Formation and Reactions of (1-Chloroalkyl)carbamoyl Chlorides. Synthesis of 1,2,4-Triazolidine-5-ones

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N-(α-Chlorobenzyl)carbaniloyl chloride and (α-chlorobenzyl)methylcarbamoyl chloride are formed by reaction of phosgene with *N*-benzylideneaniline and *N*-benzylidenemethylamine, respectively. Reaction of these carbamoyl chlorides with a number of nucleophiles is described, some of which cause cleavage of the benzyl to nitrogen bond while others give rise to substitution products without such cleavage. Of the latter type, substituted hydrazines react to effect ring closure to 1,2,4-triazolidine-5-ones. The method serves as a convenient synthesis of these new heterocyclic systems.

Le chlorure de *N*-(α-chlorobenzyl) carbaniloyle et le chlorure de (α-chlorobenzyl) méthylcarbamoyle sont formés dans la réaction entre le phosgène et la *N*-benzylidène aniline et la *N*-benzylidène méthylamine, respectivement. La réaction de ces chlorures de carbamoyle avec un certain nombre de nucléophiles est décrite, certains d'entre eux provoquent le clivage du benzyle lié à l'azote tandis que d'autres donnent lieu à des produits de substitution sans clivage. Les hydrazines substituées réagissent selon ce dernier schéma en formant un cycle de type triazolidine-1,2,4, ones-5. La méthode constitue une synthèse commode de ces nouveaux systèmes hétérocycliques. [Traduit par le journal]

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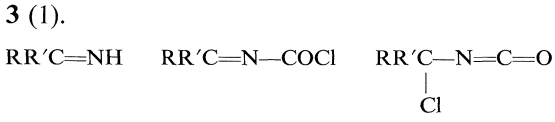
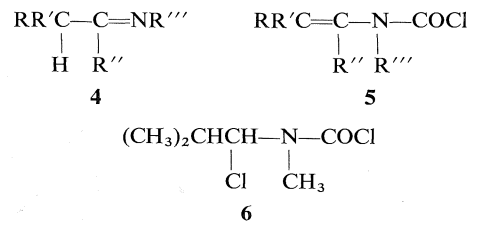
Introduction

Phosgene has been reported to react with azomethines, **1**, to produce *N*-(chloroformyl)-azomethines, **2**, and 1-chloroalkyl isocyanates, **3** (1).



1 **2** **3**

Enolizable imines of the type **4** were reported by Chupp (2) to react with phosgene to afford (1-alkenyl)carbamoyl chlorides, **5**. In an unusual example, *N*-isobutylidinemethylamine (**4**, R = R′ = R‴ = CH_3; R″ = H) was converted to (1-chloro-2-methylpropyl)methylcarbamoyl chloride (**6**) which is surprisingly stable to dehydrochlorination (3). Kiefer (4) recently reported the reaction of phosgene with some non-enolizable *N*-substituted imines to give the corresponding (1-chloroalkyl)carbamoyl chlorides.



4 **5**

6

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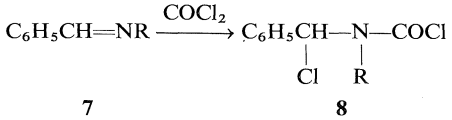
The present work was undertaken to examine the reaction of non-enolizable *N*-substituted imines with phosgene as a general route to (1-chloroalkyl)carbamoyl chlorides with a view to the use of such compounds in the synthesis of heterocyclic systems. A similar study was made of *N*-(α-chlorobenzylidene)carbamoyl chloride formed from the addition of phosgene to benzonitrile (5). In this paper, we report the formation of the (α-chlorobenzyl)carbamoyl chlorides, **8**, and some of their reactions including conversion to the 1,2,4-triazolidine-5-ones, **22**.

Results and Discussion

N-Benzylideneaniline (**7***a*) and *N*-benzylidenemethylamine (**7***b*) underwent reaction with phosgene in benzene solution to afford *N*-(α-chlorobenzyl)carbaniloyl chloride (**8***a*) and (α-chlorobenzyl)methylcarbamoyl chloride (**8***b*), respectively (see Scheme 1). The (1-chloroalkyl)carbamoyl chlorides **8** were stable and could be isolated under anhydrous conditions. The struc-



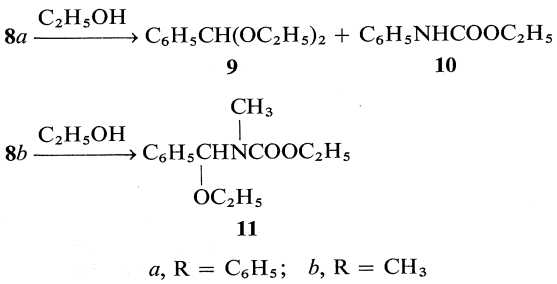
7 **8**

a, R = C_6H_5; *b*, R = CH_3

SCHEME 1

tural assignments **8** are consistent with spectral data and elemental analyses (see Experimental).

Ethanolysis of **8***a* caused cleavage to benzaldehyde diethyl acetal (**9**) and ethyl carbanilate (**10**). On the other hand, the methyl derivative, **8***b* did not undergo cleavage, but was converted to a product characterized as ethyl (α-ethoxybenzyl)-methylcarbamate (**11**) which was stable in refluxing ethanol (Scheme 2).



SCHEME 2

Reactions of the carbamoyl chlorides, **8**, with anhydrous ammonia and primary amines resulted in products which can be explained as having formed through the intermediacy of the corresponding (α-aminobenzyl)ureas, **12**, followed by base-catalyzed cleavage (see Scheme 3). From reaction with methylamine, *N*-benzylidenemethylamine (**13**, $R' = CH_3$) was obtained from both **8***a* and *b* together with 1-methyl-3-phenylurea (**14***a*, $R' = CH_3$) from **8***a*, and 1,3-dimethylurea (**14***b*, $R' = CH_3$) from **8***b*. Aniline reacted in an analogous fashion to produce *N*-benzylideneaniline (**13**, $R' = C_6H_5$) from both **8***a* and *b* along with 1,3-diphenylurea (**14***a*, $R' = C_6H_5$) from **8***a*, and 1-methyl-3-phenylurea (**14***b*, $R' = C_6H_5$) from **8***b*. Anhydrous ammonia converted **8***a* to 1,1′-benzylidenebis(3-phenylurea) (**15***a*) which, at least formally, can be viewed as having been formed through the cleavage of **12***a* ($R' = H$) to benzylidene-ammonia (**13**, $R' = H$) and phenylurea (**14***a*, $R' = H$) which reacted further to give the bisurea. In an analogous fashion, 1,1′-benzylidene-bis-(3-methylurea) (**15***b*) was obtained from **8***b*. The bisureas **15***a* (6) and *b* (7) have been reported previously as products of the condensation of benzaldehyde with phenylurea, and methylurea, respectively.

Secondary amines also would be expected to give rise to (α-aminobenzyl)ureas analogous to the intermediates **12** but which would be stable to base-catalyzed cleavage. Dimethylamine converted **8***a* and *b* to the 1,1-dimethyl-3-(α-dimethylaminobenzyl)ureas, **16***a* and *b*, respectively. These compounds react readily with moisture in the atmosphere. On hydrolysis, each forms benzaldehyde and the corresponding urea, **17***a* or *b*. The 3-phenyl-derivative, **16***a*, undergoes what appears to be slow thermal decomposition in a dry nitrogen atmosphere at ambient temperatures as well.

Reaction of the carbamoyl chlorides, **8**, with hydrazine resulted in the formation of the semicarbazones, **19**, as the main products, together with the biureas, **20**, in smaller yields. The 1,2,4-triazolidine-5-ones, **18**, could be postulated as intermediates which underwent base-catalyzed ring opening to the semicarbazones **19** (see Scheme 4).

Under oxidizing conditions, the semicarbazone (**19***a*) is known to undergo cyclization to 3,4-diphenyl-Δ^2-1,2,4-triazolin-5-one (**21**) (8) (see Scheme 5). This result also suggests the intermediacy of the triazolidinone **18**.

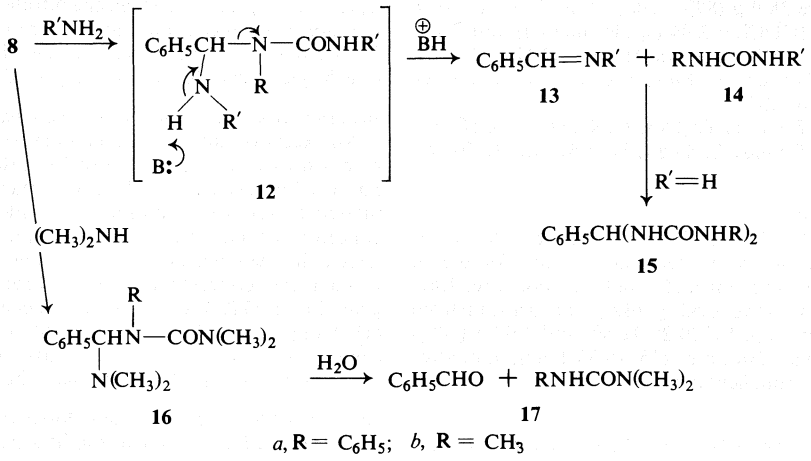
The formation of the biureas, **20**, could be explained by an analogous base-catalyzed cleavage of the corresponding 1,2-bis[(α-hydrazinobenzyl)carbamoyl]hydrazine derivative which would be expected to form, in addition to **18**, by reaction of **8***a* or *b* with hydrazine.

1,2-Disubstituted 1,2,4-triazolidine-5-ones would be expected to be stable to base-catalyzed ring opening of the type **18** → **19**. Reaction of the (α-chlorobenzyl)carbamoyl chlorides, **8**, with 1,2-dimethyl- and with 1,2-diphenylhydrazine afforded convenient routes to the new heterocycles, **22**, which appear to be the first reported 1,2,4-triazolidine-5-ones (see Scheme 6). The structures are consistent with elemental analyses and spectral data (see Experimental).

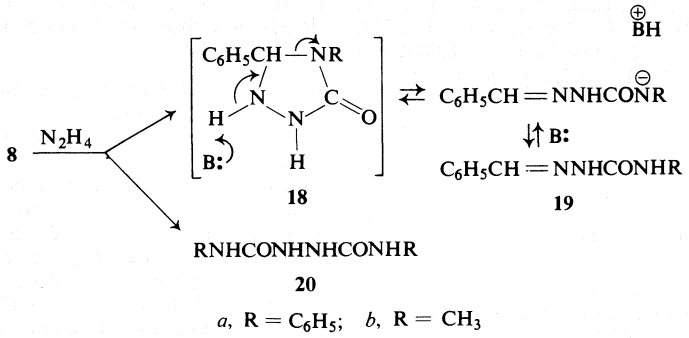
Experimental

All melting points are uncorrected. The n.m.r. spectra were recorded on a Varian HA100 (100 MHz) spectrometer using tetramethylsilane as internal standard. The i.r. spectra were recorded on a Unicam SP1000 spectrometer. Mass spectra were measured on a Hitachi–Perkin–Elmer RMU-6 mass spectrometer. Microanalyses were performed by A. B. Gygli, Toronto, Ontario.

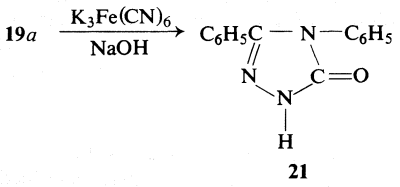
In every case in which a previously described compound was isolated as a product, the spectral data (n.m.r. and i.r.) were identical with those of an authentic sample. For each such crystalline product, the m.p. of a mixture with an authentic sample was not depressed. Each authentic sample was prepared either by the procedure cited, or if none is cited, by an unequivocal method.



SCHEME 3



SCHEME 4



SCHEME 5

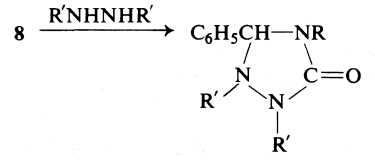
Synthesis of N-(α-Chlorobenzyl)carbaniloyl Chloride (8a)

To a stirred solution of 36.2 g (0.20 mol) of *N*-benzylideneaniline (9) in 100 ml of benzene maintained in an ice bath was added, over 1 h, 175 g of a 12.5% solution (0.22 mol) of phosgene in benzene (Matheson). The reaction mixture was stirred for an additional hour and then filtered, if necessary, to remove *N*-benzylideneaniline hydrochloride. Evaporation of solvent under reduced pressure gave 52.6 g (95% yield) of crude **8a**, m.p. 99–100.5° as white needles, m.p. after recrystallization from hexane, 102.5–103.5°; n.m.r. δ ($CDCl_3$): 7.19 (m, 10H, aromatic-H) and 7.57 p.p.m. (s, 1H, C_6H_5CH); i.r. spectrum (Nujol): $\nu_{C=O}$ 1750 cm^{-1}.

Anal. Calcd. for $C_{14}H_{11}Cl_2NO$: C, 60.03; H, 3.95; Cl, 25.32; N, 5.00. Found: C, 60.17; H, 3.85; Cl, 25.47; N, 5.00.

Synthesis of (α-Chlorobenzyl)methylcarbamoyl Chloride (8b)

By a procedure similar to that described above for the synthesis of **8a**, 22.8 g (0.20 mol) of freshly distilled *N*-benzylidenemethylamine (Aldrich) was treated with



SCHEME 6

phosgene to give 38.9 g (89% yield) of **8***b*, b.p. 116° (0.1 Torr); n.m.r. δ ($CDCl_3$): 2.94 (s, 3H, methyl) and 7.40–7.55 p.p.m. (m, 6H, aromatic-H and C_6H_5CH); i.r. (neat): $\nu_{C=O}$ 1744 cm^{-1}. Mass spectrum parent peak (*m/e*): 217; calcd., 217.

Anal. Calcd. for $C_9H_9Cl_2NO$: C, 49.57; H, 4.16; Cl, 32.51; N, 6.42. Found: C, 49.83; H, 4.41; Cl, 32.76; N, 6.47.

Ethanolysis of ***8a***

A solution of 2.7 g (0.0096 mol) of **8***a* in 50 ml of anhydrous ethanol was heated under reflux for 0.5 h. After removal of ethanol under reduced pressure, fractional distillation gave 0.85 g (49%) of benzaldehyde diethyl acetal (**9**), b.p. 58° (0.25 Torr), and 1.07 g (68%) of ethyl carbanilate (**10**), b.p. 115° (0.35 Torr), m.p. after recrystallization from heptane, 49.5–50.0°.

Ethanolysis of ***8b***

A solution of 5.0 g (0.023 mol) of **8***b* in 50 ml of ethanol was heated under reflux for 0.5 h. After removal of ethanol under reduced pressure, distillation gave 3.7 g (68%) of ethyl (α-ethoxybenzyl)methylcarbamate (**11**), b.p. 118° (0.060 Torr). An analytical sample was obtained by g.l.c.; n.m.r. δ ($CDCl_3$): 1.31, 1.32 (double t, J = 7 Hz, 6H, OCH_2CH_3), 2.57 (s, 3H, NCH_3), 3.66 (q, J = 7 Hz, 2H, $C_6H_5CH(OCH_2CH_3)$), 4.27 (q, J = 7 Hz, 2H, $COOCH_2CH_3$), 6.51 (s, 1H, C_6H_5CH), and 7.2–7.7 p.p.m. (m, 5H, aromatic-H); i.r. (neat): $\nu_{C=O}$ 1710 and ν_{C-O-C} 1160, 1100, 1030 cm^{-1}.

Anal. Calcd. for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found C, 65.91; H, 7.99; N, 5.78.

Reactions of the Carbamoyl Chlorides ***8*** *with Methylamine and with Aniline*

(i) Methylamine

An excess of methylamine was passed through a cooled (0°) stirred solution of either **8***a* or *b* (0.02 mol) in 150 ml of dry ether over a period of 1 h. The solids produced were separated by filtration. From the reaction with **8***a*, 1-methyl-3-phenylurea (**14***a*, R′ = CH_3) was obtained in 89% yield by slurrying the solids in water to dissolve methylamine hydrochloride, collecting the remaining solids by filtration, and recrystallizing them from water, m.p. 151.0–151.5°. From **8***b*, 1,3-dimethylurea (**14***b*, R′ = CH_3) was obtained by slurrying the solids in ethanol, filtering to remove insoluble ammonium chloride, concentrating the ethanol solution, and crystallizing the residue from ether. Additional **14***b* was obtained by concentration of the ether filtrate from the reaction mixture to give a total yield of 70%, m.p. 104–106°. *N*-Benzylidenemethylamine was obtained in 59% yield from the reaction with **8***a*, and in 86% yield from **8***b* by distillation (b.p. 84°, 42 Torr) of the residue from the respective concentrated ether filtrates.

(ii) Aniline

To a stirred solution of either **8***a* or *b* (0.02 mol) in 100 ml of benzene, heated under reflux was added a solution of aniline (0.11 mol) in 150 ml of benzene. The reaction mixture was heated under reflux for an additional 1.5 h, cooled, and filtered. The solid material was slurried in water to remove aniline hydrochloride and the remaining insoluble material recrystallized from ethanol to give, from **8***a*, 1,3-diphenylurea (**14***a*, R′ = C_6H_5) in 81% yield, and from **8***b*, 1-methyl-3-phenylurea (**14***b*, R′ = C_6H_5) in 77% yield. The benzene filtrate from the reaction mixture was concentrated and the residue recrystallized from ethanol to give *N*-benzylideneaniline, m.p. 48–50° in 86% yield from **8***a*, and in 81% yield from **8***b*.

Reaction of ***8a*** *with Anhydrous Ammonia*

An excess of anhydrous ammonia was passed through a cooled (0°) stirred solution of 5.6 g (0.02 mol) of **8***a* in 50 ml of benzene over 0.5 h. The reaction mixture was filtered to remove ammonium chloride, and the filtrate concentrated under reduced pressure. The residue was heated in heptane, and after cooling, the crystals that formed were collected and recrystallized from ethanol to give 2.6 g (72%) of 1,1′-benzylidenebis(3-phenylurea) (**15***a*), m.p. 206–207° (lit. (6), m.p. 198–199°). An authentic sample was prepared as previously described (6). A satisfactory elemental analysis was obtained.

Reaction of ***8b*** *with Anhydrous Ammonia*

By a procedure similar to that described above for the reaction of **8***a*, a solution of **8***b* was treated with an excess of anhydrous ammonia. 1,1′-Benzylidenebis(3-methylurea) (**15***b*) was obtained in 55% yield, m.p. after recrystallization from methanol, 188–189.5° (lit. (7), m.p. 187–188°). An authentic sample was prepared as previously described (7). A satisfactory elemental analysis was obtained.

*Synthesis of 1,1-Dimethyl-3-(α-dimethylaminobenzyl)-3-phenylurea (****16a****)*

To a stirred, cooled (0°) solution of 5.8 g (0.021 mol) of **8***a* in 100 ml of ether was added 10 g (0.22 mol) of dimethylamine over a period of 30 min. The reaction mixture was filtered to remove dimethylamine hydrochloride, and the filtrate concentrated to give 6.2 g (100%) of crude **16***a*, m.p. after recrystallization from ether, 68–70°; n.m.r. δ ($CDCl_3$): 2.37 (s, 6H, $C_6H_5CHN(CH_3)_2$); 2.61 (s, 6H, $CON(CH_3)_2$), 5.65 (s, 1H, C_6H_5CH), and 6.9–7.4 p.p.m. (m, 10H, aromatic-H); i.r. (Nujol): $\nu_{C=O}$ 1645 cm^{-1}.

Anal. Calcd. for $C_{18}H_{23}N_3O$: C, 72.77; H, 7.77; N, 14.09. Found: C, 72.61; H, 7.76; N, 14.28.

A solution of **16***a* in ether was shaken with water. Benzaldehyde and 1,1-dimethyl-3-phenylurea (**17***a*) were isolated from the reaction mixture in essentially quantitative yields.

*Synthesis of 1,1,3-Trimethyl-3-(α-dimethylaminobenzyl)urea (****16b****)*

By a procedure similar to that described for the synthesis of **16***a*, 5 g (0.023 mol) of **8***b* was treated with 10 g (0.22 mol) of dimethylamine to give 5.1 g (94.6%) of crude **16***b*, m.p. after recrystallization from ether, 45.5–47°; n.m.r. δ ($CDCl_3$): 2.27 (s, 6H, $C_6H_5CHN(CH_3)_2$), 2.70 (s, 3H, $N(CH_3)CON(CH_3)_2$), 2.76 (s, 6H, $CON(CH_3)_2$), 5.30 (s, 1H, C_6H_5CH), and 7.25–7.65 p.p.m. (m, 5H, aromatic-H); i.r. (Nujol): $\nu_{C=O}$ 1658 cm^{-1}.

Anal. Calcd. for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.12; H, 8.88; N, 17.79.

A solution of **16***b* in ether was shaken with water. Benzaldehyde and trimethylurea (**17***b*) were isolated from the reaction mixture in essentially quantitative yields.

Reaction of ***8a*** *with Hydrazine*

To a stirred solution of 8.4 g (0.03 mol) of **8***a* in 50 ml of benzene cooled in an ice bath was added, over 15 min, a

solution of 3.2 g (0.10 mol) of anhydrous hydrazine in 10 ml of dimethylformamide. The cooled reaction mixture was stirred for an additional hour and then poured into 100 ml of ice-water. The solid product was collected, slurried in ethanol, and the remaining solid recrystallized from dimethylformamide to give 1.45 g (35%) of 1,6-diphenylbiurea (**20***a*), m.p. 255–256° (lit. (10), m.p. 270°). An authentic sample was prepared from the reaction of phenyl isocyanate with hydrazine. A satisfactory elemental analysis was obtained.

The benzene filtrate from the reaction mixture, and the ethanol filtrate were concentrated and the residues recrystallized from ethanol to give a total of 4.2 g (60%) of benzaldehyde phenylsemicarbazone (**19***a*), m.p. 182–183° (lit. (8), m.p. 180°). An authentic sample was prepared as previously described (8).

*Reaction of **8***b* with Hydrazine*

By a procedure similar to that described for **8***a*, 6.54 g (0.03 mol) of **8***b* was treated with 3.2 g (0.1 mol) of anhydrous hydrazine. From the solids that formed, 0.076 g (3.5%) of 1,6-dimethylbiurea (**20***b*), m.p. after recrystallization from dimethylformamide, 258–259° (lit. (11), m.p. 260°) was obtained. An authentic sample was prepared by the reaction of methyl isocyanate with hydrazine.

The filtrate of the reaction mixture was concentrated and the residue crystallized from ethanol to give 2.2 g (41.5%) of benzaldehyde methylsemicarbazone (**19***b*), m.p. 167–169° (lit. (12), m.p. 166°). An authentic sample was prepared as previously described (12).

*Synthesis of 1,2-Dimethyl-3,4-diphenyl-1,2,4-triazolidine-5-one (**22***a*)*

To a solution of 4 g (0.03 mol) of 1,2-dimethylhydrazine dihydrochloride (13) in 15 ml of water was added a solution of 6.1 g (0.11 mol) of potassium hydroxide in 15 ml of water. Then, 120 ml of acetone was added, and the reaction mixture was filtered to remove potassium chloride.

To 30 ml of acetone cooled in an ice bath (10–12°) were added concurrently over 1 h the 1,2-dimethylhydrazine solution and a solution of 5.6 g (0.02 mol) of **8***a* in 150 ml of acetone. The reaction mixture was stirred for another 1.5 h, filtered, and concentrated. The residue was dissolved in benzene and the benzene solution washed with water, dried over magnesium sulfate and concentrated. The solid residue was recrystallized from heptane to give 3.0 g (57%) of **22***a*, m.p. 142.5–144°); n.m.r. δ ($CDCl_3$): 2.67 (s, 3H, NCH_3), 3.01 (s, 3H, NCH_3), 5.29 (s, 1H, C_6H_5CH), and 7.0–7.5 p.p.m. (m, 10H, aromatic-H), no exchange with D_2O; i.r. (Nujol): $\nu_{C=O}$ 1698 cm^{-1}; no absorptions assignable to NH. Mass spectrum parent peak (*m/e*) 267; calcd., 267.

Anal. Calcd. for $C_{16}H_{17}N_3O$: C, 71.89; H, 6.41; N, 15.72. Found: C, 71.82; H, 6.24; N, 15.88.

*Synthesis of 1,2,4-Trimethyl-3-phenyl-1,2,4-triazolidine-5-one (**22***b*)*

By a procedure similar to that described above for the synthesis of **22***a*, **8***b* was treated with 1,2-dimethylhydrazine to give **22***b* in 42% yield, b.p. 109° (0.02 Torr); n.m.r. δ ($CDCl_3$): 2.49 (s, 3H, NCH_3), 2.57 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 4.43 (s, 1H, C_6H_5CH), and 7.42 p.p.m. (s, 5H, aromatic-H); i.r. (neat): $\nu_{C=O}$ 1729 cm^{-1}; no absorptions assignable to NH. Mass spectrum parent peak (*m/e*): 205; calcd., 205.

Anal. Calcd. for $C_{11}H_{15}N_3O$: C, 64.36; H, 7.37; N, 20.47. Found: C, 64.54; H, 7.46; N, 20.28.

*Synthesis of 1,2,3,4-Tetraphenyl-1,2,4-triazolidine-5-one (**22***c*)*

A solution of 4.2 g (0.015 mol) of **8***a* in 100 ml of benzene, and another solution of 5.52 g (0.03 mol) of 1,2-diphenylhydrazine (Aldrich, freshly recrystallized from ethanol) in 100 ml of benzene were added concurrently over 1 h with stirring to 30 ml of benzene. The reaction mixture was then heated under reflux for 2 h, cooled, and filtered. Evaporation of the solution and crystallization of the residue from heptane gave 2.8 g (49.5%) of **22***c*, m.p. after recrystallization from heptane, 148–148.5°; n.m.r. δ ($CDCl_3$): 6.16 (s, 1H, C_6H_5CH), and 7.0–7.75 p.p.m. (m, 20H, aromatic-H); i.r. (Nujol): $\nu_{C=O}$ 1705 cm^{-1}; no absorption assignable to NH. Mass spectrum parent peak (*m/e*): 391; calcd., 391.

Anal. Calcd. for $C_{24}H_{21}N_3O$: C, 79.77, H, 5.41; N, 10.73. Found: C, 79.71; H, 5.54; N, 10.76.

*Synthesis of 1,2,3-Triphenyl-4-methyl-1,2,4-triazolidine-5-one (**22***d*)*

By a procedure similar to that described above for the synthesis of **22***c*, **8***b* was treated with 1,2-diphenylhydrazine to give **22***d* (33.4% yield), m.p. after recrystallization from heptane, 115.5–116.5°; n.m.r. δ ($CDCl_3$): 2.69 (s, 1H, $N—CH_3$), 5.55 (s, 1H, C_6H_5CH), and 7.0–7.75 p.p.m. (m, 15H, aromatic-H); i.r. (Nujol): $\nu_{C=O}$ 1718 cm^{-1}; no absorption assignable to NH. Mass spectrum parent peak (*m/e*): 329; calcd., 329.

Anal. Calcd. for $C_{21}H_{19}N_3O$: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.64; H, 5.98; N, 12.67.

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