Amidrazones. VII (1a). Formation of *s*-Triazines by Thermolysis of N^1-Benzyl-Substituted Amidrazone Ylides

Richard F. Smith, Richard R. Soelch, Timothy P. Feltz, Michael J. Martinelli and Susan M. Geer*

Department of Chemistry, State University, College of Arts and Science, Geneseo, N. Y. 14454

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The preparation of ylides of the general structure $RC(=NR')\bar{N}\overset{+}{N}(CH_3)_2CH_2Ar$ (**14**) is described. Thermolysis of **14a** (R = CH_3, R′ = H, Ar = C_6H_5) gave dimethylamine and 2,4-dimethyl-6-phenyl-*s*-triazine. Thermolysis of ylides **14b** (R = C_6H_5; R′ = CH_3, Ar = C_6H_5) and **14c** (R = C_6H_5, R′ = CH_3, Ar = *p*-tolyl) gave dimethylamine, ArCH = NCH_3 and 1-methyl-2-Ar-4,6-diphenyl-1,2-dihydro-*s*-triazines (**19a,b**). Triazines **19a** and **19b** were also prepared by condensation of *N*-methylbenzamidine with benzaldehyde and *p*-tolualdehyde, respectively. Thermolysis of **14d** (R = C_6H_5, R^1 = $CH_2C_6H_5$, Ar = C_6H_5) gave 1-benzyl-2,4,6-triphenyl-1,2-dihydro-*s*-triazine (**19c**) and *N*-benzylidenebenzylamine. Mechanistic aspects of these reactions are discussed.

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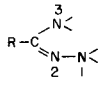
Introduction.

The recommended (2) method for designating the nitrogen atoms in amidrazones is employed throughout and is illustrated by the following structure.

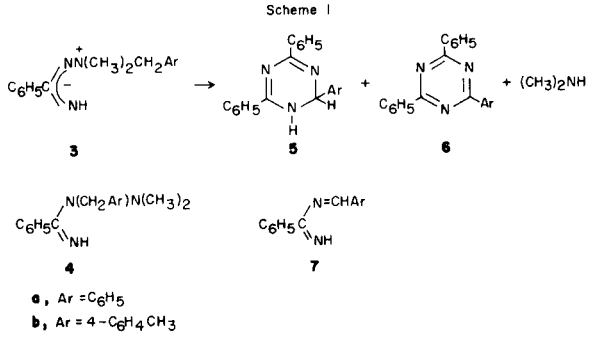


Acylaminimides (**1**) substituted with a benzyl group on the quaternary nitrogen undergo facile Stevens-type rearrangements (3) to give hydrazides (**2**). These, and analogous rearrangements involving allyl substituents (4), have been the subject of extensive mechanistic studies (5)

$$\underset{\mathbf{1}}{RCO\bar{N}\overset{+}{N}(CH_3)_2CH_2Ar} \rightarrow \underset{\mathbf{2}}{RCON(CH_2Ar)N(CH_3)_2}$$

In an earlier paper of this series (1b) we reported that thermolysis of two N^1-benzyl-substituted amidrazone ylides (**3a,b**), did not give isolable Stevens rearrangement products (**4**). The products obtained from thermolysis of **3a** and **3b** are dimethylamine and mixtures of 2-aryl-4,6-diphenyl-1,2-dihydro-*s*-triazines (**5a,b**) and the corresponding *s*-triazines (**6a,b**), which are secondary products formed by partial oxidation of **5a** and **5b**. We proposed that the dihydro-*s*-triazines may arise from the initial formation of the Stevens rearrangement products (**4**) which undergo elimination of dimethylamine to give *N*-arylidenebenzamidines (**7**). The latter compounds are probable intermediates leading to the formation of dihydro-*s*-triazines by the condensation of aldehydes with amidines (6,7). Results obtained in the current investigation require revision of this interpretation of the reaction mechanism.

Scheme I

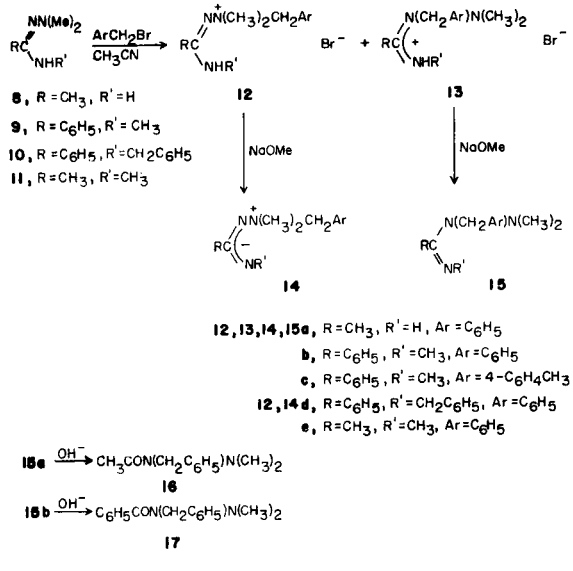


We have extended our study of the synthesis and thermolysis of N^1-benzyl-substituted amidrazone ylides to include ylides with N^3-alkyl substituents. The results of this work together with further study of N^3-unsubstituted ylides are reported herein.

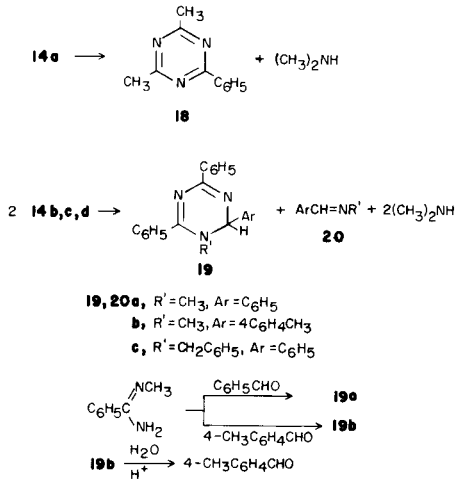
Results and Discussion.

The ylides (**14a-e**) utilized in this study were prepared by neutralization of their conjugate acids (**12a-e**) which were obtained by alkylation of amide dimethylhydrazones (**8-11**) at N^1 with either benzyl bromide or α-bromo-*p*-xylene.

Scheme 2



0022-152X/81/020319-07$02.25



The reaction of acetamide dimethylhydrazone (**8**) with benzyl bromide and the reactions of *N*-methylbenzamide dimethylhydrazone (**9**) with benzyl bromide and α-bromo-*p*-xylene gave, in addition to the ylide conjugate acids (**12a,b,c**), salts resulting from alkylation at N^2 (**13,a,b,c**). Neutralization of these salts gave the imidic acid hydrazides **15a,b,c** which are coincidently the products which would be obtained by Stevens rearrangement of the corresponding ylides. Alkaline hydrolysis of **15a** and **15b** gave hydrazides **16** and **17**, respectively. These experiments firmly establish structures **15a** and **15b**.

All of the ylides (**14**) exhibited their N^1-dimethyl nmr signals at δ 3.2-3.4; the N^1 dimethyl protons in the isomeric **15** were more shielded and their signals were observed at δ 2.3-2.4.

Confirming evidence for the ylide structures was also obtained from a hydrolysis experiment. Hydrolysis of ylide **3a** afforded, after treatment with picric acid, 1-benzyl-1,1-dimethylhydrazinium picrate.

Deuterium exchange of benzyl protons was not observed in deuterium oxide solutions of **3a**, thus ruling out the existence of tautomers in which the negative charge is accomodated on the benzylic carbon atom.

Thermolysis of ylide **14a** gave dimethylamine and a mixture of other compounds from which a low yield of 2,4-dimethyl-6-phenyl-*s*-triazine (**18**) was isolated. As with **3a** and **3b**, the Stevens rearrangement product (**15a**), was not isolated from the thermolysis of the ylide. Since **15a** was obtained as a product resulting from the alkylation of **8**, it was available for testing as an intermediate in the conversion of **14a** to **18**. When **15a** was subjected to the conditions employed for the thermolysis of **14a**, it was recovered unchanged. This observation provides evidence to invalidate our original proposal (1b) that Stevens rearrangement products may be intermediates in the formation of dihydro-*s*-triazines.

s-Triazines were also obtained from the thermolysis of the N^3-substituted ylides **14b,c,d**. Thermolysis of **14b** gave good yields of 1-methyl-2,4,6-triphenyl-1,2-dihydro-*s*-triazine (**19a**), *N*-benzylidenemethylamine (**20a**) and dimethylamine. The origin of the aryl substituents in these products was established from the results obtained by thermolysis of the methyl labelled ylide, **14c**. Isolation of 1-methyl-2-(4-methylphenyl)-4,6-diphenyl-1,2-dihydro-*s*-triazine (**19b**) and *N*-(4-methylbenzylidene)methylamine (**20b**) from the thermolysis of **14c** established that the 2-aryl substituent of the dihydro-*s*-triazine and the aryl substituent of the *N*-arylidenemethylamine originate from the benzyl group of the ylide.

Thermolysis of ylide **14d** gave a low yield of 1-benzyl-2,4,6-triphenyl-1,2-dihydro-*s*-triazine (**19c**). Tlc and analysis of the nmr spectrum of the reaction mixture also showed that *N*-benzylidenebenzylamine (**20c**) was also a component of the thermolysis mixture. Compound **19c** has been prepared by Hunter and Sim (7) by condensation of benzaldehyde with *N*-benzylbenzamidine.

Evidence was also obtained to indicate that the Stevens rearrangement product (**15b**) is an unlikely intermediate in the conversion of **14b** to **19a**. Compound **15b** (obtained from neutralization of **13b**) was found to be thermally stable and was also recovered unchanged after the **14b** → **19a** conversion was carried out utilizing an admixture of **14b** and **15b**.

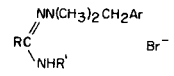
Triazines **19a** and **19b** were also synthesized by condensation of *N*-methylbenzamidine with benzaldehyde and *p*-tolualdehyde, respectively. *p*-Tolualdehyde was obtained from the acid-catalyzed hydrolysis of **19b**. This experiment established the positions of the aryl substituents in **19b**.

Thermolysis of **14e** gave a complex mixture of products that was not successfully separated.

Although *N*-arylidienemethylamines (**20a,b,c**) were obtained from the thermolysis of N^3-substituted ylides (**14b,c,d**), the thermolysis of N^1-unsubstituted ylides (**3a, 3b, 14a**) would not be expected to yield aldimines (**20**, R′ = H) since these compounds are unstable (8). For example, benzaldimine is converted to hydrobenzamide (**21**) at low temperature. Hydrobenzamide is also thermally unstable and is converted to amarine (**22**). Hunter and Sim (7) have established that the conversion of **21** → **22** is catalyzed by base. At higher temperatures hydrobenzamide is converted to lophine (**23**). Tlc indicated that in addition to the triazines **5a** and **6a**, a complex mixture containing at least 13 components is also formed from thermolysis of **3a**. We have examined this mixture with the objective of identifying the benzaldimine transformation products **21**, **22**, and **23**. Based on tlc retention times and analysis of the nmr spectrum **21**, **22**, and **23** are components of this mixture. However only lophine was isolated by preparative tlc.

Table 1

Analytical and Nmr Data



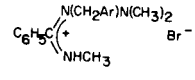
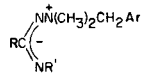
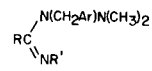
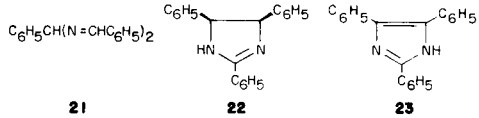
Compound No.	M.p. °C	Yield	Recrystallization Solvent	Molecular Formula	Analysis Calcd. (Found) C	H	N	Nmr (a)
3a·HBr	208-209	73	methanol	$C_{16}H_{20}N_3Br$	57.5 (57.3)	6.0 (6.0)	12.6 (12.4)	(b)
3b·HBr	189-190	63	ethanol	$C_{17}H_{22}N_3Br$	58.6 (58.9)	6.4 (6.3)	12.1 (12.0)	(b)
12a	206-207	43	acetonitrile	$C_{11}H_{18}N_3Br$	48.5 (48.7)	6.7 (6.4)	15.4 (15.6)	(polysol): 1.9 (s, 3H), 3.4 (s, 6H), 4.8 (s, 2H) 7.3-7.7 (m, 7H, aromatic and NH_2)
12b	186-188	26	ethanol	$C_{17}H_{22}N_3Br$	58.6 (59.0)	6.4 (6.3)	12.1 (11.9)	2.8 (d, 3H, J = 5 Hz, s on NH → ND) 3.7 (s, 6H), 5.3 (s, 2H), 7.0-7.8 (m 10H), 8.1 (bd, 1H, exchangeable)
12c	187-188	27	ethanol	$C_{18}H_{24}N_3Br$	59.7 (59.8)	6.7 (6.8)	11.6 (11.3)	2.3 (s, 3H), 2.8 (d, 3H, J = 5 Hz, s on NH → ND), 3.7 (s, 6H), 5.2 (s, 2H), 6.8-7.6 (m, 9H), 8.0 (bd, 1H, exchangeable)
12d	179-181	12	ethanol	$C_{23}H_{26}N_3Br$	65.1 (65.3)	6.2 (6.2)	9.9 (9.8)	3.7 (s, 6H), 4.5 (d, 2H , J = 4 Hz, s on NH → ND), 5.3 (s, 2H), 6.8-7.7 (m, 15H), 8.8 (bd, 1H, exchangeable)
12e	155-157	43	acetonitrile	$C_{12}H_{20}N_3Br$ 	50.4 (50.4)	7.0 (7.1)	14.7 (14.7)	2.1 (s, 3H), 3.1 (d, 3H, J = 4 Hz, s on NH → ND), 3.7 (s, 6H), 5.2 (s, 2H), 7.2-7.7 (m, 6H, aromatic and NH)
13b	105-107	58	ethanol-ether	$C_{17}H_{22}N_3Br$	58.6 (58.8)	6.4 (6.3)	12.1 (12.0)	(DMSO-d_6): 2.7 (s, 6H), 3.4 (s, 3H), 4.7 (s, 2H), 7.2 (s, 5H), 7.6 (s, 5H) 10.3 (bd, 1H, exchangeable)
13c	206-207	19	ethanol-ether	$C_{18}H_{24}N_3Br$ 	59.7 (60.0)	6.7 (6.7)	11.6 (11.4)	2.4 (s, 3H), 2.9 (s, CH_3N) superimposed on 3.0 (d, CH_3NH, combined integration 9H), 4.9 (s, 2H), 6.7-7.7 (10H, NH and aromatic)
3a	108-109 dec.	(c)	(d)	$C_{16}H_{19}N_3$	75.9 (75.8)	7.6 (7.6)	16.6 (16.6)	(b)
3b	126-129 dec.			$C_{17}H_{21}N_3$	76.4 (76.2)	7.9 (8.0)	15.7 (15.6)	(b)
14a	hygroscopic oil			$C_{11}H_{17}N_3$				1.8 (s, 3H), 3.2 (s, 6H), 5.0 (s, 2H), 7.3 (s, 6H, aromatic and NH)
14b	95-97 dec.			$C_{17}H_{21}N_3$	76.4 (76.1)	7.9 (8.0)	15.7 (15.6)	2.9 (s, 3H), 3.4 (s, 6H), 5.3 (s, 2H), 7.3, 7.4 singlets, 10H)
14c	118-119 dec.			$C_{18}H_{23}N_3 \cdot \frac{1}{2}H_2O$	74.5 (74.5)	8.4 (8.3)	14.5 (14.4)	2.3 (s, 3H), 2.8 (s, 3H), 3.4 (s, 6H), 5.1 (s, 2H), 6.9-7.5 (m, 9H)
14d	108-111 dec.			$C_{23}H_{25}N_3 \cdot \frac{1}{2}H_2O$	78.4 (78.2)	7.4 (7.5)	11.9 (11.7)	3.5 (s, 6H), 4.3 (s, 2H), 5.4 (s, 2H), 7.0-7.6 (m, 15H)
14e	hygroscopic oil			$C_{12}H_{19}N_3$				1.8 (s, 3H), 3.0 (s, 3H), 3.4 (s, 6H), 5.1 (s, 2H), 7.4 (s, 5H)

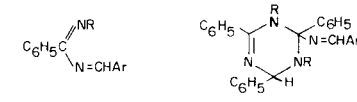
Table 1 Continued

Compound No.	M.p. °C	Yield	Recrystallization Solvent	Molecular Formula	Analysis Calcd. (Found) C	H	N	Nmr (a)
								
15a	b.p. 80-82 (0.2 mm)			$C_{11}H_{17}N_3$	69.1 (69.0)	9.0 (8.9)	22.0 (22.2)	2.0 (s, 3H), 2.3 (s, 6H), 4.5 (s, 2H), 6.1 (bd, 1H, exchangeable), 7.2 (s, 5H)
15b	74-75		ethanol	$C_{17}H_{21}N_3$	76.4 (76.6)	7.9 (7.8)	15.7 (15.6)	2.4 (s, 6H), 2.8 (s, 3H), 4.6 (s, 2H), 7.1-7.6 (m, 10H)
15c	64-65		ether	$C_{18}H_{23}N_3$	76.8 (76.7)	8.2 (8.6)	14.9 (15.2)	2.3 [s, 9H, $(CH_3)_2N$, $C_6H_4CH_3$], 2.7 (s, 3H), 4.5 (s, 2H), 6.8-7.5 (m, 9H)

(a) Chemical shifts in δ units. Unless otherwise specified, spectra were determined in deuteriochloroform. (b) Data recorded in reference 1b. (c) Yields of ylides were nearly quantitative. (d) The ylides could not be purified in crystallization. Analytical data were recorded on products obtained from neutralization of pure samples of the conjugate acids.



21 **22** **23**



7 R = H
24a, R = alkyl
b, R = CH_3, Ar = 4-$CH_3C_6H_5$
c, R = $CH_2C_6H_5$, Ar = C_6H_5

25a, R = H
b, R = alkyl

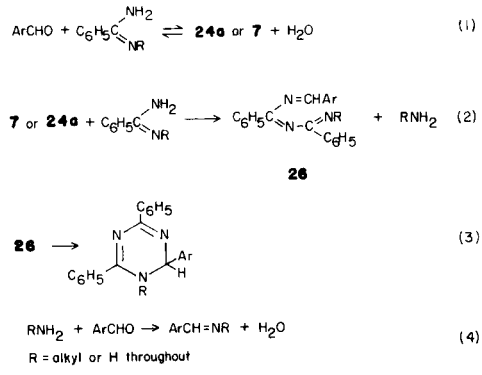
Since dihydro-*s*-triazines are products isolated from both ylide thermolysis and by condensation of aryl aldehydes with benzamidine or *N*-alkylbenzamidines, it seems appropriate to consider mechanistic similarities of these reactions. We propose that both reactions proceed *via* the formation of *N*-arylidenebenzamidines (**7**,**24a**).

The intermediacy of **7** and **24a** in the aldehyde-amidine route to dihydro-*s*-triazines seems well established. Cherkasov, Kapran and Zavitskii (6) proposed that the formation of dihydro-*s*-triazines from the reaction of aryl aldehydes and benzamidine may be accounted for by assuming that the initially formed aldehyde-amidine condensation product **7** undergoes a [2 + 4] cycloaddition reaction to give the dimer **25a** which gives the dihydro-*s*-triazine by elimination of an aldimine molecule. However, this interpretation of the reaction does not readily accomodate the formation of 1-alkyl-1,2-dihydrotriazines (*e.g.*, **19a,b,c**) from the reaction of aryl aldehydes with *N*-alkyl-substituted amidines since conversion of the intermediate dimer (**25b**) to a dihydro-*s*-triazine would require that the carbon-nitrogen double bond formation occur by elimination of an *N*-benzylidene primary amine. Formation of carbon-nitrogen double bonds by β-elimination of ammonia or secondary amines resulting from cleavage of vicinal N-H and C-N bonds in known (9). However, formation of carbon-nitrogen double bonds by the elimination of an amine from structures requiring cleavage of two vicinal carbon-nitrogen bonds (*e.g.*, **25b**) is, to our knowledge, unprecedented.

We prefer the mechanistic interpretation of the reactions that was first proposed by Hunter and Sim (7) to account for the formation of **19c** and **20c** from the condensation of benzaldehyde with *N*-benzylbenzamidine. This interpretation, which is outlined in Scheme 3, can be applied to the formation of either *N*-unsubstituted or *N*-substituted dihydro-*s*-triazines and involves transamination of *N*-arylideneamidine (**24a** or **7**) by the amidine to produce a triazatriene (**26**) which cyclizes to give the dihydrotriazine. Hunter and Sim prepared **24c** by a zinc chloride-catalyzed condensation of benzaldehyde with *N*-benzylbenzamidine and a base-catalyzed isomerization of hydrobenzamide (**21**). They found that deuteriochloroform solutions of **24c** were converted to **19c** and *N*-benzylidenebenzylamine. We were unable to prepare **24b** by a zinc chloride-catalyzed condensation of *p*-tolualdehyde with *N*-methylbenzamidine. The only product isolated from this reaction was **19b**.

Hunter and Sim proposed that the transformation of **24c** to **19c** in deuteriochloroform requires moisture which is utilized to generate the amidine by reversal of the aldehyde-amidine condensation reaction (equation 1, Scheme 3). Water is reformed in the condensation of the aldehyde with the primary amine (or ammonia) to give an *N*-arylideneamine (or aldimine) (equation 4).

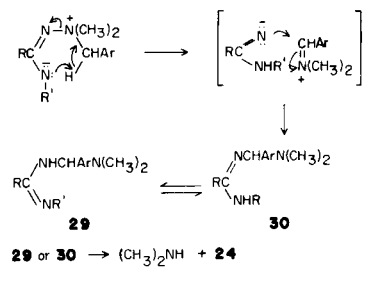
Scheme 3



If *N*-arylidenebenzamidines (**7,24a**) are also intermediates leading to the formation of 1,2-dihydro-*s*-triazines from the thermolysis of amidrazone ylides, our current work which demonstrated the stability of **15a** and **15b**, suggests that they are probably not formed by elimination of dimethylamine from the Stevens rearrangement products. In our earlier communication (1b) we also showed that *N*-benzylbenzamide dimethylhydrazone (**10**), the product which would result from **3a** undergoing a $N^1 \rightarrow N^3$ benzyl migration is also thermally stable and, therefore, an unlikely precursor to **24a**.

A possible pathway from ylide to **24** could involve elimination of dimethylamine from the aminals **29** or **30** which, in turn, could form from the dissociation-recombination process shown in Scheme 4.

Scheme 4



Subsequent conversion of **24** to dihydro-*s*-triazines and *N*-arylideneamines would involve the sequence shown in Scheme 3.

EXPERIMENTAL

Melting points were determined on a Mel-temp apparatus and are uncorrected. Nmr spectra were determined on a Hitachi Perkin-Elmer R24B instrument utilizing hexamethyldisiloxane as an internal standard. Solutions were dried over anhydrous magnesium sulfate.

Amidrazone Syntheses.

Benzamide Dimethylhydrazone.

The following represents an improved synthesis of this compound, which was employed in the synthesis of **3a** (1b). *N,N*-Dimethylhydrazine (18 g.) was added to a solution containing methyl benzimidate hydrochloride (52 g.) and triethylamine (30.3 g.) in 500 ml. of dry methanol. After 3 days, the solvent was removed under reduced pressure. The residue was partitioned between 200 ml. of 3*N* sodium hydroxide and 200 ml. of methylene chloride. The aqueous layer was extracted with three 100 ml. portions of methylene chloride. Evaporation of the dried extracts gave 44 g. of crude product, m.p. 55-63°. Recrystallization from petroleum ether (35-60°) afforded 36 g. (70%) of product, m.p. 68-71°, lit. m.p. 70-71° (10).

Acetamide Dimethylhydrazone (**8**).

Ethyl acetimidate hydrochloride (31 g.) was slowly added to *N,N*-dimethylhydrazine (46 ml.) with cooling to keep the temperature below 50°. The mixture was stirred for 1.5 hours then evaporated at reduced pressure. The residue was treated with 200 ml. of 3*N* sodium hydroxide. The basic solution was exhaustively extracted with methylene chloride. Evaporation of the dried solution gave 11.1 g. (44%) of product, m.p. 68-73°, lit. m.p. 79-80° (11). This material was used without further purification for the preparation of **14a**.

N-Benzylbenzamide Dimethylhydrazone (**10**).

N-Benzylbenzimidoyl chloride (6 g.) (12) was slowly added to a solution containing *N,N*-dimethylhydrazine (1.7 g.) and triethylamine (2.8 g.) in 20 ml. of dry benzene. After 48 hours, 50 ml. of water and 50 ml. of benzene was added. After separation of the organic layer, the aqueous solution was extracted with methylene chloride. The dried combined extracts were evaporated at reduced pressure to give 6.4 g. (91%) of crude product. Distillation of 3.0 g. of the crude material gave 2.1 g. of pure **10** as an orange oil, b.p. 135-140° (0.25 mm): nmr (deuteriochloroform): δ 2.3 (s, 6H), 4.1 (d, 2H, J = 5 Hz, s on NH → ND), 6.4 (bd, 1H, exchangeable), 6.8-7.5 (m, 10H).

Anal. Calcd. for $C_{16}H_{19}N_3$: C, 75.9; H, 7.6; N, 16.6. Found: C, 75.6; H, 7.6; N, 16.5.

N-Methylacetamide Dimethylhydrazone (**11**).

N,N-Dimethylhydrazine (12.2 ml.) was added to a solution containing triethylamine (22 ml.) and 32 g. of *N*-methylacetimidate methylsulfate (13) in 100 ml. of dry methanol. After 24 hours, the solvent was removed at reduced pressure and the residue was partitioned between 100 ml. of 3*N* sodium hydroxide and 100 ml. of methylene chloride. The aqueous layer was extracted with four 50 ml. portions of methylene chloride. Distillation of the residue remaining after removal of the dried extracts 11.2 g. (71%) of product as a colorless liquid, b.p. 62-65° (33 mm.); nmr afforded (deuteriochloroform): δ 1.9 (s, 3H), 2.3 (s, 6H), 2.8 (d, 3H, J = 5 Hz, s on NH → ND), 5.9 (bd, 1H, exchangeable).

Anal. Calcd. for $C_5H_{13}N_3$: C, 52.1; H, 11.4; N, 36.5. Found: C, 52.2; H, 11.4; N, 36.3.

s-Triazine Syntheses.

2-(4-Methylphenyl)-4,6-diphenyl-1,2-dihydro-*s*-triazine (**5b**).

A solution containing benzamidine (2.6 g.) and *p*-tolualdehyde (1.3 g.) in 15 ml. of ethanol was heated under reflux for 4 hours. On cooling, 1.2 g. of **5b** precipitated, m.p. 179-183°. Concentration of the filtrate to 5 ml. afforded an additional 0.7 g. of product, m.p. 180-184°. Recrystallization from ethanol afforded white crystals, m.p. 187-189°; nmr (deuteriochloroform): δ 2.4 (s, 3H), 4.8 (bd, 1H, exchangeable), 6.2 (s, 1H), 8.0-8.3 (m, 4H), 7.3-7.7 (m, 10H).

Anal. Calcd. for $C_{22}H_{19}N_3$: C, 81.2; H, 5.9; N, 12.9. Found: C, 81.4; H, 6.0; N, 12.8.

2-(4-Methylphenyl)-4,6-diphenyl-*s*-triazine (**6b**).

A solution containing 1.0 g. of **5b** and 0.76 g. of chloranil in 50 ml. of acetone was stirred for 1 hour. Filtration afforded 0.7 g. of **6b**, m.p. 205-209°, lit. m.p. 199-200° (14). This material was identical with the material isolated from the thermolysis of **3b** (1b).

1-Methyl-2,4,6-triphenyl-1,2-dihydro-*s*-triazine (**19a**).

A solution containing 5.1 g. of *N*-methylbenzamidine (**13**) and benz-

aldehyde (2.0 g.) in 17 ml. of dry toluene was heated under reflux for 18 hours. The reaction mixture was concentrated to half volume at reduced pressure. On cooling, 2.6 g. of crude **19a** separated, m.p. 148-155°. Recrystallization from ethanol gave white crystals, m.p. 169-170°; nmr (deuteriochloroform): δ 3.0 (s, 3H), 6.2 (s, 1H), 7.1-7.8 (m, 11H), 8.0-8.4 (m, 4H).

Anal. Calcd. for $C_{22}H_{19}N_3$: C, 81.2; H, 5.9; N, 12.9. Found: C, 81.6; H, 6.1; N, 12.6.

The picrate was recrystallized from methanol as yellow needles, m.p. 201-204°.

Anal. Calcd. for $C_{28}H_{22}N_6O_7$: C, 60.6; H, 4.0; N, 15.2. Found: C, 60.8; H, 3.9; N, 14.8.

1-Methyl-2-(4-methylphenyl)-4,6-diphenyl-1,2-dihydro-*s*-triazine (**19b**).

A solution containing *N*-methylbenzamidine (2.4 g.) and *p*-tolualdehyde (1.1 g.) in 8 ml. of dry toluene was heated under reflux for 12 hours. On cooling, 0.5 g. of crude product separated, m.p. 128-138°. Concentration of the filtate gave a second crop, 0.6 g., m.p. 154-156°. Recrystallization from ethanol gave white crystals, m.p. 163-164°; nmr (deuteriochloroform): δ 2.21 (s, 3H), 2.8 (s, 3H), 5.9 (s, 1H), 6.9-7.9 (m, 10H), 8.1-8.3 (m, 4H).

Anal. Calcd. for $C_{23}H_{21}N_3$: C, 81.4; H, 6.2; N, 12.4. Found: C, 81.5; H, 6.4; N, 12.3.

Acid Catalyzed Hydrolysis of **19b**.

A suspension of **19b** (.5 g.) in 5 ml. of 6*M* hydrochloric acid was heated on a steam bath for 7 hours. After cooling and removal of a small quantity of a white solid by filtration, the aqueous solution was extracted with ether. Evaporation of the dried extract gave an oil which after treatment with 2,4-dinitrophenylhydrazine reagent gave 0.11 g. of *p*-tolualdehyde 2,4-dinitrophenylhydrazone, m.p. 235-236°. The ir spectrum of this material was identical with that obtained from an authentic sample.

Reactions of Amidrazones with Benzyl Bromide and α-Bromo-*p*-xylene.

Preparation of **12a** and **13a**.

After 24 hours at room temperature, a reaction mixture containing 8 g. of **8** and 9.6 ml. of benzyl bromide in 80 ml. of dry acetonitrile deposited 9.3 g. of crude **12a**, m.p. 181-192°. Dilution of the filtrate with anhydrous ether afforded a viscous oil which could not be crystallized. This material was utilized for the preparation of **15a**.

Preparation of **12b** and **13b**.

A solution containing 25 g. of **9** (15), and 24.2 g. of benzyl bromide in 100 ml. of dry acetonitrile was heated under reflux for 2 hours. After 3 days at room temperature 9.6 g. of crude **12b** was isolated by filtration, m.p. 183-186°. An additional 0.57 g. of **12b**, (m.p. 174-179°) was obtained by seeding the filtrate. The filtrate was evaporated and the syrupy residue dissolved in a minimum amount of ethanol. Absolute ether was added to the ethanol solution to produce a slight turbidity and the solution was refrigerated. After three days, 28.2 g. of crude **13b** was isolated by filtration, m.p. 97-107°.

Preparation of **12c** and **13c**.

A solution containing 15 g. of **9** (15) and 15.7 g. of α-bromo-*p*-xylene in 80 ml. of dry acetonitrile was heated under reflux for 2 hours. After 24 hours at room temperature, 17.3 g. of a mixture consisting of **12c** and **13c** was isolated by filtration. Recrystallization of the mixture from ethanol gave 8.2 g. (27%) of **12c**, m.p. 177-178°. The less soluble **13c** was isolated from the ethanolic filtrate as described in the preceding experiment.

Preparation of **12d**.

After 3 days at room temperature, a reaction mixture containing 25.3 g. of **10** and 17.1 g. of benzyl bromide in 100 ml. of dry acetonitrile was evaporated at reduced pressure. The syrupy residue was dissolved in methanol and the crude product, 5.1 g. (12%) was precipitated by addition of ether, m.p. 170-174°.

Preparation of **12e**.

After 24 hours at room temperature, a reaction mixture containing 40 g. of **11** and 59.5 g. of benzyl bromide in 375 ml. of dry acetonitrile deposited 43.1 g. (43%) of crude product, m.p. 145-155°.

Preparation of Ylides.

Preparation of **14a**.

A solution of 8.54 g. of **12a** in 35 ml. of water was treated with 17 ml. of 50% sodium hydroxide and the solution extracted with four 35 ml. portions of methylene chloride. The dried extracts were evaporated at reduced pressure (40°) to give a quantitative yield of the ylide as a hygroscopic orange oil.

Preparation of **14b,c,d,e**.

These ylides were obtained by stirring 10 percent suspensions of the conjugate acids (**12b,c,d,e**) in freshly prepared solutions of sodium methoxide (1.1 equivalent) in methanol for 1 to 3 hours. The reaction mixtures were evaporated on a warm water bath (40°) at reduced pressure and the ylides were separated from inorganic material by several extractions with warm benzene. Evaporation of the benzene extracts at reduced pressure (40°) afforded the ylides in excellent yields. All the ylides were hygroscopic and the solid products could not be successfully recrystallized.

Hydrolysis of Ylide **3a**.

A solution of 0.2 g. of the ylide in 3 ml. of water was heated under reflux for 15 hours. After removal of a small quantity of gummy solid, the aqueous solution was evaporated to give 80 mg. of an oil which was converted to 1-benzyl-1,1-dimethylhydrazinium picrate. Recrystallization from ethanol gave orange crystals, m.p. 157-159°. The product was identical with the picrate obtained from 1-benzyl-1,1-dimethylhydrazinium chloride (16).

Anal. Calcd. for $C_{15}H_{17}N_5O_7$: C, 47.5; H, 4.5; N, 18.5. Found: C, 47.3; H, 4.5; N, 18.6.

Preparation of **15a**.

The gummy material (50 g.) which was obtained after isolation of **12a** was treated with 175 ml. of 6*N* sodium hydroxide and the solution extracted with six 100 ml. portions of methylene chloride. The dried extracts were evaporated and the residue on distillation afforded 9.5 g. of crude product, b.p. 87-98° (0.35 mm.). Redistillation afforded pure material.

Hydrolysis of **15a**.

A solution containing 0.66 g. of **15a**, 3.5 ml. of 6*N* sodium hydroxide and 3.5 ml. of ethanol was heated under reflux for 2 hours. The reaction mixture was concentrated to half volume and extracted with chloroform. Evaporation of the dried extract afforded 0.57 g. of 1-benzyl-1-acetyl-2,2-dimethylhydrazine (**16**) as an oil, nmr (deuteriochloroform): δ 2.2 (s, 3H), 2.4 (s, 6H), 4.6 (s, 2H), 7.2 (s, 5H). The product was identical with an authentic sample (3).

Preparation of **15b** and **15c**.

These compounds were obtained by neutralization of **13b** and **13c** with sodium methoxide in methanol by the procedure described above for the preparation of the ylides.

Hydrolysis of **15b**.

1-Benzoyl-1-benzyl-2,2-dimethylhydrazine (**17**) was obtained in 68% yield from **15b** by the procedure described for the hydrolysis of **15a**. Recrystallization from ether gave white prisms, m.p. 61-62°, nmr (deuteriochloroform): δ 2.5 (s, 6H), 4.7 (s, 2H), 6.7-7.9 (m, 10H).

Anal. Calcd. for $C_{16}H_{19}N_2O$: C, 75.6; H, 7.1; N, 11.0. Found: C, 75.4; H, 7.4; N, 10.8.

The product was identical with a sample prepared by the following procedure. Benzoyl chloride (4.17 g.) was added over 10 minutes to a stirred solution containing 5.0 g. of 2-benzyl-1,1-dimethylhydrazine (**16**) and triethylamine (3.36 g.) in 50 ml. of methylene chloride. The precipitated solid was removed by filtration and the filtrate was washed with water. Evaporation of the dried filtrate afforded the product (5.9 g.) as an oil that crystallized on seeding with a pure sample.

Thermolysis Experiments.

Thermolysis of **14a**.

A solution containing 6.0 g. of **14a** in 20 ml. of dry benzene was heated under reflux for 4 hours. After removal of a small quantity of insoluble semi-solid material, the solvent was evaporated at reduced pressure to give an orange oil. Vacuum distillation of this material afforded 0.83 g. of crude 2,4-dimethyl-6-phenyl-*s*-triazine (**18**), b.p. 100-101° (1.8 mm), lit. (17) b.p. 93-96° (1.5 mm). The product was identified by comparison of its nmr spectrum with an authentic sample [(deuteriochloroform): δ 2.6 (s, 6H), 7.2-7.6 (m, 3H), 8.3-8.6 m, 2H)] and conversion to the picrate, m.p. 149-152°, lit. m.p. 153-154° (18). Minor impurity peaks in the nmr spectrum of **18** obtained by thermolysis were noted as singlets at δ 2.1, 2.3 and 3.0. Attempts to isolate other products from the thermolysis mixture by column chromatography on silica gel and by Kugelrohr distillation were unsuccessful.

Dimethylamine was isolated in 36% yield as its benzoyl derivative from a separate experiment in which the amine was trapped in dilute hydrochloric acid. The procedure employed for conversion of the amine to *N,N*-dimethylbenzamide was identical with that employed in the following experiment.

Thermolysis of **14b**.

A sample of **14b** (8.5 g.), which had been dried on a vacuum line at 50° was transferred under nitrogen to a vacuum distillation apparatus which was connected, in turn, to a trap that was immersed in liquid nitrogen. The ylide was decomposed by heating at 130° (1.6 mm) for 15 minutes. The liquid distillate was redistilled through an 8″ Vigreaux column to give four fractions totalling 1.17 g., b.p. 30-95° (0.37 mm). A center fraction, b.p. 55° (0.37 mm) was identified as pure *N*-benzylidenemethylamine (**20a**) by nmr. Each of the other fractions was also found to consist mainly of **20a** which could be separated from the other components by gc utilizing a SE-30 on 100/120 Varaport column (165°). Based on gc analysis, the yield of **20a** obtained was 44%. The nmr spectrum of an authentic (19) sample of **20a** was obtained: (deuteriochloroform) δ 3.4 (d, 3H, J = 0.5 Hz); 7.2-7.9 (m, 5H), 8.2 (d, 1H, J = 0.5 Hz).

The contents of the liquid nitrogen trap were dissolved in 6*N* hydrochloric acid. The solution was treated with 5 ml. of benzoyl chloride and made strongly alkaline with 10*N* sodium hydroxide. After vigorous stirring for 4 hours, the solution was extracted with benzene. Evaporation of the dried extracts gave 2.1 g. (42%) of *N,N*-dimethylbenzamide as an oil which was identified by nmr and ir.

After trituration with ether, the distillation residue afforded 3.1 g. (60%) of crude **19a**, m.p. 155-165°.

Thermolysis of the ylide (0.44 g.) in refluxing dry toluene (25 ml.) for 5 hours afforded **19a**, m.p. 165-166° in 82% yield. The product was isolated by evaporating the solvent at reduced pressure and triturating the residue with ether.

Thermolysis of **14c**.

A solution containing 3.2 g. of **14c** in 100 ml. of dry toluene was heated under reflux for 4 hours. The reaction mixture was concentrated to 15 ml. and treated with 15 ml. of petroleum ether (35-60°). On cooling, 0.6 g. of **19b** precipitated, m.p. 155-158°. A second crop (0.4 g., m.p. 145-154°) was obtained after addition of 30 ml. of petroleum ether to the filtrate.

The filtrate described above was evaporated at reduced pressure. Vacuum distillation of the residue gave a fraction [0.4 g., b.p. 40-45° (1.5 mm.)] which was identified [tlc (silica gel, 50% benzene-petroleum ether) and nmr] as **20b** contaminated with approximately 10% *p*-tolualdehyde. The nmr spectrum of authentic (20) **20b** was obtained; nmr (deuteriochloroform): δ 2.2 (s, 3H), 3.3 (d, 3H, J = 0.5 Hz), 7.1 and 7.5 (aromatic AB, J = 7 Hz, 4H), 8.1 (d, 1H, J = 0.5 Hz).

Thermolysis of **14d**.

The ylide (0.5 g.) was heated at 130° for 3.5 hours. Tlc on silica gel [chloroform-ethanol (20:1)] indicated the presence of 3 major and 7 minor components. Two of the major components had R*f* values identical with authentic **19c** and **20c** (7). The nmr signals characteristic of both **19c** and **20c** were observed in the spectrum of the crude thermolysis mixture. Preparative tlc of the mixture (150 mg.) afforded, after recrystallization from ethanol, 15 mg. of **19c**, m.p. 136-140°, lit. m.p. 135-136° (7). Identity was established by nmr, ir and tlc.

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