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UNEXPECTED REACTIVITY OF THE ANION DERIVED FROM BENZOPHENONE BENZOYLHYDRAZONE IN THE PRESENCE OF ELECTROPHILES

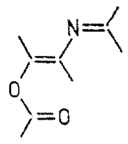
Diego Armesto,[a*] Mar G. Gallego,[a] William M. Horspool,[b] and Ana Ramos[a]

a: Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Complutense, 28040-Madrid, Spain.

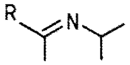
b: Department of Chemistry, The University, Dundee, DD1 4HN, Scotland.

Summary: The reactions of the anion of benzophenone benzoylhydrazone with acid chlorides are described. These afford dihydro-oxadiazoles. In the absence of acid chlorides the anion from the benzoylhydrazone yields open chain products such as enol ethers and *N*-methyl amides. An electron transfer mechanism is proposed to account for this change in behaviour.

The photochemistry of 2-azabuta-1,3-dienes (1) has proved to be of great interest. In particular some heavily arylated derivatives undergo a novel photochemical 1,2-acyl migration followed by cyclization affording dihydro-oxazoles.[1] On the other hand, we have observed that changes in the substitution on the azadiene system bring about modifications in the photochemical reactivity of this type of compounds that were unprecedented in the photochemistry of enol esters.[2] The synthesis of azadienes (1) was achieved by double aroylation of anions of imines (2a)[3] or by *O*-acylation of the anions of mono imines (2b) of 1,2-dicarbonyl compounds.[4] As an extension of this study we have sought a synthetic route to 1-acyloxy-2,3-diazabuta-1,3-dienes (3).

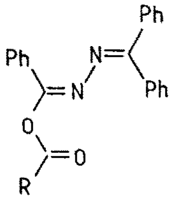


(1)



2a: R= Ar
2b: R= ArCO

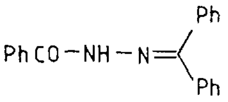
(2)



3a: R=Me
3b: R=Ar

(3)

A possible route to the synthesis of these new dienes involved the treatment of the benzoylhydrazone (4) with base under the conditions used for the synthesis of the buta-1,3-dienes (1).[5] This involves reaction of the hydrazone with sodium hydride in THF/HMPT hopefully to yield the anion (5). This anion could then be trapped by the addition of an acid chloride. It was clear from the development of a coloured solution that the anion (5) was produced readily on treatment of (4) with the base. Surprisingly on addition of acetyl chloride followed by conventional work up we were unable to obtain the desired diene (3a). Instead the only isolable products, after flash chromatography on silica gel, were the starting material (12%), benzophenone (40%) and a new compound in 42% yield, obtained as white crystals (m.p. 136-138°C). The product showed the presence of a carbonyl function (1660 cm^{-1}) in the i.r. and a C=N group (1640 cm^{-1}).[6] The ^{1}H n.m.r. (δ 2.3, 3H, s; 7.0-7.5, 13H, m; 7.7-7.9, 2H, m) and the ^{13}C n.m.r. (δ 22.7, 103.2, 124.4, 126.7-129.7, 131.3, 137.7, 153.4 (C=N), and 167.1 (C=O, amide)) spectra in conjunction with the mass spectrum and microanalytical results (m/z 342, 299, 223, 195, 165, 105, and 77; Found: C, 76.89; H, 5.05; N, 8.10. $C_{22}H_{18}N_{2}O_{2}$ requires C, 77.19; H, 5.26; N, 8.18%) identify the product as the 2,3-dihydro-oxadiazole (6a). The formation of benzophenone can be easily explained by hydrolysis of the benzoylhydrazone (4) during chromatography.



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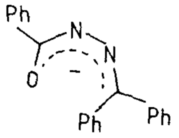

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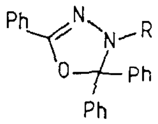


6a: R = COMe
6b: R = COPh
6c: R = H
6d: R = Me

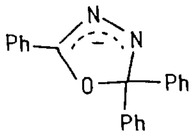
(6)

A similar reaction is observed in the trapping of the anion (5) using benzoyl chloride that gives the corresponding 2,3-dihydro-oxadiazole (6b) in 25% yield.[7] No evidence was obtained for the formation of an open chain acylated product. It is of interest to note that a related observation has been made by others in that the reaction of hydrazones analogous to (4) with acetic anhydride[8] or acetyl chloride[6] affords oxadiazoles of the type represented by (6). The reaction in these instances could also implicate the anion as the key intermediate. This means that the anion, once it is formed and since there is no evidence for the isolation of open chain acylated products, cyclises to the cyclic anion (7) and presumably is in equilibrium with the open chain species. However, there is evidence from our studies that the anion remains as the open chain species and certainly does not cyclise to anion (7). This evidence comes from two experiments:

(a) Formation of the anion by the standard sodium hydride/HMPT method followed by quenching with water affords recovered starting material only. One could argue that this result arises from the quenching of the cyclic anion (7) and that the product (6c) is unstable and undergoes ring opening to afford starting material.

(b) However, when the anion is quenched by the addition of methyl iodide the products obtained are the enol ether (8) (38%) and the *N*-methylamide (9) (54%). Both these products are readily identified by their spectroscopic and analytical data, details of which are recorded.[9,10] This is reasonable evidence that the anion does not cyclise and that it exists solely in the open chain form. There is no evidence for the formation of a product such as (6d) which would be produced from the cyclic anion.

Thus an alternative mechanism for the formation of the cyclic products (6a,b) has to be sought. The major difference in the reaction conditions between those used to form the cyclic products (6a,b) and those to yield the open chain species (8) and (9) is in the nature of the electrophile i.e. an acid chloride or water or methyl iodide. We have already observed differences in behaviour of this type with anions derived from the bisimines (10).[11] Again in these cases we observed cyclization only when acyl chlorides were used and no cyclization in their absence. Our interpretation in these instances was the involvement of an electron transfer between the anion and the acyl chloride even although acyl chlorides are not often considered to be acceptors of electrons. (Nevertheless aroyl chlorides have been reported to undergo cathodic reduction to afford benzoin derivatives).[12] However, this process provides a means for the conversion of the anion into a radical which would be more likely to undergo cyclization. Indeed there are few examples of the cyclization of open chain anions to cyclic species in the literature.[13] Thus we believe that our observations with the anion (5) also fit into this general pattern in that the anion (5) undergoes electron transfer to the acid chloride affording the radical anion/radical pair (11). Combination of these followed by extrusion of chloride anion affords the acylated cyclic product (6a). We believe, as a result of our observations, that a re-interpretation of some of the reactions of anions with acid chlorides is required.



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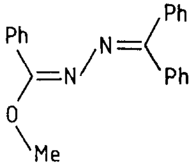

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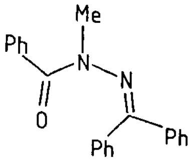

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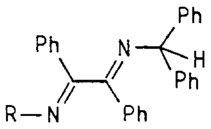

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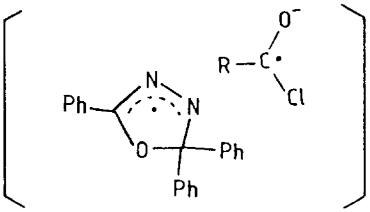

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5.- The conditions used for the synthesis and the trapping are the same as those reported previously by us.[4]

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7.- Dihydro-oxadiazole (6b) m.p. 129-130°C (lit.[14] m.p. 129°C); ν max (KBr) 1640 (C=O), 1625 (C=N); ^{1}H n.m.r. ($CDCl_3$) δ 7.1-8.2 (m, ArH); ^{13}C n.m.r. ($CDCl_3$) δ 104.2, 124.5, 126.9-131.4, 134.3, 137.6, 154.0 (C=N), 164.6 (C=O, amide); m/z 404, 165, 105, and 77.

8.- V. N. Yandovskii, *Zh. Org. Khim.*, 1976, **12**, 1093.

9.- Spectroscopic data for enol ether (8): m.p. 84-86°C; ν max (KBr) 1610, 1590, 1280; ^{1}H n.m.r. ($CDCl_3$) δ 3.6 (3H, s, CH_3), 7.1-7.9 (15H, m, ArH); ^{13}C n.m.r. ($CDCl_3$) δ 52.2 (CH_3), 126.5-137.0, 159.5 (C=N), 161.0 (C=N); Found: C, 80.15; H, 6.00; N, 8.92. $C_{21}H_{18}N_2O$ requires C, 80.25; H, 5.73; N, 8.92%.

10.- Spectroscopic data for N-methylamide (9): m.p. 65-67°C (lit.[15] m.p. 66.5-67°C); ν max (KBr) 1650 (C=O), 1600; ^{1}H n.m.r. ($CDCl_3$) δ 3.1 (3H, s, CH_3), 7.0-7.6 (15H, m, ArH); ^{13}C n.m.r. ($CDCl_3$) δ 37.6, 127.6-137.7, 163.0 (C=N), 169.4 (C=O).

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