($CDCl_3$) δ 1.0 (s, C(18)$H_3$), 1.02 (s, C(19)$H_3$), 1.38 (m, $CH_3CH_2$), 1.72, 1.79 (2s, together C(21)$H_3$), 2.0 (s, OAc), 1.2-2.4 (m), 4.2 (m, $CH_3CH_2$), 4.55 (m, C(3)$H$), 5.35 (br s, C(6)$H$), 5.8, 6.15 (2 br s, together C(16)$H$); exact mass calcd for $C_{28}H_{42}NO_5P$ $m/e$ 503.280, found 503.280.

**Pregna-4,16-diene-3,20-dione (7a).** An aqueous solution of 5% $HClO_4$ (2 mL) was added to a stirred solution of crude **6a** (0.24 g, 0.50 mmol) in 1,4-dioxane (6 mL) at rt. The mixture was refluxed for 12 h. After the solution was cooled a saturated aqueous solution of $Na_2CO_3$ (5 mL) was added. The residue was dissolved in 25 mL of $CH_2Cl_2$, and the organic layer was washed with water (10 mL) and brine (10 mL), dried ($Na_2SO_4$), and concentrated to give 0.164 g of a slowly solidifying yellow oil. Pure **7a** was obtained by column chromatography (silica, $CH_2Cl_2$) followed by one crystallization from ether/acetone, in a yield of 0.134 g (86%), mp 185-188 °C: $[\alpha]^{20}_D$ +156° (c 1, EtOH) [lit.[18] mp 186-188 °C, $[\alpha]_D$ +155° (c 1, EtOH)]. This material was identical with a commercial sample according to IR and $^1H$ NMR.

**3-Methoxy-19-norpregna-1,3,5(10),16-tetraen-20-one (7b)** was prepared analogously to the procedure given for **7a**, using **6b** (0.137 g, 0.30 mmol). Pure **7b** (0.071 g, 76%) was obtained by chromatography, mp 194-195 °C: $[\alpha]^{20}_D$ +118 (c = 1, $CHCl_3$) [lit.[19] mp 193-194 °C, $[\alpha]^{15}_D$ +115° (c 1, $CHCl_3$)]. This material was identical by IR and $^1H$ NMR with a commercial sample.

**3β-Hydroxypregna-5,16-dien-20-one (7c)** was prepared analogously to the procedure given for **7a** using **6c** (0.22 g, 0.44 mmol). After purification by filtration over a short column of silica and crystallization from EtOAc 0.098 g (71%) of **7c** was obtained, mp 211-212 °C. This material was identical by IR and $^1H$ NMR with an authentic sample,[20] mp 212-214 °C.

**(20ξ)-17β-[(Diethylphosphono)isocyanomethyl]-3-methoxyandrosta-3,5-diene (8).** A mixture of **5a** (0.56 g, 1.0 mmol) and $NaBH_4$ (0.04 g, 1.0 mmol) in THF (10 mL) and 96% EtOH (10 mL) was stirred at 20 °C for 3 h. The solvents were removed, and the resulting residue was dissolved in 25 mL of water and extracted with two portions of 25 mL of $CH_2Cl_2$. The combined extracts were washed with brine (10 mL), dried ($Na_2SO_4$) and concentrated to yield 0.43 g (93%) of **8**, mp 59-62 °C: IR (neat) 2137 (N=C), 1654, 1629 (C=C), 1256, 1022 $cm^{-1}$ (P(O)(OEt)$_2$); $^1H$ NMR ($CDCl_3$) δ 0.78, 0.80 (2s, together C(18)$H_3$), 0.95 (s, C(19)$H_3$), 1.35 (m, $CH_3CH_2$), 1.4-2.4 (m), 3.52 (s, $CH_3O$), 3.70 (dd, C(17)$H$, $J$ = 13, 17 Hz), 3.92 (d, C(20)$H$, $J$ = 22 Hz), 4.20 (m, $CH_3CH_2$), 5.10(s, C(4)$H$), 5.20 (t, C(6)$H$); exact mass calcd for $C_{26}H_{40}NO_4P$ $m/e$ 461.269, found 461.269.

**20ξ-(Diethylphosphono)-20ξ-isocyano-3-methoxypregna-3,5-diene (9).** $t$-BuOK (0.24 g, 2.0 mmol) was added to a solution of **8** (0.92 g, 2.0 mmol) in THF (20 mL) at -40 °C. After the solution was stirred for 10 min, MeI (150 μL, 2.4 mmol) was added. Stirring was continued for 15 min at -40 °C, and then the temperature was raised to 0 °C. The suspension was poured into 50 mL of water, and the mixture was extracted with two portions of 25 mL of $CH_2Cl_2$. The combined extracts were washed with brine (10 mL), dried ($Na_2SO_4$), and concentrated to give 0.86 g (90%) of **9**, mp 127-129 °C: IR (neat); 2125 (N=C), 1654, 1628 (C=C), 1255, 1025 $cm^{-1}$ (P(O)(OEt)$_2$); $^1H$ NMR ($CDCl_3$) δ 0.94 (2s, together C(18)$H_3$ and C(19)$H_3$), 1.38 (m, $CH_3CH_2$), 1.60, 1.65 (2s, together C(21)$H_3$), 2.55 (2t, C(17)$H$, $J$ = 15 Hz), 3.55 (s, $CH_3O$), 4.20 (m, $CH_3CH_2$), 5.10 (s, C(4)$H$), 5.20 (br s, C(6)$H$); exact mass calcd for $C_{27}H_{42}NO_4P$ $m/e$ 475.285, found 475.285.

**Progesterone (10)** was prepared analogously to the procedure given for **7a**, using **9** (0.176 g, 0.37 mmol). After chromatography (silica, $CH_2Cl_2$) 0.083 g (71%) of **10** was obtained as a 1:6 mixture of 17α- and 17β-progesterone **10** (mp 126-129 °C), as established by $^1H$ NMR integration of the C18 and C19 signals: $^1H$ NMR ($CDCl_3$) δ 0.65 (s, C(18)-β), 0.90 (s, C(18)-α), 1.10 (s, C(19)-α), 1.18 (s, C(19)-β), 2.07 (s, C(20)-α), 2.12 (s, C(20)-β), 2.55 (C(17)-β), 2.75 (C(17)-α), 5.70 (s, C(4)).

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**Supplementary Material Available:** $^1H$ NMR spectra of compounds **4**, **5**, **6**, **8**, **9**, and **10** (14 pages). Ordering information is given on any current masthead page.

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# 1,2,3-Triazol-1-imines. 1. The Synthesis and Lead Tetraacetate Oxidation of Biacetyl Benzoylhydrazone Arylhydrazones to the Novel 2-Aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines

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The synthesis and the $Pb(OAc)_4$ oxidation of the mixed bishydrazones of biacetyl **7** was studied. The formation of the novel *N*-benzoyl-1,2,3-triazol-1-imines **9** from the oxidation of **7** provided support to the proposed in the past mechanism for the oxidation of bis-aroylhydrazones of α-dicarbonyl compounds **4**. Thermolysis and photolysis of **9a** in DMSO was carried out. The results suggested that benzoylnitrene was formed in the photochemical reaction, and therefore compounds such as **9** could serve as non-azide aroyl nitrene precursors. For **9a** the results of the X-ray analysis were correlated with charge densities and bond orders gleaned by the MNDO method. Product **9d** was alternatively synthesized by the addition of photochemically generated benzoylnitrene to the 1,2,3-triazole **21**.

The oxidation of bis-arylhydrazones of 1,2-dicarbonyl compounds **1** with a variety of oxidants generally leads to the formation of the corresponding bis-areneazoethylenes **2**[1-7] (Scheme I). Compounds **2** exist in dynamic equilibrium with the isomeric *N*-aryl-1,2,3-triazol-1-imines **3**. The presence of the form **3** has been correctly inferred from

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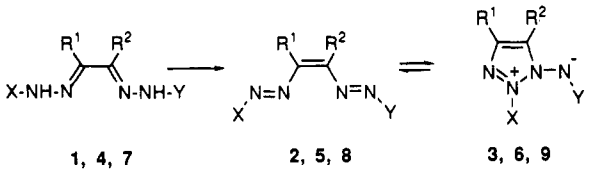
0022-3263/92/1957-2252$03.00/0 

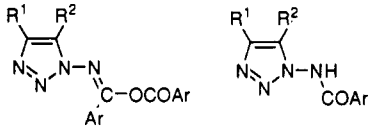
**Scheme I**



1, 4, 7 2, 5, 8 3, 6, 9

1, 2 3: X=Y=Ar, $R^1$= R or Ar, $R^2$= R or Ar
4, 5, 6: X=Y=COAr, $R^1$= R or Ar, $R^2$= R or Ar
7, 8, 9: X=Ar, Y=COPh, $R^1$=$R^2$=$CH_3$

its photochemical and thermal transformations and from trapping in a range of 1,3-dipolar cycloadditions with various dipolarophiles[8-13] while both isomeric forms **2** and **3** were directly observed by variable-temperature $^1$H NMR spectroscopy.[14] On the other hand, bis-aroylhydrazones of 1,2-dicarbonyl compounds **4** are known to undergo oxidative cyclization to 1-amino-1,2,3-triazole derivatives. Thus, depending upon the nature of the aroyl group in the starting hydrazone, they yield either 1-[[(aroyloxy)arylidene]amino]-1,2,3-triazoles (isoimides, **10**) or 1-(aroylamino)-1,2,3-triazoles **11**.[15-18] Both products **10** and **11**



10 11

a, $R^1$=$R^2$= $CH_3$, Ar=Ph
b, $R^1$=$R^2$= Ph, Ar= 2-Br-Ph

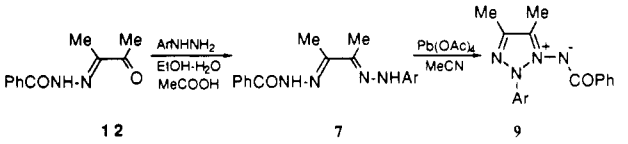
presumably result by a reaction sequence (**4** → **5** → **6**, Scheme I) analogous to that implied for the oxidation of bis-arylhydrazones (**1** → **2** → **3**, Scheme I) which in this case is further extended by an intra- or intermolecular nucleophilic capture of the aroyl group in the acyl-*N*-imine **3** to yield the isoimide **10** or the amide **11**, respectively.

Of the intermediates proposed in the reaction sequence **4** → **5** → **6** → **10** (or **11**) none has been isolated. In fact, for some time the proposed structure **6** was considered to be the end product of the oxidation reaction by some workers in the field.[19,20]

In the present work, in order to succeed in isolating the relatively stable *N*-acyl-1,2,3-triazolimines **9** and, at the same time, provide the "missing link" in the oxidation reaction of bis-aroylhydrazones of 1,2-dicarbonyl compounds **4**, we had to increase the ability of group X to stabilize the positive charge in **9** (X = Ar instead of COAr) while retaining the stabilization of the negative charge by the acyl group (Y = COPh) in the same intermediate.

We undertook, therefore, the synthesis of the unknown[21] unsymmetric hydrazones **7**. Oxidation of the latter compounds with $Pb(OAc)_4$ led to the isolation of the novel 2-aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines **9** as stable crystalline compounds in good yields.

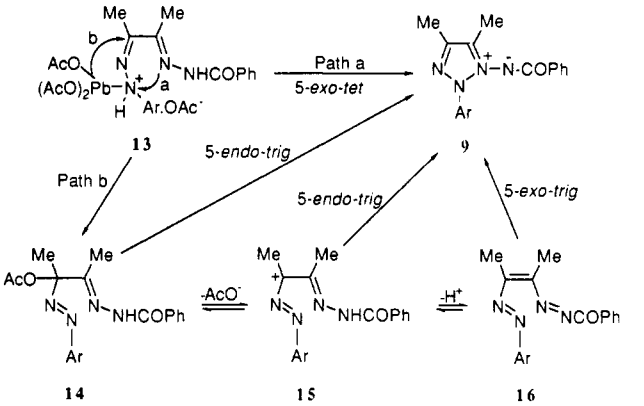
**Table I. Preparation of Biacetyl Benzoylhydrazone Arylhydrazones 7 and Their $Pb(OAc)_4$ Oxidation to 2-Aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines 9**



12 7 9

| entry | Ar | isolated yields, % 7 | 9 |
|---|---|---|---|
| a | Ph | 72 | 76 |
| b | *p*-$CH_3$Ph | 56 | 57 |
| c | *p*-$CH_3O$Ph | 40 | 32 |
| d | *p*-ClPh | 80 | 54 |
| e | *p*-$O_2N$Ph | 39 | 57 |

**Scheme II**



13 9 14 15 16

## Results and Discussion

The mixed hydrazones of biacetyl **7** were synthesized from biacetyl monobenzoyl hydrazone and the appropriate arylhydrazine (Table I). The reverse procedure, i.e., the addition of benzoylhydrazine to the monoarylhydrazone of biacetyl leads to mixtures of bis-arylhydrazone **1** and bis-aroylhydrazone **4**. Presumably benzoylhydrazine displaces arylhydrazine faster than it adds to the free carbonyl of the monoarylhydrazone in much the same way semicarbazide reacts faster with *N*-benzylideneaniline than with benzaldehyde itself.[22] The displaced arylhydrazine adds to the starting material to give the bis-arylhydrazone **1**, while the resulting monobenzoylhydrazone with benzoylhydrazine yields bis-aroylhydrazone **4**.

By analogous reasoning the isolation from the present reaction mixture, in addition to hydrazones **7**, of small amounts (up to 20%) of bis-arylhydrazones **1** can be explained. The yield of such products increases with increasing nucleophilicity of the aroylhydrazine used (i.e., from **7a** to **7c**).

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**Table II. Selected Bond Lengths and Bond Angles in 9a with Their Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| C1–C2 | 1.389 (2) | N1–N2 | 1.353 (1) |
| N1–C2 | 1.334 (2) | N1–N4 | 1.384 (1) |
| N3–C1 | 1.333 (2) | C5–N4 | 1.335 (2) |
| N2–N3 | 1.332 (2) | O–C5 | 1.229 (2) |
| | Angles (deg) | | |
| N1–C2–C1 | 105.8 (1) | C14–C13–C12 | 118.8 (1) |
| N3–C1–C2 | 109.9 (1) | C15–C14–C13 | 120.2 (2) |
| N2–N3–C1 | 105.9 (1) | C16–C15–C14 | 120.0 (2) |
| N1–N2–N3 | 110.6 (1) | C17–C16–C15 | 120.9 (2) |
| N2–N1–C2 | 107.8 (1) | C16–C17–C12 | 118.0 (1) |
| C17–C12–C13 | 122.1 (1) | | |

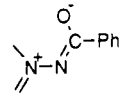
The oxidative cyclization of the title hydrazones **7** to 2-aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines **9** in good yields (Table I) may be rationalized, in the light of previous mechanistic studies in substituted phenylhydrazones,[23] in terms of the initial formation of an N-metallo intermediate **13** (Scheme II) on the arylhydrazone residue, since the nucleophilicity of the corresponding site on the aroylhydrazone moiety is very much diminished due to the neighboring carbonyl group. The intermediate **13** may yield **9**, the product of a formal 5-*exo-tet* cyclization[24] (path a).

Alternatively, this cyclization may proceed via any intermediate involved in path b such as the azoacetate **14**, the azocarbocation **15**, or the bis-azoethylene **16**, since all these possible intermediates are also capable, at least in principle, of cyclizing to the same end product **9**.

While an equilibrium between **9** and **16** is possible it should favor strongly the former. Ab initio calculations have shown that the related 1,2,3-triazolium oxides are strongly favored in the cyclic form while the *N*-aryl-1,2,3-triazol-1-imines **3** are borderline.[25] In the case of the present *N*-benzoylimines **9** the extra stabilization of the negative charge exerted by the carbonyl group makes the cyclic form **9** the favored one.

The structure proof for the products **7** and **9** rests upon their (IR, NMR, and MS) spectra and elemental analyses. The structure of **9a** was confirmed by an X-ray crystal structure determination and that of **9d** by an alternative synthesis.

In particular, the IR spectrum of the benzoylimines **9** shows a strong carbonyl absorption around 1600–1614 $cm^{-1}$. This low frequency absorption, with respect to the higher absorbing carbonyl (1660–1680 $cm^{-1}$) of the aroylamino group in the 1-(aroylamino)-4,5-dimethyl-1,2,3-triazoles **11**,[26] is caused by the existence of canonical forms such as **17** and is always found in the IR spectra of the various heteroaromatic *N*-acylimines.[27]



**17**

The molecular structure of **9a** has been ascertained by X-ray analysis. A representation of the molecule is shown in Figure 1. The intramolecular bond lengths and angles

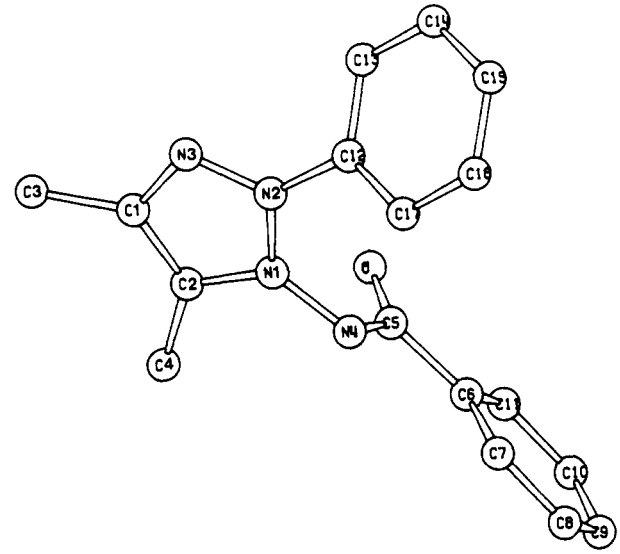



**Figure 1.** Perspective drawing of **9a** with the numbering scheme.

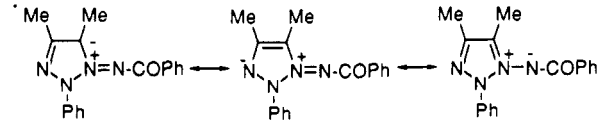
for selected atoms and their estimated standard deviations are listed in Table II.

The deformations of the endocyclic angles in the phenyl ring attached to the triazole group are symmetric around the C12–C15 line with an angle of 122.1° at the ipso position. This is caused by the highly electronegative nature of the triazolium group.[28]

The triazole ring is planar, and both methyl groups are included in the plane. The almost identical values of the angles at N1 and N3 show that these are unaffected by the asymmetry induced by the *N*-benzoylimino group and must be due to the minimal interaction between the former and the triazole ring (vide infra).

The triazole ring distances are midway between single and double bond (i.e., C1–C2 1.389 Å cf. benzene 1.397 Å;[29] N1–C2 1.334 and N3–C1 1.333 Å cf. pyridine 1.340 Å;[30] N2–N3 1.332 and N1–N2 1.353 Å cf. 1,2,4-triazole 1.359 Å[31]) and very close in value to those reported for the 1-[[α-(benzoyloxy)benzylidene]amino]-4,5-dimethyl-1,2,3-triazole (**10a**)[18] and 1-[α-[(2-bromobenzoyl)oxy](2′-bromobenzylidene)amino]-4,5-diphenyl-1,2,3-triazole (**10b**).[32]

Of special interest is the bond length value (1.384 Å) found for the exocyclic N1–N4 bond, which is very close to the corresponding N–N bond value in the previously mentioned isoimides **10a** (1.39 Å[18]) and **10b** (1.37 Å[32]) and implies that there is no significant dispersion of the exocyclic nitrogen negative charge into the triazole ring and consequently that the contribution of resonance forms such as **18** and **19** to the hybrid is minimal. The benzene ring




**18** **19** **20**

attached at N2 and the triazole ring lie in planes whose

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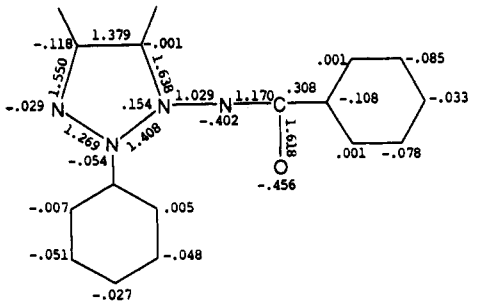



**Figure 2.** Charge densities and bond orders for **9a** by the MNDO method.

dihedral angle is 44.7°, while the angle between the N—C=O system and the triazole ring is 77.1°. The latter points to the same conclusion (with respect to the significance of forms **18** and **19**) as above since an inhibition of resonance must be expected.

Finally, the N4–C5 bond (1.335 Å) is longer than the corresponding (double) bond in the isoimides **10a** (1.26 Å[18]) and **10b** (1.27 Å[32]) but much shorter than the usual N–C single-bond distance (1.47 Å[33]). The latter taken in conjunction with the longer than expected O–C5 bond (1.229 vs 1.20 Å for **10a**[18] and 1.196 Å for **10b**[32]) indicates that some interaction exists between the negatively charged nitrogen and the carbonyl group contributing to the shortening of this covalency.

The charge densities (atomic units) and the bond orders in the molecule of **9a** were calculated using the bond lengths and angles obtained from the X-ray analysis by the MNDO method[34] and are shown in Figure 2.

The description generally agrees with that gleaned from the X-ray analysis. The exocyclic nitrogen and oxygen carry considerable negative charge (–0.402 and –0.456, respectively) while C2 is practically neutral. This in conjunction with the significant contribution of N4 AOs in the HOMO and C2 AOs in the LUMO which indicate that the molecule is a potential 1,3-dipole.[35]

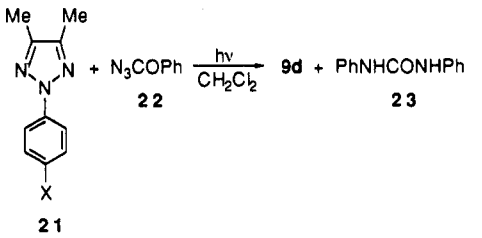
From the bond order values it is concluded that there is significant electron delocalization in the triazole ring and that in valence bond terms no simple structure of all possible resonance forms can adequately describe the molecule. However, structure **20** can be considered as the most contributing to the hybrid.

In the $^1$H NMR spectra the signals of Me-4 are observed in the $\delta$ 2.30–2.40 range and are very close in value to those due to the methyl groups of the parent 2-aryl-4,5-dimethyl-1,2,3-triazoles **21**.[36] The signals of the Me-5 are shifted downfield by ca. 0.05–0.1 ppm, and this fact is attributed to the reduced electron density at that position.

The signals of the benzoyl group protons are in accord with those reported for the same protons in the *N*-benzoylpyridin-1-imine,[37] while those for the 2-aryl group generally agree with the ones found for the same group in the triazole **21**[36] and the corresponding *N*-oxides.[38]

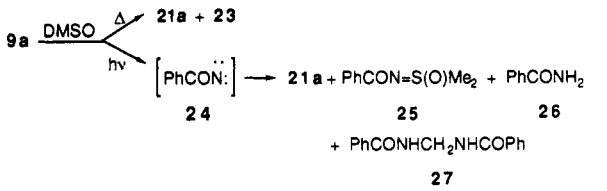
The $^{13}$C NMR spectra of compounds **9** show all the expected carbon signals and will be reported in full together with other $^{13}$C NMR data gleaned from additional

**Scheme III**




a, X= H, b, X= Cl

**Table III. Thermolysis[a] and Photolysis[b] of 9a in DMSO**




| | % yield | |
|---|---|---|
| product | thermolysis | photolysis |
| **21a** | 77 | 78 |
| **23** | 78 | 0 |
| **25** | 0 | 28 |
| **26** | 0 | 45 |
| **27** | 0 | 27 |

[a] At 190 °C (refluxing DMSO). [b] Unfiltered light from a medium-pressure mercury arc.

*N*-acyl-1,2,3-triazol-1-imines.[39]

In the mass spectroscopic fragmentation of compounds **9** the exocyclic N–N bond cleavage is dominant leading to the triazole ion or to $C_7H_5NO$ ion. The latter could be attributed to an ionized benzoylnitrene or phenyl isocyanate fragment. In this respect the MS spectra of compounds **9** resemble the spectra of *N*-acyl-1,2,4-triazol- and *N*-sulfinyl-1,2,4-triazol-4-imines.[40] The instability of the molecule as a result of this easy N–N bond cleavage results in low-intensity (1–7%) molecular ions, and it is in accord with the observed photolytic and thermolytic behavior of these compounds which will be presented later in this paper.

As a final structure proof and before the results of the X-ray analysis were available to us, we successfully synthesized *N*-benzoyl-2-(4′-chlorophenyl)-4,5-dimethyl-1,2,3-triazol-1-imine (**9d**) by irradiating benzoyl azide (**22**) in methylene chloride in the presence of 2-(4′-chlorophenyl)-4,5-dimethyl-1,2,3-triazole (**21b**, Scheme III). The product obtained, albeit in small yield (9%), owed to its photoinstability, was identical with the corresponding product of the oxidative cyclization. In addition to **9d** diphenylurea (**23**) was also obtained. This type of reaction has precedent in the synthesis of pyridin-*N*-imines.[41]

Finally, the obvious structural similarity of compounds **9** to well-known acylnitrene and isocyanate precursors, such as the acyl azides[42] and the trialkylammonio *N*-imines,[43] and also the anticipated good leaving-group ability of the triazole group in these compounds, prompted

(33) Higginbotham, H. K.; Bartell, L. S. *J. Chem. Phys.* **1965**, *42*, 1131.
(34) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(35) Preliminary experiments indicated that compound **9a** gives a 1:1 adduct with dimethyl acetylenedicarboxylate the structure analysis of which shows that it must have resulted from an initial addition to the 1,3-azomethine dipole.
(36) Maroulis, A. J. Unpublished results.
(37) (a) Katritzky, A. R.; Kinns, M. *Org. Magn. Reson.* **1975**, *7*, 569. (b) Dias, A. S.; Downs, A. W.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* **1975**, 162.
(38) Kiouplidis, K. Ph.D. Thesis, University of Zürich, 1980, p 78.
(39) Maroulis, A. J.; Hadjiantoniou-Maroulis, C. P.; Rodios, N. A. Manuscript in preparation.
(40) Reference 27a, 237; ref 27b, 86.
(41) Reference 27a, 220; ref 27b, 78.
(42) Lwowski, W. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: Orlando, 1984; Chapter 4.
(43) Lwowski, W. In *Nitrenes*; Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 6.

us to initiate a study of their thermal and photochemical reactions. The results are summarized in Table III.

In refluxing DMSO **9a** produces very good yields of **21a** and **23**. The latter originates from phenyl isocyanate which in turn results from a Curtius-type rearrangement[44] in the starting material **9a** and does not apparently involve the trappable by DMSO benzoyl nitrene (**24**).[45] This behavior contrasts the *N*-benzoyl-1,2,3-triazolimines **9** with the *N*-acyl-1,2,4-triazolimines which also decompose on heating but do not yield isocyanates,[46] while it resembles the thermolysis of **22** in DMSO which yields also exclusively **23**.[47]

In the photolytic decomposition, besides the very good yield of **21a**, fair yields of *N*-benzoyldimethylsulfoximine (**25**) and -benzamide (**26**) together with minor product methylenebisbenzamide (**27**) were obtained. These results parallel the benzophenone-sensitized irradiation of **22**[48] and indicate that nitrene **24** is most likely involved.

However, we must add that it is still possible to write mechanisms that avoid postulating a benzoylnitrene intermediate for this photoreaction should one decide to ignore the striking analogy to the known behavior of **22**.[48]

## Concluding Remarks

The synthesis of biacetyl benzoylhydrazone arylhydrazones **7** has allowed us to prepare via their oxidative cyclization the first examples of *N*-acyl-1,2,3-triazol-1-imines **9**. The isolation of this type of compound supports already proposed mechanistic interpretations concerning the oxidation of bis-aroylhydrazones of $\alpha$-dicarbonyl compounds **4** by providing the hitherto "missing link" in these reactions. Moreover, the present method can potentially be extended toward the synthesis of other mixed bishydrazones of $\alpha$-dicarbonyl compounds (such as arylhydrazone sulfonyl hydrazones, arylhydrazone semicarbazones, etc.) in order to obtain, after oxidation, the corresponding N-substituted 1,2,3-triazol-1-imines.

The preliminary results presented in this paper with regard to the photolytic and thermolytic decomposition of the acylimines **9** justify our belief that these compounds can be considered as potential nonazide precursors for the generation of acyl nitrenes and for this reason further work to explore the scope of this reaction is in progress.

Alternatively, the photolysis and thermolysis of the same compounds **9** can be effectively used as a method for the synthesis of triazoles **21**, since the yields realized in both the thermal and the photochemical reactions of **9a** (ca. 80%) equal or exceed by far those realized by the known methods of synthesis.[49]

Lastly, the title imines **9** represent an azomethineimine system and therefore should be capable of undergoing 1,3-dipolar cycloaddition reactions. Preliminary experiments, now in progress, with acetylene dicarboxylate confirm this hypothesis.[35]

## Experimental Section

All melting points were determined on a hot-stage apparatus and are uncorrected. $^1$H NMR spectra were obtained at 80 MHz. For the X-ray analysis the density was measured by flotation. Precise lattice constants have been derived from a least-squares refinement of the setting angles of 28 automatically centered reflections on a Syntex P21 diffractometer upgrated by Crystal Logic with Ni-filtered Cu-K$\alpha$ radiation. Three standard reflections measured every 97 reflections showed less than 3% intensity fluctuation. Lorentz and polarization corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares using SHELX76[50] with all non-H atoms refined anisotropically. Unit weights were used giving satisfactory analysis of the variance. Photochemical reactions were carried out using commercially available 125- or 250-W medium-pressure mercury lamps at 20 °C. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh) and mixtures of petroleum ether (bp 40–60 °C)–ethyl acetate of increasing polarity. The reactions were monitored by TLC using precoated 0.25-mm Merck silica gel 60 $F_{254}$ plates, and the spots were visualized under UV light. All commercial reagents were purchased from Fluka. The literature procedures were employed for the synthesis of the known **12**,[51] **21a**,[52] **21b**,[53] **22**,[54] **25**,[55] and **27**.[56]

**Preparation of Biacetyl Benzoylhydrazone Phenylhydrazone (7a).** To an almost saturated boiling solution of **12** (2.4 g, 0.01 mol) in EtOH (60 mL)–$H_2O$ (30 mL) was added phenylhydrazine (1.5 g, 0.01 mol). The solution was acidified by the addition of 0.3 mL of acetic acid, boiled for about 1 min, filtered, while hot, to remove the less soluble side product bisphenylhydrazone, and left to cool. Gradually crystals separated and were collected by suction. Besides the first, usually the richest crop, more product was obtained in successive filtrations (total yield 2.55 g, 72%). The product was further purified by recrystallization from EtOH and was assigned as the mixed bishydrazone **7a**: mp 186–8 °C; IR (Nujol) 3396, 3222, 1671, 1602, 1576, 1303, 1252, 1138, 746, 691 cm$^{-1}$; MS (70 eV) $m/z$ 294 (M$^+$, 33.1), 105 (51.8), 93 (100.0). Anal. Calcd for $C_{17}H_{18}N_4O$: C, 69.37; H, 6.16; N, 19.04. Found: C, 69.21; H, 5.98; N, 18.95.

According to the above general procedure all mixed hydrazones **7** were prepared. Since the substituted hydrazines were purchased as hydrochlorides they had to be neutralized with KOH–EtOH solution prior to their addition. Yields are reported in Table I.

**7b**: mp 178–9 °C; IR (Nujol) 3293, 1651, 1611, 1561, 1509, 1272, 1248, 1136, 806, 711 cm$^{-1}$; MS (70 eV) $m/z$ 308 (M$^+$, 54.7), 106 (100), 105 (99.6). Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.10; H, 6.54; N, 18.17. Found: C, 70.03; H, 6.68; N, 18.08.

**7c**: mp 183–4 °C; IR (Nujol) 3230, 1655, 1568, 1514, 1242, 1178, 1139, 1028, 822, 718 cm$^{-1}$; MS (70 eV) $m/z$ 324 (M$^+$, 49.0), 123 (65.3), 108 (100), 105 (75.1). Anal. Calcd for $C_{18}H_{20}N_4O_2$: C, 66.65; H, 6.22; N, 17.27. Found: C, 66.39; H, 6.11; N, 17.15.

**7d**: mp 204–6 °C; IR (Nujol) 3280, 1673, 1600, 1582, 1518, 1488, 1257, 1143, 824 cm$^{-1}$; MS (70 eV) $m/z$ 330 and 328 (M$^+$, 6.3 and 16.5), 129 and 127 (35 and 100), 105 (58.3). Anal. Calcd for $C_{17}H_{17}N_4OCl$: C, 62.10; H, 5.21; N, 17.04. Found: C, 62.24; H, 5.38; N, 17.07.

**7e**: mp 264–6 °C; IR (Nujol) 3303, 3218, 1673, 1590, 1520, 1300, 1265, 1108, 843 cm$^{-1}$; MS (70 eV) $m/z$ 339 (M$^+$, 14), 105 (100), 77 (95.4). Anal. Calcd for $C_{17}H_{17}N_5O_3$: C, 60.17; H, 5.05; N, 20.64. Found: C, 59.89; H, 4.98; N, 20.64.

**Oxidation of Biacetyl Benzoylhydrazone Phenylhydrazone (7a) to *N*-Benzoyl-2-phenyl-4,5-dimethyl-1,2,3-triazol-1-imine (9a).** To a stirred solution of $Pb(OAc)_4$ (2.2 g, 0.05 mol) in dry $CH_3CN$ (20 mL) was added the mixed hydrazone **7a** (1.01 g, 0.034 mol) over a period of a few min. The slight excess of $Pb(OAc)_4$ was checked throughout the experiment by the use of KI–starch paper and maintained, if necessary, by the addition of extra amounts of $Pb(OAc)_4$. After the starting material was consumed (usually after 0.5–1 h) workup of the mixture involved

(44) Smith, P. A. S. In *Molecular Rearrangements*; DeMayo, P., Ed.; Interscience: New York, 1963; Vol. 1, p 528.
(45) In a separate control experiment we have refluxed *N*-benzoyldimethylsulfoximine (**25**) in DMSO, for at least 5 h. No reaction took place; therefore, **25** was not formed and subsequently decomposed during the thermolysis of **9a**.
(46) Reference 27a, footnote 147.
(47) Horner, L.; Bauer, G.; Dörges, J. *Chem. Ber.* **1965**, *98*, 2631.
(48) Hayashi, Y.; Swern, D. *J. Am. Chem. Soc.* **1973**, *95*, 5205.
(49) (a) Finley, K. T. In *Triazoles: 1,2,3*; Montgomery, J. A., Ed.; Interscience: New York, 1980; Chapter 3 and references cited therein. (b) Maroulis, A. J.; Theocharis, A. B.; Alexandrou, N. E. *Abstracts of Papers*; 11th ICHC, Heidelberg, Germany, 1987, Abstr. P 12.14, p 387.
(50) Sheldrick, G. M. *SHELX76. A program for crystal structure determination*; University of Cambridge, England, 1976.
(51) Pechmann, H. V.; Bauer, W. *Ber.* **1909**, *42*, 659.
(52) Pechmann, H. V.; Bauer, W. *Ber.* **1888**, *21*, 2751.
(53) Prepared as described in ref 49b. Identified from its spectra and reported mp: Ponzio, G. *Gazz. Chim. Ital.* **1898**, *28*(I), 280.
(54) Barret, E. W.; Porter, C. W. *J. Am. Chem. Soc.* **1941**, *63*, 3434.
(55) Horner, L.; Christmann, A. *Chem. Ber.* **1963**, *96*, 388.
(56) Magat, E. E.; Chandler, L. B.; Faris, B. F.; Reith, J. E.; Salisbury, L. F. *J. Am. Chem. Soc.* **1951**, *73*, 1031.

filtration of the (mostly) insoluble Pb(II) salts, evaporation of the solvent, and chromatography of the residue on a flash column. A mixture of petroleum ether–ethyl acetate in varying proportions was used as eluant, and only for the last few fractions, which contain **9a**, a 10% mixture of methanol in ethyl acetate was used.

The product was further purified by recrystallization from ethyl acetate–petroleum ether and was assigned as the *N*-acylimine **9a**: mp 119–20 °C; IR (Nujol) 1613, 1570, 1328, 1319, 1298, 1138, 902, 767, 752, 713 $cm^{-1}$; MS (70 eV) *m/z* 292 ($M^+$, 1), 173 (15), 119 (29), 77 (100); $^1H$ NMR ($CDCl_3$) δ 2.34 (s, 3 H, Me-4), 2.41 (s, 3 H, Me-5), 7.22–7.54 (m, 6 H, H-3′, H-4′, H-5′, H-3″, H-4″, H-5″), 7.57–7.80 (m, 2 H, H-2′, H-6′), 7.93–8.12 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{17}H_{16}N_4O$: C, 69.84; H, 5.52; N, 19.17. Found: C, 70.00; H, 5.73; N, 18.84.

According to the general procedure described earlier all *N*-acylimines **9** were prepared. In some cases bisazoethylenes **2** in very small yields (<3%) were obtained in the early fractions. Yields reported in Table I are after isolation and recrystallization from ethyl acetate–petroleum ether.

**9b**: mp 100–1 °C; IR (Nujol) 1601, 1515, 1324, 1298, 1138, 1069, 903, 847, 829, 715 $cm^{-1}$; MS (70 eV) *m/z* 306 ($M^+$, 9), 187 (47), 91 (100); $^1H$ NMR ($CDCl_3$) δ 2.35 (s, 6 H, Me-4, Me-4′), 2.42 (s, 3 H, Me-5), 7.05–7.48 (m, 5 H, H-3′, H-5′, H-3″, H-4″, H-5″), 7.61 (d, *J* = 10.6 Hz, 2 H, H-2′, H-6′), 7.91–8.17 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{18}H_{18}N_4O$: C, 70.56; H, 5.92; N, 18.29. Found: C, 70.64; H, 6.03; N, 18.38.

**9c**: mp 95–6 °C; IR (Nujol) 1608, 1570, 1518, 1324, 1299, 1266, 1031, 904, 846, 721 $cm^{-1}$; MS (70 eV) *m/z* 322 ($M^+$, 1), 203 (34), 119 (55), 64 (100); $^1H$ NMR ($CDCl_3$) δ 2.33 (s, 3 H, Me-4), 2.41 (s, 3 H, Me-5), 3.78 (s, 3 H, $CH_3O$), 6.91 (d, *J* = 8.7 Hz, 2 H, H-3′, H-5′), 7.37–7.45 (m, 3 H, H-3″, H-4″, H-5″), 7.58 (d, *J* = 8.7 Hz, 2 H, H-2′, H-6′), 7.91–8.13 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{18}H_{18}N_4O_2$: C, 67.06; H, 5.63; N, 17.38. Found: C, 67.18; H, 5.78; N, 17.44.

**9d**: mp 129–31 °C; IR (Nujol) 1610, 1568, 1490, 1322, 1297, 1138, 1092, 850, 828, 715 $cm^{-1}$; MS (70 eV) *m/z* 328 and 326 ($M^+$, 1 and 3), 209 and 207 (27 and 75), 127 and 125 (34 and 100), 119 (95); $^1H$ NMR ($CDCl_3$) δ 2.30 (s, 3 H, Me-4), 2.35 (s, 3 H, Me-5), 7.20–7.47 (m, 3 H, H-3″, H-4″, H-5″), 7.36 (d, *J* = 8.8 Hz, 2 H, H-3′, H-5′), 7.68 (d, *J* = 8.8 Hz, 2 H, H-2′, H-6′), 7.90–8.17 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{17}H_{15}N_4OCl$: C, 62.48; H, 4.63; N, 17.15. Found: C, 62.47; H, 4.82; N, 17.23.

**9e**: mp 133–4 °C; IR (Nujol) 1601, 1569, 1520, 1317, 1288, 1138, 962, 908, 860, 722 $cm^{-1}$; MS (70 eV) *m/z* 337 ($M^+$, 3), 218 (32), 119 (36), 105 (100); $^1H$ NMR ($CDCl_3$) δ 2.40 (s, 3 H, Me-4), 2.48 (s, 3 H, Me-5), 7.21–7.56 (m, 3 H, H-3″, H-4″, H-5″), 7.90–8.13 (m, 4 H, H-2′, H-6′, H-2″, H-6″), 8.34 (d, *J* = 8.6 Hz, 2 H, H-3′, H-5′). Anal. Calcd for $C_{17}H_{15}N_5O_3$: C, 60.53; H, 4.48; N, 20.76. Found: C, 60.51, H, 4.68; N, 20.87.

**Irradiation of 22 in the Presence of 21b.** A solution of 300 mg (2 mmol) of **22** and 50 mg (0.25 mmol) of **21b** in 2 mL of methylene chloride was irradiated in a quartz vessel, using a 250-W medium-pressure mercury arc at 20 °C. When the nitrogen evolution subsided (ca. 0.5 h) the resulting orange-brown solution was chromatographed. Apart from the unreacted **22** (111 mg), **23** (157 mg, 57%, based on the amount of consumed **22**) and **9d** (7 mg, 9%, based on the amount of starting **21b**) were obtained.

**Thermolysis of 9a in DMSO.** A solution of 292 mg (1 mmol) of **9a** in 2 mL of DMSO was refluxed for 35 min. From the mixture, after chromatography, 133 mg (77%) of **21a** and 83 mg (78%) of **23** were obtained.

**Photolysis of 9a in DMSO.** A stirred solution of 292 mg (1 mmol) of **9a** in 2 mL of DMSO was irradiated with an immersed 125-W medium-pressure mercury arc for 10 h. From the resulting brown solution the solvent was removed in vacuo and from the oily residue, after chromatography, 135 mg (78%) of **21a**, 34 mg (27%) of **27**, 54 mg (45%) of **26**, and 54 mg (28%) of **25** were obtained.

**Acknowledgment.** We are indebted to Dr. P. D. Akrivos for performing the MNDO calculations.

**Registry No.** **7a**, 31400-24-5; **7b**, 138815-25-5; **7c**, 138815-26-6; **7d**, 138815-27-7; **7e**, 138815-28-8; **9a**, 138815-29-9; **9b**, 138815-30-2; **9c**, 138815-31-3; **9d**, 138815-32-4; **9e**, 138815-33-5; **12**, 55590-53-9; **21a**, 58737-90-9; **21b**, 90799-28-3; **22**, 582-61-6; **23**, 102-07-8; **25**, 31280-33-8; **26**, 55-21-0; **27**, 1575-94-6; phenylhydrazine, 100-63-0; *p*-tolylhydrazine, 539-44-6; *p*-anisylhydrazine, 3471-32-7; (*p*-chlorophenyl)hydrazine, 1073-69-4; (*p*-nitrophenyl)hydrazine, 100-16-3; lead tetraacetate, 546-67-8; benzoylnitrene, 50401-20-2.

**Supplementary Material Available:** X-ray crystallographic data for **9a** and tables of atomic coordinates, atomic thermal parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

# Acid-Induced Ring Opening of α-[Bis(methylthio)methylene]alkyl Cyclopropyl Ketones: A Novel Route to Substituted Cyclopentanones through Carbocationic Cyclizations

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α-[Bis(methylthio)methylene]alkyl 2-styrylcyclopropyl ketones **10a–d,f** and their higher enyl analogues **10e,g** undergo acid-induced ring opening and carbocationic cyclizations to afford substituted cyclopentanone derivatives. The structures of these products depend on the reaction conditions and the nature of the substituent in the aryl ring. The methodology has been extended to the synthesis of 11-oxosteroid precursors **22** and **25**.

## Introduction

Cyclopentanone chemistry enjoys current interest due to its widespread occurrence in many natural products.[1] Their synthesis by classical reactions such as Dieckmann cyclization, Friedel–Crafts acylation, and aldol condensation etc. have limitations.[1a] Thus, the most common classical approach involving the cyclization of an enolate anion of γ-halo ketones or the corresponding β-keto esters leads to the corresponding alkylidenetetrahydrofurans instead of cyclopentanones owing to stereoelectronic factors.[1a] However, some ingenious efforts have been made to convert these alkylidenetetrahydrofurans to the desired cyclopentanones under the influence of Pd(0)-assisted rearrangements.[1a,2] Interestingly, no efforts seem to have

(1) Reviews: (a) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141. (b) Ramaiah, M. *Synthesis* **1984**, 529.

(2) (a) Trost, B. M.; Jungheim, L. N. *J. Am. Chem. Soc.* **1980**, *102*, 7910. (b) Trost, B. M.; Runge, T. A. *Ibid.* **1981**, *103*, 7550. (c) Trost, B. M.; Runge, T. A. *Ibid.* **1981**, *103*, 7559.

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