2-Acetylimino-4-methyl-5-phenyl-1,3,4-thiadiazole (IIg). A 3.13 g (3 mmole) sample of acetyl isothiocyanate and 3.13 g (2 mmole) of 1-thiobenzoyl-1-methylhydrazine were mixed in 20 ml of absolute toluene. After the violent reaction had ceased, the mixture was refluxed for 4 h. The precipitate (3.5 g) was recrystallized (after decolorization with charcoal) from alcohol to give 1.18 g of IIg (with an impurity with R_f 0.08). Treatment of the filtrate with ether gave 1.28 g of pure IIg with R_f 0.25.

Mesoionic 2-Benzoylimino-4-methyl-5-phenyl-1,3,4-thiadiazole (IIa). A 0.59 g (3 mmole) sample of the benzoyliminocarbonic acid dichloride [9] and 0.47 g (3 mmole) of 1-thiobenzoyl-1-methylhydrazine were mixed in 15 ml of benzene. After the vigorous reaction had ceased, the mixture was refluxed for 30 min and worked up to give 0.82 g (96%) of a compound identical (according to the IR spectrum) to VII. Treatment with aqueous bicarbonate gave a quantitative yield of thiadiazole IIa.

2-Benzoylimino-4-methyl-5-phenyl-1,3,4-thiadiazolium Chloride (VII). An 0.4 g sample of IIa was allowed to stand for 12 h in 30 ml of methylene chloride saturated with dry HCl. The addition of absolute ether precipitated 0.4 g (90%) of VII with mp 230° (dec.). IR spectrum: 1670, 1550, 1310, 1270 cm^{-1}. Found,%: Cl 10.1. $C_{16}H_{13}N_3OS \cdot HCl$. Calculated,%: Cl 10.2.

2-(N-Methyl-N-benzoylimino)-4-methyl-5-phenyl-1,3,4-thiadiazolium Iodide (VIII). An 0.50 g sample of IIa was heated in a sealed ampul at 100° with 5 ml of absolute alcohol and 1 ml of methyl iodide for 1.5 h. The alcohol was evaporated, and the residue was treated with ether and acetone to give 0.50 g (68%) of VIII with mp 144-145°. IR spectrum: 1671, 1556, 1338, 1310, 1270 cm^{-1}. Found,%: N 9.6. $C_{17}H_{16}IN_3O$. Calculated,%: N 9.6.

4-Methyl-5-phenyl-1,3,4-triazole-2-thione (VI). A. A 1 g sample of IIa was refluxed in a solution containing 20 ml of alcohol, 5 ml of water, and 0.4 g of KOH for 3 h, after which the mixture was acidified to pH 2 with concentrated hydrochloric acid. The precipitate was washed with water, dried, and extracted with heptane. The heptane yielded 0.26 g (63%) of benzoic acid, while the residue [0.52 g (80%)] was found to be VI with mp 206-208° (from dimethylformamide–acetone). IR spectrum: 2500-3100 (broad band), 1512, 1483, 1437, 1373, 1218 cm^{-1}. UV spectrum (CH_3OH), λ_{max}, nm (log ε): 242 (4.25), 304-308 (3.44). Mass spectrum, m/e: 191 (92) $M^{+\cdot}$, 118 (9.6) $C_6H_5\equiv\overset{+}{N}CH_3$, 104 (100) $C_6H_5CNH^+$, 103 (33.8), $C_6H_5C\overset{+}{N}\cdot$; 88 (74) CH_3N_2CSH. Found,%: C 56.2; H 4.9; S 16.7. $C_9H_9N_3S$. Calculated,%: C 56.5; H 4.7; S 16.8.

B. A 0.5 g sample of 1,4-dibenzoyl-1-methylthiosemicarbazide was refluxed for 3 h in a solution of 0.11 g of sodium in 20 ml of absolute alcohol, after which the mixture was diluted with an equal volume of water and acidified to pH 5-6 with concentrated hydrochloric acid. Brief standing yielded 0.25 g of a precipitate that was identical to VI according to its melting point and IR spectrum.

1,4-Dibenzyl-1-methylthiosemicarbazide (IX). A 0.9 g sample of IIa was added to a solution of 0.6 g of $LiAlH_4$ in 20 ml of absolute ether at such a rate that the ether continued to boil, after which the mixture was allowed to stand for 2 h. The excess hydride was decomposed, initially with ether and then with water, and the mixture was made weakly acidic with 1 N HNO_3. It was then extracted continuously with ether for 8 h, after which the ether was evaporated and the residue was recrystallized from alcohol to give 0.35 g (45%) of IX with mp 144-145°. IR spectrum: 3350, 3180, 3018, 2842, 1560, 1535, 1470, and 1250 cm^{-1}. Mass spectrum, m/e: 285 (0.3) M^+, 252 (19) $(M-SH)^+$, 120 (17) $(CH_3NCH_2C_6H_5)^+$, 50.5* (285 → 120), 91 (100) $(C_6H_5CH_2)^+$, 69* (120 → 91). Found,%: C 66.6; H 6.6; N 15.0; S 11.1. $C_{16}H_{19}N_3S$. Calculated,%: C 67.3; H 6.7; N 14.7; S 11.2.

1-Benzoyl-4-phenylsulfonyl-1-methylthiosemicarbazide (X). A. A 0.5 g sample of IId was refluxed for 2 h in a mixture of 10 ml of alcohol, 3 ml of water, and 0.2 g of KOH. Acidification with concentrated HCl yielded 0.35 g (52%) of X with mp 167-168° (from aqueous alcohol). IR spectrum: 3260, 3070, 1664, 1365, 1183, 1143, 1083 cm^{-1}. Found,%: C 51.3; H 4.5; N 2.0; S 18.4. $C_{15}H_{15}N_3O_3S_2$. Calculated,%: C 51.6; H 4.3; N 12.0; S 18.4.

B. A mixture of 0.76 g (5 mmole) of 1-benzoyl-1-methylhydrazine and 0.70 ml (5 mmole) of benzenesulfonyl isothiocyanate was heated at 100° for 5 min, after which it was cooled, and the precipitate was recrystallized from methanol–CCl_4 to give 0.3 g of a substance that was identical to X according to its melting point and IR spectrum.

Mesoionic 2-Benzoylimino-4,5-diphenyl-1,3,4-oxadiazole (IV). A mixture of 1.10 g (5 mmole) of the benzoyliminocarbonic acid dichloride and 1.15 g (5 mmole) of 1-benzoyl-1-diphenylhydrazine in 20 ml of absolute benzene was refluxed for 1.5 h, after which 3.0 ml of triethylamine was added, and the mixture was refluxed for another 40 min. The precipitate was dried and then washed with water, 5% sodium bicarbonate solution, again with water, and dried to give 0.96 g (51%) of IV with mp 205-206.5° (from benzene–acetonitrile). UV spectrum (CH_3OH), λ_{max}, nm (log ε): 330 (3.80), 234 (3.40). Absorption at 330 nm is observed immediately after dissolving, since, probably in connection with the low stability of IV in acids, it falls rapidly with time. IR spectrum: 1645, 1535, 1355, 1300 cm^{-1}. Mass spectrum, m/e: 147 (24) $C_6H_5CONCO^+$, 105 (100) $C_6H_5CO^+$, 75.5* (147 → 105), 77 (67) $C_6H_5^+$, 56.5* (105 → 77). Found,%: C 73.4; H 4.4; N 12.3. $C_{12}H_{15}N_3O_2$. Calculated,%: C 73.9; H 4.4; N 12.3.

2-Benzoylimino-4,5-diphenyl-1,3,4-oxadiazolium Chloride (XV). A suspension of 0.5 g of IV in 25 ml of absolute ether was saturated at 10° with dry HCl. The precipitate was washed with absolute ether to give 0.40 g (70%) of XV with mp 234-240° (dec.). IR spectrum: 1745, 1558, 1370 cm^{-1}. Found,%: Cl 10.7. $C_{21}H_{15}N_3O_2 \cdot HCl$. Calculated,%: Cl 11.1.

4,5-Diphenyl-1,3,4-triazol-2-one (XI). A. A 0.7 g sample of IV was refluxed in a mixture of 10 ml of alcohol, 2 ml of water, and 0.2 g of KOH for 40 min. The mixture was diluted with two volumes of water and acidified to pH 2 with concentrated HCl. The precipitate was separated, dried, and extracted with heptane. The heptane extract yielded 0.15 g (60%) of benzoic acid. The heptane-insoluble solid was recrystallized from DMF–acetone to give 0.30 g (60%) of a substance that did not melt up to 300°. IR spectrum: 1610, 1580, 1520, 1470, 1430 cm^{-1}. Mass spectrum, m/e: 237 (100) $M^{+\cdot}$, 134 (32.6) $C_6H_5NNHCO^+$, 76* (237 → 134), 106 (21.5) $C_6H_5NNH^+$, 105 (15) $C_6H_5N_2^+$, 104 (84.5) $C_6H_5CNH^+$, 45.5* (237 → 104), 91 (26.6) $C_6H_5N^+$, 77 (50) $C_6H_5^+$, 57* (104 → 77). Found,%: C 70.0; H 4.5; N 17.6. $C_{14}H_{11}N_3O$. Calculated,%: C 70.9; H 4.7; N 17.7.

B. A 0.5 g sample of 1,4-dibenzoyl-1-diphenylsemicarbazide was refluxed for 30 min in 20 ml of absolute alcohol in which 0.39 g of sodium had been dissolved. The precipitate was removed by filtration and dissolved in water. The solution was acidified to pH 5 to give 0.15 g of a substance that did not melt up to 300° and was identical to XI according to the IR spectrum.

1,4-Dibenzoyl-1-phenylsemicarbazide (XIII). A 0.5 g sample of IV was refluxed for 40 min in a mixture of 5 ml of alcohol and 1 ml of concentrated HCl. After 12 h, the precipitate was removed by filtration to give 0.36 g (68%) of XIII with mp 214-215° (from acetonitrile–alcohol). IR spectrum: 3330, 3260, 3080, 1725, 1625, 1510, and 1480 cm^{-1}. Found,%: C 69.9; H 4.8; N 11.8. $C_{12}H_{17}N_3O_3$. Calculated,%: C 70.2; H 4.8; N 11.7. Evaporation of the filtrate in vacuo gave 0.10 g of a substance that was identical to XI according to its melting point and IR spectrum.

B. A 0.83 g sample of benzoyl isocyanate and 1.2 g of 1-benzoyl-1-phenylhydrazine were mixed in 10 ml of absolute tetrahydrofuran, after which the mixture was refluxed for 4 h and worked up to give 1.5 g of a substance that was identical to XIII according to its melting point and IR spectrum.

1,4-Dibenzyl-1-phenylsemicarbazide (XIV). A 1.0 g sample of IV was added gradually, while maintaining continuous refluxing, to 0.82 g of $LiAlH_4$ in 25 ml of absolute ether. After 12 h, the mixture was decomposed with moist ether and water, and 2 N HNO_3 was added to completely dissolve the aluminum oxide. The mixture was extracted continuously with ether for 6 h. The ether solution was evaporated, and the residue was recrystallized from aqueous alcohol to give 0.47 g (48%) of XIV with mp 148.5-149°. IR spectrum: 3420, 3210, 3025, 3075, 3032, 2925, 1680, 1540, 1495, 1450 cm^{-1}. Mass spectrum, m/e: 331 (8) $M^{+\cdot}$, 198 (5) $C_6H_5N(CH_2C_6H_5)NH_2^{+\cdot}$, 182 (34) $C_6H_5NCH_2C_6H_5^+$, 181 (76) $C_6H_5NCHC_6H_5^+$, 99.5* (331 → 181), 133 (6) $C_6H_5CH_2NCO^{+\cdot}$, 107 (92) $C_6H_5NNH_2^+$, 57.9* (198 → 107), 91 (100) $C_6H_5CH_2^+$.

1-Phenyl-1-(N-phenylbenzamido)-4-benzoylsemicarbazide (XII). A mixture of 1 g of IV and 0.7 ml of aniline in 5 ml of absolute alcohol was refluxed for 1.5 h and worked up to give 0.82 g of XII with mp 162-163° (from alcohol). IR spectrum: 3380, 3280, 1740, 1645, 1650, 1610, 1530, 1515, 1475, 1365, and 1282 cm^{-1}. Mass spectrum, m/e: 180 (72.5) $C_6H_5NCC_6H_5^+$, 75* (434 → 180), 147 (12.5) $C_6H_5CONCO^+$, 121 (46.0) $C_6H_5CONH_2^{+\cdot}$, 105 (78) $C_6H_5CO^+$, 77 (100) $C_6H_5^+$. Found,%: C 74.5; H 5.1; N 13.0. $C_{27}H_{22}N_4O_2$. Calculated,%: C 74.6; H 5.1; N 12.9.

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