Synthesis and Some Addition Reactions of 1-Aryl-3-cyclopropyl-prop-1-en-3-ones

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Summary: Condensation of cyclopropyl methyl ketone with aromatic aldehydes gave 1-Aryl-3-cyclopropyl-prop-1-ene-3-ones (I). Addition reactions of bromine, hydrazines, and some active methylene compounds to (I) have been investigated. Structures of the products have been established by elemental analysis, IR, and PMR spectroscopic methods.

Claisen-Schmidt condensation of cyclopropyl methyl ketone with benzaldehyde or anisaldehyde in presence of potassium hydroxide gave 3-cyclopropyl-1-phenyl/4'-methoxy-phenyl-prop-1-en-3-one(Ia and b). The IR spectra* of I showed bands at 1685 (C=O), and 1595 (C=C). [1]

Treatment of I with bromine in carbon tetrachloride yielded 2,3-dibromo-1-cyclopropyl-3-phenyl/4'-methoxyphenyl-propan-1-one(IIa and b). The IR spectra of II showed band at 1700 (C=O) [2].

Reaction of Ib with hydrazine hydrate or phenyl-hydrazine in boiling acetic acid yielded the corresponding 3-cyclopropyl-5-(4'-methoxyphenyl)-2-pyrazolines (IIIa and b). The IR spectrum of IIIa showed bands at 1605 (C=N), and 3420 (NH) [3].

Base catalyzed addition of cyclohexanone, ethyl aceto-acetate, ethyl benzoylacetate, [4] and 1,3-diphenyl-2-pyrazolin-5-one [5] to (I) gave the corresponding Michael adducts 3-substituted-1-cycloproyl-3-phenyl/4'-methoxyphenyl-propan-1-ones (IVa-f). The IR spectra of IVa and b showed bands at 1690 and 1705 (C=O), and 2860-3080 (aliphatic CH). The IR spectra of IVc and d showed bands at 1740 and 1675 (C=O of ester ketone), while the IR spectra of IVe and f showed bands at 1690, and 1670 (C=O of 5-pyrazolone and ketone). The IR spectra of IV showed a broad band at 3410 (enolic OH).

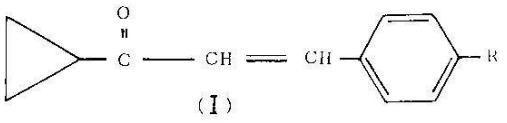
Experimental

Melting points reported are uncorrected. IR spectra in KBr were recorded on a Beckman IR 20 spectrophotometer and the PMR spectra in $CDCl_3$ on a Bruker WP-80-CW spectrophotomter using TMS as internal standard (Chemical shifts in ppm). Cyclopropyl methyl ketone is a Fluka product No. 29960.

3-Cyclopropyl-1-phenyl/4'-methyoxy-phenyl-prop-1-en-3-ones (1a and b)

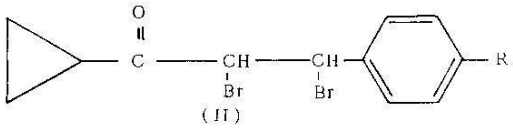
To a solution of cyclopropyl methyl ketone (0.1 mol) in ethanol (100 ml) containing KOH (4 g in 2 ml H_2O), benzaldehyde/or anisaldehyde (0.1 mol) was added dropwise during 30 minutes at room temperature with continuous stirring for 2 hours. The solid product was precipitated quantitatively, filtered, washed with hydrochloric acid (100 ml, 2 %) followed

*IR ν_{max} in cm^{-1} throughout the article.



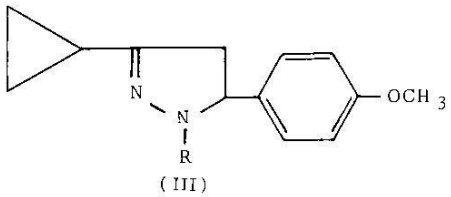
(I)

a) R = H ; b) R = OCH_3



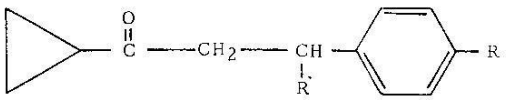
(II)

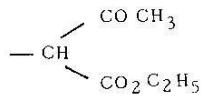
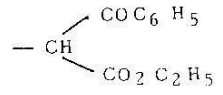
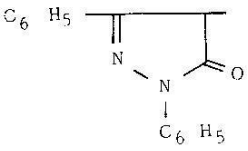
a) R = H ; b) R = OCH_3



(III)

a) R = H ; b) R = C_6H_6



	R	R'
a)	H	2-oxocyclohexyl
b)	OCH_3	2-oxocyclohexyl
c)	H	
d)	OCH_3	
e)	H	
f)	OCH_3	

(IV)

by water (3 x 100 ml) and dried. The products were crystallized from benzene-petroleum ether (60-80°) mixture to give Ia and b as pale yellow crystals (Table 1).

2,3-Dibromo-1-cyclopropyl-3-phenyl/ 4'-methoxyphenyl-propan-1-ones(IIa and b)

To a solution of I (0.01 mol) in carbon tetrachloride (60 ml), bromine (1.6 g, 0.5 ml, 0.01 mol) was added dropwise at room temperature with stirring. After complete addition, carbon tetrachloride was slowly evaporated at room temperature and the solid residue was crystallised from petroleum ether (80-100°) to give II as colourless crystals (Table 1).

3-Cyclopropyl-5-(4'-methoxyphenyl)-2-pyrazolines (IIIa and b)

A solution of I (0.01 mol), hydrazine hydrate or phenylhydrazine (0.01 mol) in acetic acid (30 ml) was refluxed for 4 hours. The solution was poured after cooling in ice. The solid product which separated was filtered and crystallized from petroleum ether (60-80°) to give IIIa or b as yellow crystals (Table 1).

3-Substituted-1-cyclopropyl-3-phenyl /1'-methoxyphenyl-propan-1-ones (Michael adducts IVa-f)

A mixture of I (0.01 mol), the appropriate active methylene compounds, and few drops of piperidine in ethanol (30 ml) was refluxed for 6 hours. The solid product obtained on evaporation of most of the solvent and cooling was crystallized from petroleum ether (80-100°) to give IVa-f as colourless crystals (Table-1).

Table-1: Physical Data of Various Compounds Prepared.

Comp.	M.P. °C	Yield %	Mol.Formula		Analysis (%) Calcd.	Found
Ia	57	68	$C_{12}H_{12}O$	C	83.72	83.66
				H	6.98	6.90
Ib*	74	73	$C_{13}H_{14}O_2$	C	77.23	77.17
				H	6.93	6.87
IIa**	116	76	$C_{12}H_{12}Br_2O$	C	43.37	43.32
				H	3.61	3.60
IIb	112	84	$C_{13}H_{14}Br_2O_2$	C	43.09	43.00
				H	3.87	3.81
IIIa*	61	57	$C_{13}H_{16}N_2O$	C	72.22	72.13
				H	7.41	7.36
				N	12.96	12.72
IIIb	93	63	$C_{19}H_{20}N_2O$	C	78.08	78.00
				H	6.85	6.72
				N	9.59	9.34
IVa++	118	68	$C_{18}H_{22}O_2$	C	80.00	79.91
				H	8.15	8.09
IVb	110	72	$C_{19}H_{24}O_3$	C	76.00	75.91
				H	8.00	7.97
IVc@	83	62	$C_{18}H_{22}O_4$	C	71.52	71.46
				H	7.28	7.22
IVd	96	74	$C_{24}H_{26}O_5$	C	73.10	73.03
				H	6.60	6.54
IVe	97	60	$C_{27}H_{24}N_2O_2$	C	79.41	79.30
				H	5.88	5.83
				N	6.86	6.62
IVf	124	68	$C_{28}H_{26}N_2O_3$	C	76.71	76.61
				H	5.94	5.87
				N	6.39	6.19

*PMR: 0.9 (hump, 4H, cyclopropyl-CH_2-), 1.9 (m, 1H, cyclopropyl-CH-), 3.5 (s, 3H, OCH_3), 6.5 (d, 2H, -CH=CH-), 7.2 (d x d, 4H, Ar-H).

**PMR: 0.9 (hump, 4H, cyclopropyl-CH_2-), 1.9 (m, 1H, cyclopropyl-CH-), 4.6 (d, 1H, C_3-H), 5.0 (d, 1H, C_2H), 7.1 (s, 5H, Ar-).

$^{+}$PMR: 0.8 (hump, 4H, cyclopropyl-CH_2), 1.7 (m,1H, cyclopropyl-CH-), 2.8 (m, 2H, C_4-H_2), 3.7 (s, 3H, OCH_3), 5.1 (d, 1H, C_5-H), 6.7 (d x d, 4H, Ar-H).

$^{++}$PMR: 0.8(hump, 4H, cyclopropyl-CH_2-), 1.8 (m,1H, cyclopropyl-CH-), 2-2.8 (hump, 9H, cyclohexylprotons) 2.9 (m, 1H, C_3-H), 3.5 (d, 2H, C_2-H_2), 7.1 (s, 5H, Ar-H).

$^{@}$PMR: 0.8 (hump, 4H, cyclopropyl-CH_2-), 1.1 (t, 3H, O-CH_2-CH_3), 1.7 (m, 1H, cyclopropyl-CH-), 2.2 (s, 3H, $COCH_3$) 2.8 (m, 1H, C_3-H), 3.4 (d, 2H, C_2-H_2), 3.9 (q, 2H, -OCH_2-CH_3), 5.7 (s, 1H, CO.CH.CO), 7.1 (s, 5H, Ar-H).

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