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Reactions of Ethyl α-Naphthylpropiolate with Phenylacetamide, Benzyl Cyanide, Ethyl Phenylacetate and 1-Acetylindole

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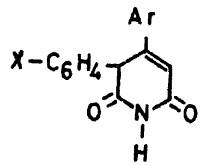
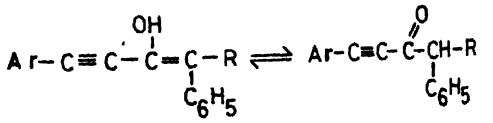
THE condensation between arylacetamide[1-4], benzyl cyanides[3,5], ethyl acetate[6,7] and *N*-acetylindole[8] with ethyl phenylpropiolate has been reported earlier. The results of the analogous condensation of the above nucleophiles with ethyl α-naphthylpropiolate are reported here.

The reaction of arylacetamide with ethyl α-naphthylpropiolate in boiling benzene in presence of powdered sodium afforded **1** (Table 1). The reaction proceeded either by Claisen ester condensation of the amide anion or Michael addition of the carbanion generated from $ArCH_2CONH_2$ to the acetylenic ester followed by cyclisation. The Claisen route seems more likely by analogy to the condensation of benzyl cyanide[3-5] or ethyl phenylacetate[6,7] with acetylenic ester. The condensation of ethyl α-naphthylpropiolate with benzyl cyanide and ethyl phenylacetate gave **2** and **3**, respectively, as the main products, evidently arising by Claisen ester condensation of the reactants. Ir and pmr spectra (Table 1) indicate that these two products exist predominatly, if not exclusively, in the enolic form.

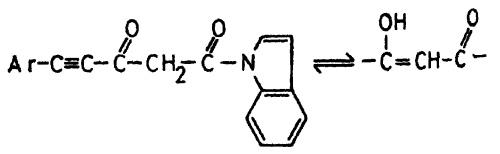
The condensation of ethyl α-naphthylpropiolate with 1-acetylindole in the presence of sodium ethoxide at 0° yielded the β-ketoamide (**4**) as the only product. Here also the reaction proceeds via a Claisen addition of the carbanion of the 1-acetylindole to the ester function of the propiolate. It should be mentioned here that the reaction of phenylpropiolic ester with 1-acetylindole yielded two products, 5-aryl-1-(indol-1-yl)-pent-4-yn-1,3-diones and ethyl β-(indol-1-yl)cinnamates as a result of Claisen and Michael reactions, respectively[8]. Compound **4** gave positive ferric chloride test, but attempt to convert it into the corresponding 4-pyrones was unsuccessful.



1; X = H, *p*-Cl and *m*-F



2; R = CN
3; R = CO_2Et



4
1-4; Ar = α-Naphthyl

Experimental

Ir spectra were measured with a Unicam SP-200 spectrophotometer and ^1H nmr spectra with a Varian A-60 D spectrometer for solutions in deuteriochloroform containing TMS as the internal standard. The compounds were analysed at the Max Planck Institute, Ruhr, West Germany. Melting points were determined on a Kofler hot stage and are uncorrected. All the compounds gave satisfactory elemental analysis.

TABLE 1—PHYSICAL AND SPECTRAL DATA OF THE PYRIDIN-2,6-DIONES (**1**)

Substituent x	Yield %	M.p. °C	ν_{max} (cm^{-1})		δ ($CDCl_3$)			
			NH	CO	NH (br, s, exchangable)	3-H (d, *J* 2Hz)	ArH (m)	5-H (d, *J* ~ 2Hz)
H	41	178	3 400	1 750, 1 710	11.90	8,30	7.50	5.20
p-Cl	40	182	3 410	1 745, 1 715	11.95	8.25	7.40	5.18
m-F	47	220	3 390	1 740, 1 710	11.85	8.20	7.55	5.30

Ethyl α-naphthylpropiolate: It was prepared from α-formylnaphthalene by the same procedure as described for ethyl phenylpropiolate from benzaldehyde[8]. 3-α-Naphthylacrylic acid, prepared by

reacting α-formylnaphthalene with malonic acid, had m.p 212°. Its ethyl ester, m.p. 37°, on bromination gave the corresponding dibromo-derivative, m.p. 70°. The latter was converted by literature methods[9] to α-naphthylpropiolic acid, m.p, 135°. Its ethyl ester had b.p. 120/0.2 mm ; ν_{max} 2 220 (C=C) and 1 700 cm^{-1} (CO) ; δ 1.38 (3H, t, CH_2CH_3), 4 35 (2H, q, OCH_2Me) and 7.5 (7H, m, ArH).

Condensation of arylacetamides with ethyl α-naphthylpropiolate : Arylacetamide (0.0172 mol) and powdered sodium (0.0172 g-atom) in dry benzene (150 ml) was kept under reflux for 20 h. α-Naphthylpropiolic ester (0.0172 mol) was then added, and heated under reflux for further 3 h. The mixture was then poured into ice-cold water (150 ml) and the benzene layer separated. The alkaline aqueous layer was acidified with dilute sulphuric acid, extracted with ether and the ethreal extract shaken with sodium hydrogen carbonate solution. The non-acidic ethereal and benzene extracts were combined, dried and evaporated. The residual solid was crystallised from benzene–petroleum ether (b.p. 30–40°) to give 1 as pale yellow needles (Table 1). The sodium hydrogen carbonate washings after acidification, extraction with ether and evaporation gave a solid, which was mainly α-naphthylpropiolic acid, m.p. 135°.

Condensation of ethyl α-naphthylpropiolate with benzyl cyanide, ethylphenylacetate and N*-acetylindole:* The condensations were carried out as described for the analogous condensation of ethyl phenylpropiolate with the above nucleophiles[4,5,7,8]. The physical data of the products are as follows : 2 (35%), m.p. 202° ; ν_{max} 3 500–3 000 (OH) and 2 220 cm^{-1} (C=C and N=N); δ7 5–8.0 (m); 3 (15%), m.p. 75° ; ν_{max} 3 500(OH) and 2 230 cm^{-1} (C=C) ; δ2.2 (3H, t, CH_2CH_3), 4.2 (2H, q, OCH_2Me) and 7.6–8 0 (13H, m, ArH+OH); 4 (45%), m.p. 45° ; ν_{max} 3 500–3 200 (OH), 2 230 (C=C), 1 700 and 1 670 cm^{-1} (CO) ; δ6.3 (1H, s, C(OH)=CH–CO), 6.6 (1H, d, indole 3-H), 7.5–8.0 (12H, m, other ArH) and 11.0 (1H, s, exchangable enolic OH).

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Action of Grignard Reagents on 8-Bromo-3(*H*)-oxonaphtho[2,1-*b*]pyran Derivatives

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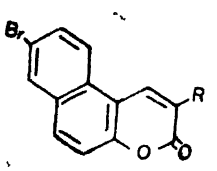
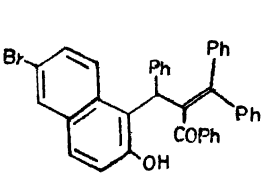
SEVERAL studies[1-7] are already being reported on reactions between Grignard reagents and coumarins having an ethyl ester function. In the present investigation, ethyl 8-bromo-3(*H*)-oxonaphtho[2,1-*b*]pyran-2-carboxylate (**1a**)[8] and the corresponding carboxamide (**1b**)[8] were treated with various Grignard reagents.

Thus, excess phenylmagnesium bromide reacted with **1a** to furnish only one isolable product which gave a violet colouration with alcoholic ferric chloride solution. This together with analytical and spectroscopic data (Table 1) led to the formulation of this product as 1,1,3-triphenyl-2-benzoyl-3-(6-bromo-2-hydroxy-1-naphthyl)propene-1 (**2**). However, reaction of **1b** with excess phenylmagnesium bromide under reflux for 3 h furnished 8-bromo-1,3-diphenyl-1,2-dihydro-3-hydroxy-naphtho[2,1-*b*]pyran-2-*N*-phenylcarboxamide (**3**) as the only isolable product. It seems that the reaction in this case involves 1,2-addition to the carbonyl group of pyran moiety of **1b** along with 1,4-addition. The interaction of **1a** with excess alkylmagnesium halides affords ethyl 1-alkyl-8-bromo-1,2-dihydro-3(*H*)-oxonaphtho[2,1-*b*]pyran-2-carboxylates (**4a-c**), while **1b** furnished 1-alkyl-8-bromo-1,2-dihydro-3(*H*)-oxonaphtho[2,1-*b*]pyran-2-*N*-phenylcarboxamides (**4d-f**). Evidently compounds **4** were produced as a result of the 1,4-addition of the alkylmagnesium halides. These results are in full agreement with that obtained by Abou-Assali *et al.*[9] for coumarin itself.



1a ; R = CO_2Et
1b ; R = CONHPh



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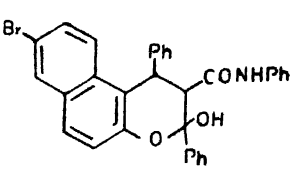

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