Pergamon

Tetrahedron Letters, Vol. 35, No. 36, pp. 6753-6754, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01414-0

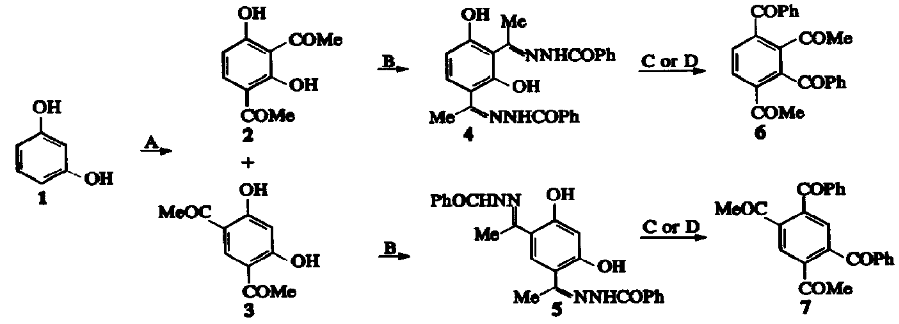
A Novel and Facile Synthesis of Tetraacylbenzenes

Antigoni Kotali

Laboratory of Organic Chemistry, College of Engineering, University of Thessaloniki,
Thessaloniki GR-54006, Greece

***Abstract** : 1,3-Dibenzoyl-2,4-diacyl- and 1,5-Dibenzoyl-2,4-diacylbenzene are prepared in good yields via a further application of a recently reported two step replacement of phenolic hydroxyl by an acyl group.*

Lead tetraacetate (LTA) has been a useful reagent in organic synthesis.[1] Recently, in our laboratories, it has been employed to prepare 1,2-diacylbenzenes in a generalized and simple route *via* oxidation of o-hydroxyaryl ketone hydrazones.[2] This methodology was extended to the preparation of 1,2,3-triacylbenzenes[3] and o-acylaryl esters[4] from acyl hydrazones of 2,6-diacylcresols and (ethoxycarbonyl)hydrazones of o-hydroxyarylketones respectively. To further explore the above reaction and to extend its synthetic potential, we investigated the reactivity of hydrazones **4** and **5** towards LTA and we now report a new high yield route to 1,2,3,4- and 1,2,4,5-tetraacylbenzenes **6** and **7**, otherwise inaccessible molecules.



A= $AlCl_3$ / MeCOCl / 2 h / 120 °C ; B= $PhCONHNH_2$ / 2-propanol / 24 h / reflux ;
C= $Pb(OAc)_4$ / THF / 2 h / r. t. ; D= $PhI(OAc)_2$ / CH_2Cl_2 / 2 h / r. t.

This oxidation process further generalizes the replacement of phenolic hydroxyl by an acyl group. It is reasonable to assume that the reaction follows the same route as that established recently.[5] The starting materials **2** and **3** were obtained from resorcinol **1** by a typical Friedel-Crafts reaction and isolated by column chromatography (silica gel 70-230 mesh, pet. ether/ chloroform 1 : 1). Hydrazones **4** and **5** were prepared by treatment of benzoic hydrazide with the diacyl compounds **2** and **3** (2 : 1 ratio). The LTA oxidation of **4** and **5** led to the formation of the desired compounds **6** and **7** in very good yields, 73% and 55% respectively. In a typical oxidation procedure LTA (1.2 mmol) is added to a solution of the corresponding hydrazone (1 mmol) in THF and the mixture is stirred at r.t. for 2 hours. The oily product, obtained after filtration of lead diacetate and condensation of the filtrate was crystallized by treatment with chloroform/pet. ether to give **6** and **7**. The compounds **2-7** were characterized by elemental analysis and by their ^1H and ^{13}C nmr spectra (Table 1).

Finally, [(diacetoxy)iodo]benzene (PID) was also examined as an alternative oxidative agent for hydrazones **4** and **5**. It is very well known that PID has very similar reactivity to that of LTA.[6] Recently it has been also used as an alternative to LTA oxidant in the synthesis of 1,2-diacylbenzenes.[7] In a typical oxidation procedure PID (4 mmol) is added to a solution of the corresponding hydrazone (1 mmol) in dichloromethane and the mixture is stirred for 2 hours. After evaporation of the solvent the mixture was subjected to column chromatography (silica gel 70-230 mesh, pet. ether/ chloroform 2 : 1) to give **6** and **7** in 68% and 50% yield respectively. Thus, both LTA as well as PID lead to the desired products in good yields. PID has the advantage of being less toxic than LTA and the disadvantage to need column chromatography for the purification of the products. This was also observed in the synthesis of 1,2-diacylbenzenes.[7]

In conclusion, both methods proved to be synthetically useful in the preparation of tetraacylbenzenes. The simplicity of the experimental, the high yields of the products and the low cost of the starting materials add to the synthetic value of the reaction. Furthermore, tetraacylbenzenes could be proved very interesting precursors in the synthesis of heterocycles.

Table 1. Preparation, ^1H- NMR and ^{13}C-NMR Data of Compounds 2-7.

Prodt	Yld (%)	m.p.[b] (°C)	Molecular Formula[c]	^1H-NMR[d] δ, J (Hz)	^{13}C-NMR[d] Chemical Shifts (δ)
2	40	96-97	$C_{10}H_{10}O_4$	2.50(s, 3H), 2.70(s, 3H), 6.40(d, 1H, J=9) 7.70(d, 1H, J=9)	26.2, 33.5, 109.5, 109.9, 112.0, 137.8, 168.2, 170.8, 203.0
3	24	176-77	$C_{10}H_{10}O_4$	2.59(s, 6H), 6.34(s, 1H) 8.15(s, 1H), 12.88(s, 2H)	26.1, 104.9, 113.6, 136.3, 168.9, 202.5
4	88	243-44	$C_{24}H_{22}N_4O_4$	2.48(s, 3H), 2.53(s, 3H), 6.52(d, 1H, J=8.5), 7.59(m, 8H) 7.93(d, 4H, J=5.6), 11.26(s, 1H), 11.31(s, 1H), 12.65(s, 1H)	14.2, 19.3, 107.5, 111.1, 111.2, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 130.8, 131.8, 131.9, 133.0, 133.2, 159.0, 159.3, 159.9, 164.2
5	82	292-93	$C_{24}H_{22}N_4O_4$	2.51(s, 6H), 6.40(s, 2H), 7.53(m, 6H) 7.80(m, 2H) 7.92(m, 4H), 11.30 (s, 2H)	14.0, 104.3, 111.9, 126.9, 127.4, 128.0, 128.3, 128.4, 128.5, 128.6, 129.6 129.7, 131.0, 131.9, 132.0, 132.1, 133.0, 133.3, 133.4, 164.2, 165.9
6	73 68[a]	169-70	$C_{24}H_{18}O_4$	2.24(s, 3H), 2.48(s, 3H), 7.61(m, 12H)	27.6, 31.8, 128.5, 128.7, 128.8, 128.9, 130.15, 130.2, 133.2, 133.9, 135.9, 137.3, 139.2, 139.25, 140.6, 143.5, 195.2, 196.5, 197.2, 202.2
7	55 50[a]	182-83	$C_{24}H_{18}O_4$	2.59(s, 6H), 7.40(m, 6H) 7.57(m, 2H) 7.72(m, 4H)	27.9, 118.5, 128.0, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.1, 129.5, 129.6, 129.7, 133.3, 133.8, 133.9, 136.1, 138.9, 143.8, 196.0, 197.8

[a] Yield with PID.

[b] Melting points were determined on a Kofler apparatus and are uncorrected.

[c] Satisfactory microanalyses were obtained for the new compounds **4-7**.

[d] $CDCl_3$ for the compounds **2**, **3**, **6** and **7** and DMSO/TMS for the compounds **4** and **5**.

References

1. Butler, R. N. *Chem. Rev.*, 1984, 89, 249.
2. Kotali, A.; Tsoungas, P. G. *Tetrahedron Lett.*, 1987, 28, 4321.
3. Kotali, A.; Glaveri, U.; Pavlidou, E.; Tsoungas, P. G. *Synthesis*, 1990, 1172.
4. Katritzky, A. R.; Kotali, A. *Tetrahedron Lett.*, 1990, 31, 6781.
5. Katritzky, A. R. ; Harris, P. A.; Kotali, A. *J. Org. Chem.*, 1991, 56, 5049.
6. Griegee R.; *Oxidations in Organic Chemistry*, Academic, NY, 1965, p. 365.
7. Moriarty, R.; Berglund, B. A.; Rao, M. S. C. *Synthesis*, 1993, 318.

The author thanks the Royal Society of Chemistry for financial support of this research.

(*Received in UK* 23 *May* 1994; *revised* 18 *July* 1994; *accepted* 22 *July* 1994)