

Short Communication

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**MICHAEL CONDENSATION OF
3-CARBETHOXY-5, 6-BENZOCOUMARIN WITH
ETHYL ACETOACETATE, ETHYL
BENZOYLACETATE, ETHYL CYANOACETATE
AND ACETYLACETONE**

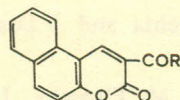
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Recently [1,2] some of the reactions of 3-carbethoxycoumarin were studied. The C_3-C_4 olefinic double bond in I is activated due to conjugation to both carbethoxy (or carboxanilide) and carbonyl groups, this prompted us to investigate the behaviour of I towards the action of compounds with active methylene groups under Michael conditions [3-9].

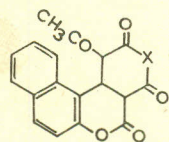
In this investigation, it has been found that the addition of active methylene compounds to I under Michael conditions depends on the nature of both reactants and reaction temperature to give normal open chain or cyclic addition products.



(I)

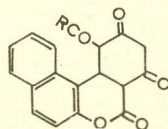
R, (a) OC_2H_5 ; (b) NHC_6H_5 ;
(c) NCH_6H_4Me-p

The base-catalyzed cycloaddition of ethylacetoacetate with Ia at room temperature leads to l-acetyltetrahydropyranonaphthopyrantrione (IIa). When Ia-c were allowed to react with ethyl acetoacetate at 170° , it gave ethyl hexahydrotrioxobenzonaphthopyrantrione (IIIa) and l-acetyldihydro-3-arylnaphthopyranpyridinetrione derivatives IIb and c respectively.



(II)

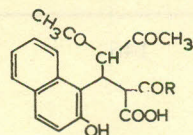
X, (a) O; (b) NC_6H_5 ;
(c) NC_6H_4Me-p



(III)

R, (a) OC_2H_5 ; (b) $NHNHC_6H_5$;
(c) $NHCH_2C_6H_5$.

The Michael reaction of Ia-c with acetylacetone at room temperature gave the normal addition with subsequent hydrolysis of the lactone ring leading to the formation of α -(1-acetylacetyl)-hydroxynaphthoalimonic IVa and malonilic acids IVb, and c respectively.

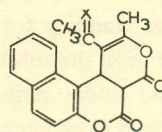


(IV)

R, (a) OH; (b) NHC_6H_5 ;
(c) NHC_6H_4Me-p .

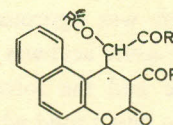
On the other hand at 170° , acetylacetone reacts with Ia-c to give l-acetyldihydro-2-methyl-4H,5H-pyrano (3,4) [1] naphthopyran-4,5-dione (Va) and 4-(1-acetylacetyl)-2-oxo-3-benzochromancarboxanilide (VIa and b). Compounds IVb and c were converted to VIa and b by heating with acetic anhydride.

When 3-carbethoxycoumarin (Ia) was allowed to react with ethyl benzoylacetate and ethyl cyanoacetate in the presence of sodium methoxide it gave ethyl-4-substituted-2-oxo-3-benzochromancarboxylates (VIc and d).



(V)

X, (a) O; (b) $NNHC_6H_5$;
(c) NNH_2 ; (d) NC_6H_5 .

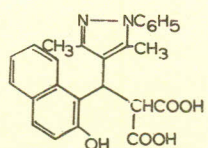


(VI)

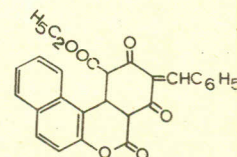
	R	R'	R''
(a)	NHC_6H_5	CH_3	CH_3
(b)	NHC_6H_4Me-p	CH_3	CH_3
(c)	OC_2H_5	C_6H_5	OC_2H_5
(d)	OC_2H_5	NH_2	OC_2H_5

All the structures of the given compounds were established chemically and confirmed from the correct analytical data, and expected IR spectra [10].

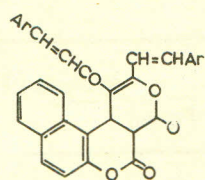
Compounds IIIa, IVa and Va with phenylhydrazine, hydrazinehydrate, aniline and aldehyde gave IIIb, c; VII-IX respectively. The IR data of some of the compounds are given in Table 1.



(VII)



(VIII)



(IX)

Ar, (a) C_6H_5 ;
(b) C_6H_4OMe-p

EXPERIMENTAL

The IR spectra were obtained with Perkin-Elmer IR

spectrometer model 577 using KBr pellet technique. M.p.'s are uncorrected.

Condensation of I with Ethyl acetoacetate, Acetylacetone, Ethyl benzoylacetate and Ethyl cyanoacetate. (A) At Room temperature: To a solution of I (0.01 mole) and ethyl acetoacetate, acetylacetone, ethyl benzoylacetate and ethylcyanoacetate (0.015 mole) in methanol (30 ml), sodium methoxide (0.02 mole) was added. The reaction mixture was allowed to stand at room temperature for three days, then poured into water (100 ml) and acidified with dil HCl. The solid product which separated was crystallized from a suitable solvent to give IIa, IVa-c and VIc and d(65-80%). The results are listed in Table 2.

(B) Fusion at 170° : A mixture of I (0.01 mole),

Table 1.

Compound	ν C=O				ν C=N	ν C=C	ν NH and ν OH
	δ -Lactone	Acetyl Co	Acid/ Ester	Amide			
IIa	1665	1685	—	—	—	—	—
IIb,c	1660	1685	—	1640	—	—	—
IIIa	1660	—	Ester 1745	—	—	—	—
IIIb,c	1665	—	—	1635	—	—	3300
IVa	—	1685	Acid 1754 1724	—	—	—	3540-3225
IVb,c	—	1685	Acid 1735	1645	—	—	3370, 3130
Va	1665	1675	—	—	—	1590 ^a	—
Vb-d	1660	—	—	—	1618	1590	3300 not for Vd
VIa,b	1655	1690	—	1640	—	—	3310
VIc,d	1660	—	Ester 1740	—	—	—	—
VII	—	—	Acid 1754 1724	—	1620	1600	3450-3250
VIII	1660	Conjugated 1670	Ester 1750	—	—	1580	—
IX	1655	Conjugated 1670	—	—	—	1580	—

Table 2. Michael adducts of I.

Compound	Solvent of crystn	M. p (°C)	Formula (mol. wt.)	Analysis (%)		
					Found	Calcd
IIa	B	179	C ₁₈ H ₁₂ O ₆ (324)	C	66.94	66.66
				H	3.66	3.70
IIb	E	245	C ₂₄ H ₁₇ NO ₅ (399)	C	72.33	72.18
				H	4.25	4.26
				N	3.52	3.51
IIc	E	>250	C ₂₅ H ₁₉ NO ₅ (413)	C	72.80	72.64
				H	4.60	3.38
				N	3.40	3.38
IIIa	B	215	C ₂₀ H ₁₆ O ₆ (352)	C	68.30	68.18
				H	4.53	4.54
IVa	E	205	C ₁₉ H ₁₈ O ₇ (358)	C	63.80	63.68
				H	5.00	5.03
IVb	M	>250	C ₂₅ H ₂₃ NO ₆ (433)	C	69.50	69.28
				H	5.29	5.31
				N	3.25	3.23
IVc	Ac	>250	C ₂₆ H ₂₅ NO ₆ (447)	C	69.90	69.79
				H	5.56	5.59
				N	3.15	3.13
Va	B	192	C ₁₉ H ₁₄ O ₅ (322)	C	70.92	70.80
				H	4.33	4.35
VIa	E	210	C ₂₅ H ₂₁ NO ₅ (415)	C	72.51	72.29
				H	5.02	5.06
				N	3.36	3.37
VIb	E	225	C ₂₆ H ₂₃ NO ₅ (429)	C	72.93	72.72
				H	5.33	5.36
				N	3.26	3.26
VIc	Ac	>250	C ₂₇ H ₂₄ O ₇ (460)	C	70.60	70.43
				H	5.20	5.22
VIId	Ac	>250	C ₂₁ H ₂₁ NO ₇ (399)	C	63.00	63.16
				H	5.29	5.26
				N	3.50	3.51

B benzene, E ethanol, M methanol, Ac acetic acid.

sodium methoxide (0.015 mole) and ethyl acetoacetate or acetylacetone (0.02 mole) was heated for 4 hr at 170°, after cooling, the reaction mixture was washed with dil HCl and the residue was crystallized from a suitable solvent to give IIIa, IIb, c; Va, b respectively (60–70%) (cf. Table 2).

Conversion of IVb or c to VIa and b. This was effected by refluxing IVb or c (1 g) with acetic anhydride (20 ml) for 20 hr. The solid obtained after pouring on ice was crystallized for ethanol to give VIa and b respectively (mixed m.p. and their IR spectra).

Condensation of IIIa, IVa and Va with Phenylhydra-

Table 3. Products of amines and hydrazines.

Compound	Solvent of crystn	M.p. (°C)	Formual (mol. wt.)	Analysis (%)		
				Found	Calcd	
IIIb	E	245	$C_{24}H_{18}N_2O_5$ (414)	C	70.24	69.56
				H	4.36	4.34
				N	6.90	6.76
IIIc	M	>250	$C_{25}H_{19}NO_5$ (413)	C	72.90	72.64
				H	4.56	4.60
				N	3.42	3.39
VII	E	218	$C_{25}N_{22}N_2O_5$ (430)	C	69.93	69.76
				H	5.10	5.12
				N	6.60	6.51
Vb	B	>250	$C_{19}H_{16}N_2O_4$ (336)	C	67.72	67.86
				H	4.80	4.76
				N	8.50	8.33
Vc	T	>250	$C_{25}H_{20}N_2O_4$ (412)	C	72.97	72.81
				H	4.82	4.85
				N	6.90	6.80
Vd	T	>250	$C_{25}H_{19}NO_4$ (397)	C	75.67	75.56
				H	4.75	4.78
				N	3.54	3.53

E ethanol, M methanol, B benzene, T toluene.

Table 4. Products of condensation of aldehydes.

Compound	solvent of crystn	M.p. (°C)	Formula (mol. wt.)	Analysis (%)		
				Found	Calcd	
VIII	E	185	$C_{27}H_{20}O_6$ (440)	C	73.94	73.63
				H	4.50	4.54
IXa	B	234	$C_{33}H_{22}O_5$ (498)	C	79.23	79.52
				H	4.44	4.42
IXb	Bu	>250	$C_{34}H_{24}O_6$ (528)	C	77.50	77.27
				H	4.50	4.54

E ethanol, Bu butanol (n)

zine, Hydrazinehydrate and Amines. A mixture of IIIa, IVa or Va (0.01 mole), phenylhydrazine (0.02 mole), hydrazinehydrate (0.015 mole) 95%, benzylamine or aniline (0.015 mole) and a few drops of acetic acid in ethanol or butanol in case of amine 60 ml was refluxed for 10 hr. The solid product obtained after concentration and cooling was crystallized from a suitable solvent to give IIIb, c, VII

and Vb-d (70-80%), cf. Table 3.

Condensation of IIIa and Va with Aldehyde. A solution of IIIa or Va (0.01 mole), aromatic aldehyde e.g. benzaldehyde, anisaldehyde (0.03 mole) and piperidine 1 ml in n-butanol (50 ml) was refluxed for 10 hr, on cooling it gives VIII and IXa, b respectively (50-65%). The results were listed in Table 4..

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