Short Communication

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Behaviour of 2,2'-(1,4-Phenylene) Bis (4-Phenylmethylene) -5(4H)-Oxazolone Towards Carbon Nucleophiles under Friedel-crafts and Michael Reactions Conditions

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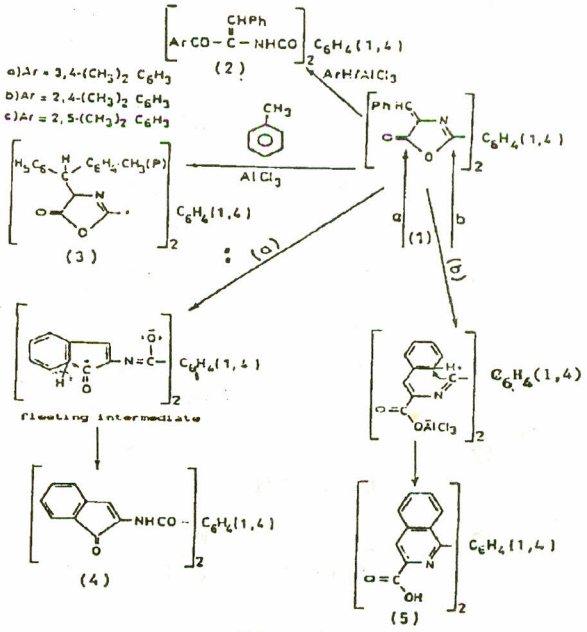
The reaction of 2,2'-(1,4-phenylene)bis (4-phenylmethylene)-5(4H)-oxazolone (1) with aromatic hydrocarbons such as m-xylene, o- xylene, p-xylene and toluene in the presence of anhydrous aluminium chloride as a catalyst gave compounds (2 a-c) and (3). With 1,1,2,2, tetrachloroethane as an inert solvent, the reaction underwent an intramolecular acylation to give the indenone and isoquinoline derivatives (4) and (5). The behaviour of (1) towards active methylene compounds has also been studied.

Recently we have reported the behaviour of 3,1-benzoxazine-4- one [1] and 5(4H)-oxazolone [2] toward aromatic hydrocarbons under Friedel-Crafts reaction conditions. Oxazole derivatives and the pharmacological properties of some oxazoles and oxazolidine derivatives as antiepileptic, appectite depressants and other effects were reported [3,4]. This prompted us to investigate the behaviour of the title compound towards aromatic hydrocarbons, to synthesise some compounds which may have medicinal effects.

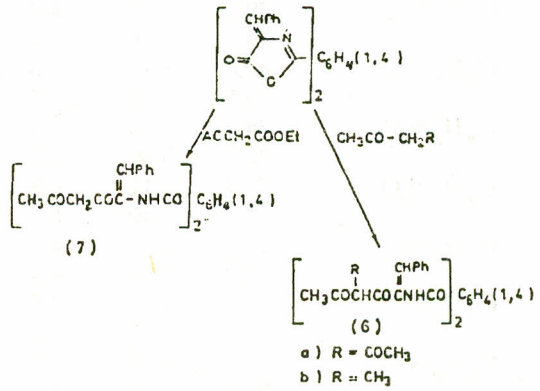
Thus 2,2'-(1,4-phenylene) bis(4-phenylmethylene)-5 (4H)- oxazolone [5], (1) reacts with aromatic hydrocarbons namely, o- xylene, m-xylene, and p-xylene in the presence of anhydrous aluminium chloride to form N,N'-bis-(1-(3,4-dimethylbenzoyl), (2,4-dimethylbenzoyl) or (2,5-dimethylbenzoyl)-2-phenylmethylene)-1,4-benzenedicarboxamide (2a-c) in high yield. Also, compound (1) react with toulene and aluminium chloride to give 2,2'-(1,4-phenylene)bis-4-(phenyl-p-tolyl)methyl-5(4H)-oxazolone (3). In inert solvents (e.g. 1,1,2,2-tetrachloroethane) under Friedel- Crafts conditions, compound (1) undergoes an intramolecular acylation to yield a mixture of N,N'-bis(2-indanone)-1, 4-benzene-dicarboxamide (4) and 1.4-bis (3-carboxy-2-isoquinoline)benzene (5). Compound (4) is formed by acyl-oxygen fission followed by ring closure according to route (a). Compound (5) is formed by alkyl-oxygen fission



Scheme 1.

(C=N) and recyclization with the benzylidine moiety according to route (b).

The behaviour of some 3,1-benzoxazin-4-ones toward active methylene compounds have been investigated [6], but in case of 5(4H)-oxazolones it have not been reported. In this work we report the behaviour of (1) towards active methylene compounds namely acetylacetone, ethylmethylketone and ethyl-acetoacetate under Michael reaction conditions. Thus when compound (1) was allowed to react with acetylacetone or ethylmethylketone in the presence of sodium ethoxide as a catalyst in ethanol, N,N'-bis(3-acetyl or methyl-2,4-dioxo-1-(phenylmetheylene)phenyl)-1, 4-benzenedicarboxamide (6 a-b) was obtained. Similarly, when a mixture of (1), ethylacetoacetate and sodium ethoxide was stirred in ethanol, N,N'bis(2,4-dioxo-1-(phenylmethylene)phenyl)-1,4-benzene



Scheme 2.

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TABLE 1. COMPOUNDS 2–7 PREPARED (CHARACTERISATION AND PHYSICAL DATA).

Product No.	Yield (%)	M.P. (°C) (Solvent)	Molecular formula	I.R. (KBr) υ (cm^{-1})	^{1}H-N.M.R. (DMSO-d_6) δ (ppm)
2a	62	293 Ethanol	$C_{42}H_{36}N_2O_4$ 632	1670 (α,β-unsat. $\upsilon_{C=O}$); 1655(amide $\upsilon_{C=O}$); 3300 (υ_{NH})	
2b	65	271 Toluene	$C_{42}H_{36}N_2O_4$ 632	1675(α,β-unsat. $\upsilon_{C=O}$); 1655 (amide $\upsilon_{C=O}$) 3330 (υ_{NH})	2.35(s, 6H, CH_3 in position-4) 2.45 (S,6H, CH_3 in Position -2) 6.7(s, 2H, =CH): 7.3-7 g (m,
2c	52	276 Toluene	$C_{42}H_{36}N_2O_4$ 632	1665 (α,β-unsat. $\upsilon_{C=O}$); 1650 (amide $\upsilon_{C=O}$); 3295 (υ_{NH})	20H, Ar-H): 8.5-9(2H, NH, broad)
3	43	253 Ethanol	$C_{40}H_{32}N_2O_4$ 604	1825 ($\upsilon_{C=O}$) 1630 ($\upsilon_{C=N}$)	1.7(d, 2H, methine H's): 2.3(s, 6H CH_3) 2.1(d, 2H, benzylic H's): 7.1-7.8 (m, 22H, Ar-H)
4	17	268 Xylene	$C_{26}H_{16}N_2O_4$ 420	1720($\upsilon_{C=O}$, cyclicketone); 1645 ($\upsilon_{C=O}$amide) 3350 (υ_{NH})	6.8 (s, 2H, =CH); 7.3-8.1 (m, 12H, Ar-H); 8.6-9.1 (2H, NH, broad)
5	12	300 CH_3COOH	$C_{26}H_{16}N_2O_4$ 420	1690 (acid $\upsilon_{C=O}$); 2700–3000(basin υ_{OH}); 1640 ($\upsilon_{C=N}$)	7.2–8.1 (m, 14H, Ar-H); 11.7 (s, 2H, COOH)
6a	42	265 (CH_3OH)	$C_{36}H_{32}N_2O_8$ 620	1710 ($\upsilon_{C=O}$ sat.); 1680 ($\upsilon_{C=O}$ α,β-unsat.); 1665 ($\upsilon_{C=O}$ amide); 3300 (υ_{NH})	2.1(s, 12H, $COCH_3$; 4.6 (s, 2H COCHCO); 6.5 (S, 2H, =CH): 7.1–7.8 (m, 14H, Ar-H); 8.5-9 (2H, NH, broad)
6b	37	243 (CH_3OH)	$C_{34}H_{32}N_2O_6$ 564	1715 ($\upsilon_{C=O}$ sat.); 1675 ($\upsilon_{C=O}$, α,β-unsat.); 1660 ($\upsilon_{C=O}$ amide); 3330 (υ_{NH})	
7	35	227 Acetic acid	$C_{32}H_{28}N_2O_6$ 536	1715 ($\upsilon_{C=O}$) sat.); 1700 ($\upsilon_{C=O}$, α,β-unsat.); 1650 (υ_{CO} amide); 3300 (υ_{NH})	2.0 (s, 6H, $COCH_3$); 3.4 (S, 4H, $COCH_2CO$); 6.6 (s, 2H, =CH); 7.2–7.9 (m, 14H, Ar-H); 8.5–9 (2H, NH, broad)

TABLE 2. COMPOUNDS 2-7 PREPARED (MICROANALYTICAL DATA).

Product	Molecular formula	Analysis Found/Calculated (%) C	H	N
2a	$C_{42}H_{36}N_2O_4$	79.5	5.72	4.5
		79.7	5.69	4.4
2b	$C_{42}H_{36}N_2O_4$	80.2	5.43	4.7
		79.7	5.69	4.43
2c	$C_{42}H_{36}N_2O_4$	79.3	5.81	4.8
		79.7	5.69	4.4
3	$C_{40}H_{32}N_2O_4$	80.0	5.13	4.8
		79.5	5.29	4.6
4	$C_{26}H_{16}N_2O_4$	74.7	4.15	7.1
		74.3	3.80	6.7
5	$C_{26}H_{16}N_2O_4$	73.9	4.12	6.8
		74.3	3.80	6.7
6a	$C_{36}H_{32}N_2O_8$	70.2	5.52	4.35
		69.7	5.16	4.51
6b	$C_{34}H_{32}N_2O_6$	71.8	5.72	4.8
		72.3	5.67	5.0
7	$C_{32}H_{28}N_2O_6$	72.1	4.88	5.3
		71.6	5.22	5.2

dicarboxamide (7) was obtained via hetero-ring fission by deethoxycarbonylation.

Experimental. Melting points are uncorrected, IR spectra (KBr): Unicam SP 1200 'H-NMR spectra: Varian S-60 T, TMS as internal reference (Chemical shift in δ scale), $CDC1_3$ or $CC1_4$ as a solvent.

Prepration of compounds (2a-c), (3), (4) and (5). A solution of compound (1) (0.01 mol) in o-xylene, or m-xylene, or p-xylene or toluene or 1,1,2,2-tetrachloroethane (50 ml) was added slowly at room temperature to a mixture of anyd. $AlCl_3$ (0.09 mol) and the appropriate aromatic hydrocarbon (50 ml) with stirring. After 10hrs the reaction mixture was hydrolyzed by ice-dilute HCl. The product was extracted with ether, the ethereal extract washed with cold H_2O and dried (anhyd. Na_2SO_4). Slow evaporation of ether left solid product which was washed with benzene and crystallized from a proper solvent to give (2 a-c), (3), (4) and (5).

Preparation of compounds (6a-b) and (7). A solution of NaOEt (0.02 mol) in EtOH (40 ml) was added to a mixture of ehtyl acetoacetate and (1) (0.01 mol). The mixture was stirred

for 15 hrs. at room temperature, then diluted with cold H_2O (50 ml) and acidified with dil. HCl to give (6 a-b) and (7).

Key words: 5(4H)-oxazolone, Aromatic hydrocarbons, Active methylene compounds.

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