The Lead Tetraacetate Oxidation of Bisacetylhydrazones of α-Dicarbonyl Compounds

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Dedicated to the memory of Professor Nicholas Alexandrou

The oxidative cyclization of the title compounds results in generally two different kinds of products. The first, 1-(*N*,*N*-bisacetylamino)-1,2,3-triazole **7** ($R^3 = CH_3$) is the primary product, while the second, 1-*N*-acetylamino-1,2,3-triazole **8** ($R^3 = CH_3$), when observed, is obtained *via* hydrolysis from the former during work-up and separation of the reaction mixture. The primary products are considered as resulting from intramolecular nucleophilic attack on the acetyl group, of the presumed zwitterionic intermediate **5** ($R^3 = CH_3$), by the *N* of the ambident *N*-acetylimine site of **5**.

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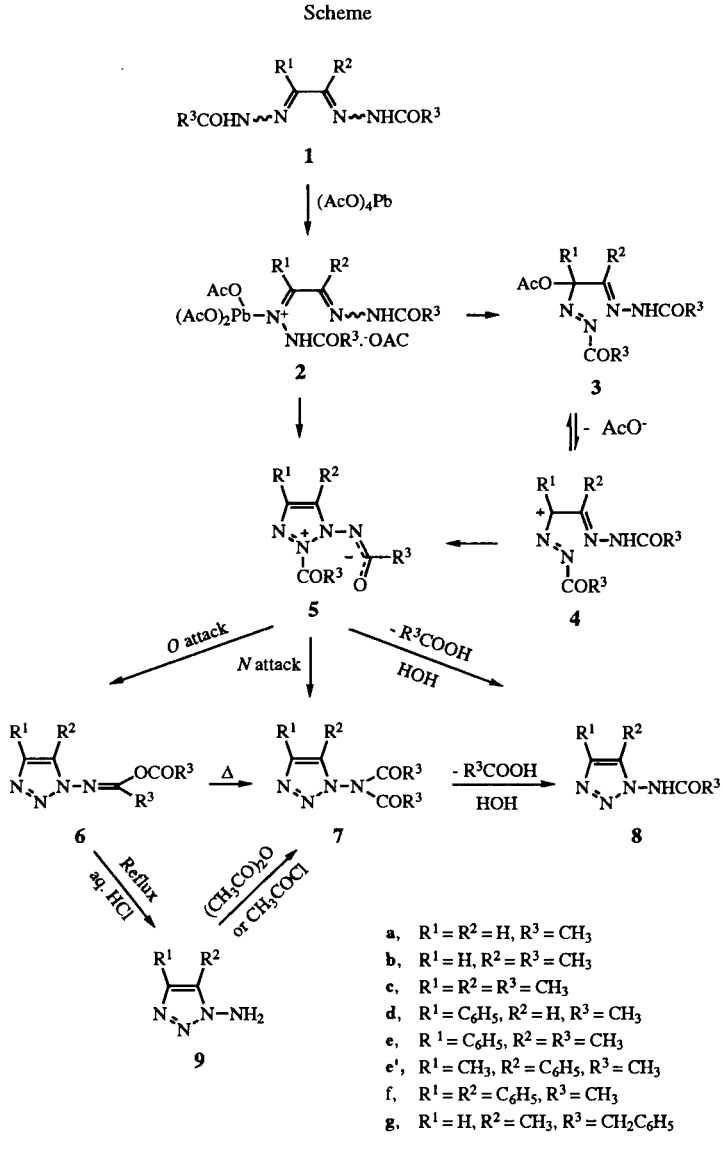
Bisaroylhydrazones of 1,2-dicarbonyl compounds **1** (R^3 = Ar), are known to undergo oxidative cyclization to 1-amino-1,2,3-triazole derivatives. In most instances, they yield either 1-(α-aroyloxyarylideneamino-1,2,3-triazoles (isoimides, **6**) or 1-*N*-aroylamino-1,2,3-triazoles (amides, **8**) [1-6] (Scheme). On the other hand, the oxidation of bisarylacetylhydrazones of 1,2-dicarbonyl compounds **1** ($R^3 = CH_2Ar$) was reported to yield 1-(*N*-arylacetylamino)-1,2,3-triazoles **8** ($R^3 = CH_2Ar$) as the main products [7].

Continuing our work on the oxidative cyclization of 1,2-bis- and 1,2-mixed heteroallylic systems such as bisaroylhydrazones of a-diketones [6], α-hydroxyiminoaroylhydrazones of biacetyl [8] and biacetyl benzoylhydrazone arylhydrazones [9], we report here the preparation and oxidative cyclization with lead tetraacetate of bisacetylhydrazones of 1,2-dicarbonyl compounds **1** ($R^3 = CH_3$). It is of interest to note that in marked contrast to all bisacylhydrazones **1** studied to date, the title bishydrazones yield, upon oxidation with lead tetraacetate, exclusively 1-(*N*,*N*-bisacetylamino)-1,2,3-triazoles (imides, $R^3 = CH_3$, **8**) as the primary products. The 1-*N*-acetylamino-1,2,3-triazoles **8**, which in some cases are also isolated, are believed to be merely the hydrolysis products of the 1,2,3-triazole imides **7**.

Results and Discussion.

The oxidative cyclization of the bisacetylhydrazones **1a-g** results in two different kinds of products (Table 1). The first, 1-(*N*,*N*-bisacetylamino)-1,2,3-triazole **7a-g** is in our view the primary product, while the second, 1-*N*-acetylamino-1,2,3-triazole **8a-g**, when observed, is formed during the aqueous work-up and mostly during the following chromatographic separation on silica gel. The above conclusion is substantiated by the increased yields of **7f** and **7g**, which were obtained when the aqueous work-up of the oxidation mixture was omitted and the

Scheme



latter was loaded directly on the silica gel column (Table 1, entries 6 and 9 respectively). It was also supported by the observed elution of phenylacetic acid from the column, in the case of the oxidation of **1g** (Table 1, entry 8). Since treatment of the oxidation mixture with sodium carbonate would have removed all the acid the latter must have come from hydrolysis of **7g**.

Table 1

Preparation and Oxidation of Bisacylhydrazones **1** with Lead Tetraacetate [a]

Entry	Hydrazone **1**	Isolated Yields % Triazole **7**	Triazole **8**	Total Cyclization (**7** + **8**)
1 **a**	73	15	-	15
2 **b**	63	14	-	14
3 **c**	76	33	-	33
4 **d**		26	32	58
5 **e**	75	3 [c]	59 [c]	62
6 **e** [b]		6 [c]	57 [c]	63
7 **f**	76	7	51	58
8 **g**	92	trace	32	32
9 **g** [b]		9	30	39

[a] Solvent methylene chloride at room temperature. [b] Without aqueous work-up. [c] The regioisomers **7e**, **7e'** and **8e**, **8e'** were not separated. They were identified in the mixture.

From the results of Table 1 it can be seen that, as the substitution on R^1 and R^2 changes from H and CH_3 to Ph the overall cyclization yield increases. Actually, the presence of only one phenyl group in the starting bisacetylhydrazone **1** results in a four-fold increase in the cyclization yield. This can be possibly rationalized in terms of the increased stabilization afforded by the phenyl group in the presumed [10] azacarbonium ion intermediate **4** (Scheme 1). The azacarbonium ion **4**, is in equilibrium with the azoacetate **3** and can lead by cyclization *via* an allowed 5-endo-trig process [11] to the *N*-acetyl-1,2,3-triazol-1-imine **5**. It is reasonable then to assume that favorable substitution at R^1 and R^2 of the starting hydrazone exerts important influence on the cyclization yield.

On the basis of the results obtained for analogous reactions (*i.e.* the acylation of the sodium enolate of ethyl acetoacetate for which a C/O ratio of 99 for benzoyl chloride and of 0.39 for acetyl chloride was reported [12]), one would expect the intramolecular nucleophilic attack of the acetyl group by the *O* of the ambident *N*-acetylimine site in **5**, which yields isoimides **6** ($R^3 = CH_3$), to dominate. Especially so, when comparison is made with the corresponding step in the oxidation of most bisaroylhydrazones which generally leads to the formation of isoimides **6** (R^3 = Ar). However, it is clear that the reactivity in acylation reactions is governed also by steric factors [13] and that the aroyl group is definitely subjected to those more than the acetyl group does.

Our results with respect to formation of imide **7** can be rationalized also in terms of an initial *O* attack followed by a fast thermal isomerization of the resulting isoimide **6** to imide **7**. However, the *c.a.* five-fold faster migration rate constant (for *O* to *N* migration) expected for the acetyl when compared to that of benzoyl group [14] cannot explain the absence of isoimides **6** in the reaction mixture. Particularly so, since at room temperature, the 1-(α-aroyloxyarylideneamino)-1,2,3-triazoles **6** (R^3 = Ar) are stable for years.

Our findings in the case of, the related to the title compounds, bisphenylacetylhydrazone of methylglyoxal **1g**, indicate that bisarylacetylhydrazones of α-dicarbonyl compounds most likely behave upon oxidation with lead tetraacetate similarly, *i.e.* yielding 1-(*N*,*N*-bisarylacetylamino)-1,2,3-triazoles **7** ($R^3 = CH_2Ar$). The latter are further easily hydrolyzed to the corresponding 1-(*N*-arylacetylamino)-1,2,3-triazoles **8** ($R^3 = CH_2Ar$) during work-up and chromatographic separation [15]. The same holds true in our opinion with the inadequately described oxidation of **1d** to **8d**. The primary product **7d** was missed, apparently because it was hydrolyzed to **8d** [16].

The structural assignment of the new compounds was provided by their elemental analyses and spectroscopic characteristics. In addition the 1-(*N*,*N*-bisacetylamino)-1,2,3-triazoles **7a-f** and the 1-*N*-acetylamino-1,2,3-triazoles **8a,b,e** were independently synthesized by treating the corresponding known 1-amino-1,2,3-triazoles **9** with boiling acetic anhydride or with acetyl chloride in the presence of pyridine. The yields are shown in Table 2.

Table 2

Acetylation of 1-Amino-1,2,3-triazoles **9** to 1-(*N*,*N*-Bisacetylamino)-1,2,3-triazoles **7** and 1-*N*-Acetylamino-1,2,3-triazoles **8** with Acetic Anhydride [a] or Acetyl Chloride [b]

1-Aminotriazole **9**	Isolated Yield % 1-(*N*,*N*-Bisacetylamino)-triazole **7**	1-Acetylamino-triazole **8**
a [a]	12	35
b [a]	14	30
c [b]	86	-
d [a]	92	-
e [b]	45	15
f [a]	79	-

[a] Reflux for 1-2 hours in acetic anhydride. [b] Treatment with acetyl chloride in benzene solution in the presence of pyridine.

It should be pointed here that refluxing **9f** with acetic anhydride was reported to give **8f**, instead of **7f**. Moreover, different melting points and carbonyl stretching frequencies than ours were given for **8f** [17].

The regioisomers **7e**, **7e'** and **8e**, **8e'** were not separated and were identified as mixtures. The decision between the two possible regioisomers (4- or 5-substituted-1,2,3-triazoles) in compounds **7b**, **7d** and **7g** was based on the independent synthesis.

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded as nujol mulls on a Perkin-Elmer 297 or 257 spectrometer calibrated with the 1602 cm^{-1} absorption of polystyrene. Proton nmr spectra were obtained in deuteriochloroform solution with tetramethyl silane as internal standard, using a Bruker AM-300 spectrometer. The mass spectra were recorded with a VG TS-250 spectrometer and elemental microanalyses were performed with a Perkin-Elmer 240B analyzer. The reactions were monitored by tlc using pre-coated 0.25 mm Merck silica gel 60 F_{254} plates and the spots were visualized under uv light. All solvents were purchased from Fluka and were purified according to established procedures [18].

Bisacetylhydrazone of biacetyl **1c** [19] and of phenylglyoxal [16] were prepared as described in the appropriate section (preparation of bisacetylhydrazones **1**) and were identified from their reported melting points and spectra. The 1-amino-1,2,3-triazoles **9a** [20], **9b** [21], **9c** [22], **9d** [23], **9e** [24] and **9f** [25] were prepared by hydrolysis of the corresponding 1-(α-benzoyloxybenzylidene)amino-1,2,3-triazoles **6** ($R^3 = C_6H_5$) and were similarly identified. Their acetylation was carried out when acetic anhydride was the reagent as described in the literature [17]. The acetylation with acetyl chloride involved dropwise addition of acetic chloride (0.5 ml) in a solution of **9** (0.5 mmole) in benzene (4 ml) containing pyridine (0.5 ml) at room temperature, followed by a few minutes heating of the mixture at 60-70°.

Work-up of the acetylation mixture involved decomposition of the acetylating agent in ice, washing of the benzene solution successively with sodium carbonate and water and removal of the solvent under reduced pressure, after drying with anhydrous sodium sulfate. Yields of the products **7** and **8** are given in Table 2.

Preparation of Bisacylhydrazones of α-Dicarbonyl Compounds **1** ($R^3 = CH_3$ or $CH_2C_6H_5$). General Procedure.

A solution of of the α-dicarbonyl compound (10 mmoles) and of the appropriate hydrazide (22 mmoles) in ethanol-water 2:1 (*ca* 30 ml) and glacial acetic acid (0.5 ml) was refluxed until all the dicarbonyl compound was consumed (a few minutes to several days). In most cases the resulting bisacylhydrazone was insoluble in the hot solvent mixture and was filtered before cooling. In a few cases however, (*i.e.* **1d** and **1e**) concentration of the solution under reduced pressure and cooling was necessary for the crystallization to occur. The relatively soluble hydrazones were purified by recrystallization from ethanol while the insoluble such by repeated washings with hot ethanol.

Glyoxal Bisacetylhydrazone (**1a**).

This compound was obtained as colorless crystals in 73% yield, mp 317-320°; ir (nujol): 1670, 1338, 1125, 1029, 932, 875, 631 cm^{-1}; ms: m/z 170 (9) [M^+], 127 (26), 85 (26), 57 (26), 43 (100).

Anal. Calcd. for $C_6H_{10}N_4O_2$: C, 42.35; H, 5.92; N, 32.93. Found: C, 42.11; H, 5.79; N, 32.89.

Methylglyoxal Bisacetylhydrazone (**1b**).

This compound was obtained as colorless crystals in 63% yield, mp 277-279°; ir (nujol): 3168, 1670, 1590, 1331, 1122, 1042, 725 cm^{-1}; ms: m/z 185 (37) [M^++1], 141 (39), 113 (22), 99 (22), 43 (100).

Anal. Calcd. for $C_7H_{12}N_4O_2$: C, 45.64; H, 6.57; N, 30.42. Found: C, 45.48; H, 6.60; N, 30.28.

Biacetyl Bisacetylhydrazone (**1c**).

This compound was obtained as colorless crystals in 76% yield, mp >320° (lit [19], >320°); ir (nujol): 3190, 1675, 1334, 1158, 1109, 1018, 725 cm^{-1}; ms: m/z 198 (5) [M^+], 155 (31), 99 (40), 57 (52), 43 (100).

Phenylglyoxal Bisacetylhydrazone (**1d**).

This compound was obtained as colorless crystals in 31% yield, mp 238-240° (lit [16], 240-241°); ir (nujol): 3200, 1662, 1309, 1240, 1091, 954, 715 cm^{-1}; ms: m/z 247 (19) [M^++1], 203 (25), 134 (36), 46 (55), 43 (100).

1-Phenyl-1,2-propanedione Bisacetylhydrazone (**1e**).

This compound was obtained as colorless crystals in 75% yield, mp 244-245°; ir (nujol): 3190, 1657, 1320, 1200, 1105, 760, 708 cm^{-1}; ms: m/z 260 (1) [M^+], 148 (37), 130 (89), 103 (16), 43 (100).

Anal. Calcd. for $C_{13}H_{16}N_4O_2$: C, 59.98; H, 6.20; N, 21.53. Found: C, 59.96; H, 6.10; N, 21.11.

Benzyl Bisacetylhydrazone (**1f**).

This compound was obtained as colorless crystals in 76% yield, mp 248-249°; ir (nujol): 3200, 1690, 1365, 1263, 1110, 752, 690 cm^{-1}; ms: m/z 324 (6) [M^++2], 211 (15), 178 (25), 165 (20), 43 (100).

Anal. Calcd. for $C_{18}H_{18}N_4O_2$: C, 67.06; H, 5.63; N, 17.38. Found: C, 66.95; H, 5.66; N, 17.34.

Methylglyoxal Bisphenylacetylhydrazone (**1g**).

This compound was obtained as colorless crystals in 92% yield, mp 263-265°; ir (nujol): 3180, 1658, 1540, 1235, 1148, 1069, 720, 692 cm^{-1}; ms: m/z 337 (11) [M^++1], 217 (13), 190 (9), 118 (14), 91 (100).

Anal. Calcd. for $C_{19}H_{20}N_4O_2$: C, 67.84; H, 5.99; N, 16.66. Found: C, 67.98; H, 6.00; N, 16.37.

Lead Tetraacetate Oxidation of Bisacylhydrazones **1**, to 1-(*N,N*-Bisacylamino)-1,2,3-triazoles **7** and 1-Acylamino-1,2,3-triazoles **8**. General Procedure.

To a stirred suspension of **1** (2-4 mmoles) in methylene chloride (20 ml), lead tetraacetate (2.4-4.8 mmoles) dissolved in the same solvent (20 ml) was added. The slight excess of the oxidant was checked throughout the experiment by the use of potassium iodide-starch paper and maintained, if necessary, by the addition of extra amounts of lead tetraacetate. When all the starting material was consumed the mixture was filtered and the filtrate was extracted successively with sodium thiosulfate and sodium carbonate. The dried solution was evaporated under reduced pressure and the residue was chromatographed on a medium pressure silica gel column using mixtures of petroleum ether-ethyl acetate of increasing polarity. First, the imides **7** were eluted in analytically pure conditions. Then, in most cases, the amides **8** were further purified by recrystallization.

1-(*N,N*-Bisacetyl)amino-1,2,3-triazole (**7a**).

This compound was obtained as colorless oil in 15% yield; ir (neat): 1749, 1374, 1220, 1004, 940, 795, 705 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.34 (s, 6H, $N(COCH_3)_2$), 7.71 (s, 1H, 5-H), 7.89 (s, 1H, 4-H); ms: m/z 169 (100) [M^++1], 127 (65), 126 (40), 98 (25), 43 (57).

Anal. Calcd. for $C_6H_8N_4O_2$: C, 42.85; H, 4.80; N, 33.32. Found: C, 42.87; H, 5.00; N, 33.57.

1-(*N,N*-Bisacetyl)amino-5-methyl-1,2,3-triazole (**7b**).

This compound was obtained as colorless oil in 14% yield; ir (neat): 1737, 1562, 1192, 1023, 960, 835, 640 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.21 (s, 3H, 5-CH_3), 2.33 (s, 6H, $N(COCH_3)_2$), 7.63 (s, 1H, 4-H); ms: m/z 183 (22) [M^++1], 141 (10), 131 (23), 112 (12), 101 (6), 69 (79), 43 (100).

Anal. Calcd. for $C_7H_{10}N_4O_2$: C, 46.15; H, 5.52; N, 30.76. Found: C, 46.15; H, 5.61; N, 30.81.

1-(*N,N*-Bisacetyl)amino-4,5-dimethyl-1,2,3-triazole (**7c**).

This compound was obtained as colorless oil in 33% yield; ir (neat): 1740, 1416, 1362, 1198, 1012, 930, 723 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.12 (s, 3H, 5-CH_3), 2.32 (s, 6H, $N(COCH_3)_2$), 2.34 (s, 3H, 4-CH_3); ms: m/z 197 (13) [M^++1], 155 (62), 126 (38), 68 (60), 43 (100).

Anal. Calcd. for $C_8H_{12}N_4O_2$: C, 48.97; H, 6.17; N, 28.56. Found: C, 49.15; H, 6.28; N, 28.68.

1-(*N,N*-Bisacetyl)amino-4-phenyl-1,2,3-triazole (**7d**).

This compound was obtained as colorless crystals in 26% yield, mp 152-153° (ethyl acetate); ir (nujol): 1755, 1730, 1218, 1010, 811, 694 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.37 (s, 6H, $N(COCH_3)_2$), 7.33-7.49 (m, 3H, 3',4', 5'-H), 7.85 (m, 2H, 2',6'-H), 7.92 (s, 1H, 5-H); ms: m/z 245 (100) [M^++1], 203 (48), 174 (36), 105 (10), 43 (32).

Anal. Calcd. for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.06; H, 5.04; N, 22.96.

1-(*N*-Acetyl)amino-4-phenyl-1,2,3-triazole (**8d**).

This compound was obtained as colorless crystals in 32% yield, mp 155-157° (ethyl acetate); ir (nujol): 3160, 1682, 1270, 1229, 810, 755, 692 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.64 (s, 3H, $COCH_3$), 7.28-7.47 (m, 3H, 3',4',5'-H), 7.79 (m, 2H, 2',6'-H), 7.90 (s, 1H, 5-H); ms: m/z 203 (25) [M^++1], 174 (30), 116 (47), 104 (58), 43 (100).

Anal. Calcd. for $C_{10}H_{10}N_4O$: C, 59.39; H, 4.98; N, 27.71. Found: C, 59.11; H, 5.01; N, 27.38.

1-(*N,N*-Bisacetyl)amino-5(4)-methyl-4(5)-phenyl-1,2,3-triazole (**7e** and **7e'**).

These compounds were obtained as a mixture of colorless crystals not possible to isolate by column chromatography in 3% yield, mp 108-112° (ethyl acetate-petroleum ether); ir (nujol): 1745, 1200, 1018, 940, 900, 772, 700 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.16 (s, 3H, 5-CH_3), 2.43 (s, 12H, $N(COCH_3)_2$), 2.55 (s, 3H, 4-CH_3), 7.23-7.78 (m, 6H, 3',4',5'-H), 8.12 (m, 4H, 2',6'-H); ms: m/z 259 (100) [M^++1], 217 (43), 188 (64), 130 (23), 43 (36).

Anal. Calcd. for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.70. Found: C, 60.29; H, 5.30; N, 21.48.

1-(*N*-Acetyl)amino-5(4)-methyl-4(5)-phenyl-1,2,3-triazole (**8e** and **8e'**).

These compounds were obtained as a mixture of colorless crystals not possible to isolate by column chromatography in 59% yield, mp 207-211° (ethyl acetate); ir (nujol): 3140, 1720, 1260, 1248, 777, 745, 705 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.07 (s, 3H), 2.25 (s, 3H), 2.31 (s, 3H), 2.35 (s, 3H), 7.24-7.50 (m, 6H, 3',4',5'-H), 7.58 (m, 4H, 2',6'-H); ms: m/z 217 (100) [M^++1], 130 (39), 115 (31), 104 (46), 43 (34).

Anal. Calcd. for $C_{11}H_{12}N_4O$: C, 61.09; H, 5.59; N, 25.91. Found: C, 61.18; H, 5.66; N, 25.75.

1-(*N,N*-Bisacetyl)amino-4,5-diphenyl-1,2,3-triazole (**7f**).

This compound was obtained as colorless crystals in 7% yield, mp 152-153° (ethyl acetate-petroleum ether); ir (nujol): 1742, 1250, 1212, 1005, 780, 715, 700 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.30 (s, 6H, $N(COCH_3)_2$), 7.25-7.65 (m, 10H, aromatic); ms: m/z 321 (26) [M^++1], 250 (80), 192 (47), 104 (56), 43 (100).

Anal. Calcd. for $C_{18}H_{16}N_4O_2$: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.11; H, 5.08; N, 17.82.

1-(*N*-Acetyl)amino-4,5-diphenyl-1,2,3-triazole (**8f**).

This compound was obtained as colorless crystals in 51% yield, mp 246-247° (chloroform-ether); ir (nujol): 3145, 1730, 1269, 1240, 1002, 761, 705 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.60 (s, 3H, $COCH_3$), 7.25-7.60 (m, 10H, aromatic); ms: m/z 279 (99) [M^++1], 250 (100), 178 (100), 165 (63), 43 (94).

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 69.17; H, 4.96; N, 20.30.

1-(*N,N*-Bisphenylacetyl)amino-5-methyl-1,2,3-triazole (**7g**).

This compound was obtained as colorless oil in 9% yield; ir (neat): 1742, 1230, 1125, 725, 699 cm^{-1}; ms: m/z 336 (7) [M^++2], 188 (16), 161 (8), 118 (17), 91 (100).

This compound was too sensitive to purify it for elemental analysis and to record ^1H nmr spectrum because of its hydrolysis to **8g**.

1-(*N*-Phenylacetyl)amino-5-methyl-1,2,3-triazole (**8g**).

This compound was obtained as colorless crystals in 30% yield, mp 132-133° (ethanol); ir (nujol): 3165, 1710, 1108, 980, 950, 818, 722 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.13 (s, 3H, 5-CH_3), 3.77 (s, 2H, $CH_2C_6H_5$), 7.23-7.40 (m, 5H, aromatic), 7.43 (s, 1H, 4-H); ms: m/z 217 (13) [M^++1], 216 (12), 188 (56), 118 (16), 91 (100).

Anal. Calcd. for $C_{11}H_{12}N_4O$: C, 61.09; H, 5.59; N, 25.91. Found: C, 61.12; H, 5.68; N, 25.93.

REFERENCES AND NOTES

[1] D. Y. Curtin and N. E. Alexandrou, *Tetrahedron*, **19**, 1697 (1963).

[2] N. E. Alexandrou, *Tetrahedron*, **22**, 1309 (1966).

[3] H. El Khadem and M. A. E. Shaban, *J. Chem. Soc. (C)*, 519 (1967).

[4] H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza and A. Vaciago, *J. Chem. Soc., Perkin Trans.* 2, 662 (1972).

[5a] H. Wamhoff, Comprehensive Heterocyclic Chemistry, Vol 5, A. R. Katritzky and C. W. Rees, eds, Pergamon Press, Oxford, 1984, p 669; [b] R. N. Butler, Synthetic Reagents, Vol 3, J. P. Pizey, ed, Wiley, New York, 1977, p 277.

[6] A. J. Maroulis, P. D. Akrivos and C. P. Hadjiantoniou-Maroulis, *J. Heterocyclic Chem.*, **30**, 913 (1993).

[7] J. Stefanidou-Stefanatou, E. Varella, E. D. Micromastoras and N. E. Alexandrou, *J. Heterocyclic Chem.*, **16**, 1373 (1979).

[8] A. B. Theocharis, A. J. Maroulis, C. P. Hadjiantoniou-Maroulis and N. E. Alexandrou, *J. Chem. Soc., Perkin Trans. 1*, 619 (1989).

[9] C. P. Hadjiantoniou-Maroulis, A. J. Maroulis, A. Terzis and D. Mentzafos, *J. Org. Chem.*, **57**, 2252 (1992).

[10] R. W. Hoffmann and H. J. Luthardt, *Tetrahedron Letters*, 3501 (1967).

[11] J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).

[12] R. Gelin, S. Gelin and A. Galliaud, *Bull. Soc. Chim. France*, 3416 (1973).

[13] L. M. Jackman and B. C. Lange, *Tetrahedron*, **33**, 2737 (1977).

[14] D. G. McCarthy and A. F. Hegarthy, *J. Chem. Soc., Perkin Trans. 2*, 1085 (1977).

[15] Support for this explanation is offered by the isolation of phenylacetic acid during chromatography of the oxidation mixture, washed with sodium carbonate solution. See ref [7], Experimental.

[16] H. El Khadem and M. Shaban. *J. Chem. Soc. C*, 2167 (1970).

[17] M. A. E. Shaban and M. A. M. Nassr, *Bull. Chem. Soc. Japan*, **49**, 2606 (1976).

[18] D. D. Perrin, W. L. F. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1966.

[19] K. Ronco, B. Prijs and H. Herlenmeyer, *Helv. Chim. Acta*, **39**, 2088 (1956).

[20] R. Stollé, *Chem. Ber.*, **59**, 1743 (1926).

[21] L. Wolff and A. A. Hall, *Chem. Ber.*, **36**, 3617 (1903).

[22] V. von Pechmann and W. Bauer, *Chem. Ber.*, **33**, 645 (1900).

[23] S. Hauptmann, H. Wilde and K. Moser, *Tetrahedron Letters*, 3295 (1967).

[24] T. L. Gilchrist, G. E. Gymer and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 555 (1973).

[25] S. Munch and H. Kind, *J. Prakt. Chem.*, **68**, 441 (1856).