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PREPARATION AND REACTIONS OF ALKYL AND ARYL ISOPROPENYL CARBONATES

NOVEL ALKOXY- AND ARYLOXYCARBONYLATIONS OF AMINES

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It is well documented that isopropenyl acetate is a most convenient, mild and high-yield acetylating reagent for amines, alcohols and carboxylic acids, and also an extremely useful reagent for enol acetylation of all enolizable carbonyl compounds[1]. Therefore, the corresponding isopropenyl carbonates are expected to be particularly useful reagents for alkoxy- and aryloxycarbonylations We wish to report here the preparation of the heretofore unknown alkyl and aryl isopropenyl carbonates (I) and some preliminary results of alkoxy- and aryloxycarbonylations by the reaction of (I) and amines.

Preparation of alkyl and aryl isopropenyl carbonates (Ia-e)

At first, direct alkoxy- and aryloxycarbonylations of acetone-enolate would seem to be a simple route to (I) and the reaction of ethyl chloroformate with the enolate of acetone generated by the following methods were examined in various conditions; a) 2-(trimethylsiloxy)propene with CH_3Li[2], b) isopropenyl acetate with CH_3Li[3], c) acetone with lithium diisopropylamide[4] and d) 2,5-dimethyl tetrahydrofuran with n-BuLi[5]. However, none of these methods gave satisfactory results probably because of complication caused by the ambident nature of the enolate and facile base-catalyzed polymerization of the starting material and/or products. Finally, the desired carbonates (I) were obtained by treatment of chloromercuriacetone ($ClHgCH_2COCH_3$, II) as the acetone-enolate equivalent[6] with alkyl and aryl chloroformates (III) in hexamethylphosphoric triamide (HMPA) in considerable yields.

A typical experimental procedure is illustrated by the reaction of (II) with ethyl chloroformate (IIIa) in HMPA leading to the formation of ethyl isopropenyl carbonate (Ia). Ethyl chloroformate (IIIa) was added dropwise with stirring to a previously warmed solution of (II) in HMPA at 65-70° over 4 hr under argon, and stirring was continued at the same temperature for 20 hours (The reaction was monitored by t.l.c. and i.r.). After cooling the reaction mixture to room temperature, it was poured into ice-water and extracted with n-pentane. From the extract, 78% yield of pure (Ia) was obtained as a colorless liquid. The structure was established by elemental analysis, i.r., n.m.r., and mass spectral data. The reaction was very much influenced by the solvent used.

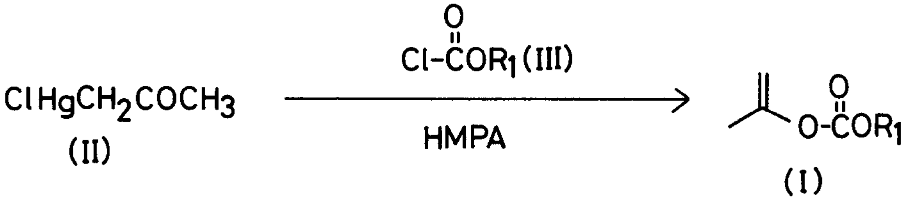


Table I

	R_1	Isolated Yield(%)	b.p. (°C/mmHg)	$\nu_{max}^{CHCl_3}$ cm^{-1}	Vinyl Protons of Isopropenyl Group δ ($CDCl_3$)	m/e(M^+)
Ia	C_2H_5	78	59-60/48	1750,1675	4.80 (d, 1H) 4.70 (d, 1H)	130
lb	CH_3	48	51/57	1755,1670	4.82 (d, 1H) 4.70 (d, 1H)	116
Ic	$CH_2CH{=}CH_2$	72	59-60/16	1750,1680	4.82 (d, 1H) 4.70*	142
Id	$CH_2C_6H_5$	56	104-105/0.45	1750,1680	4.80 (d, 1H) 4.68 (d, 1H)	192
Ie	C_6H_5	76	101/10**	1760,1670	4.94 (d, 1H) 4.75 (d, 1H)	178

* The signals of $C\underline{H}_2C{=}$ protons are overlapped with those of $-OC\underline{H}_2$ protons.

** The distillate was kept in a refrigerator to solidify as colorless crystals, m.p. 36-37°.

No reaction occurred in other solvents such as xylene, dimethyl ethylene glycol, methylene chloride and tetrahydrofuran. The reaction temperature of 65-70° was quite sufficient and all other reactions were done at this temperature in HMPA. The yields, b.p. and spectral data of some representative alkyl and aryl carbonates (Ia-e) are summarized in Table I. The ease with which chloromercuriacetone (II) is obtained by aqueous mercuration of isopropenyl acetate, the high-specific O-isopropenylation and the easiness of isolation of the products make this procedure especially valuable for the synthesis of the title carbonates (I).

Alkoxy- and aryloxycarbonylations of Amines

Alkoxy- and aryloxycarbonylations of amines were examined by using alkyl

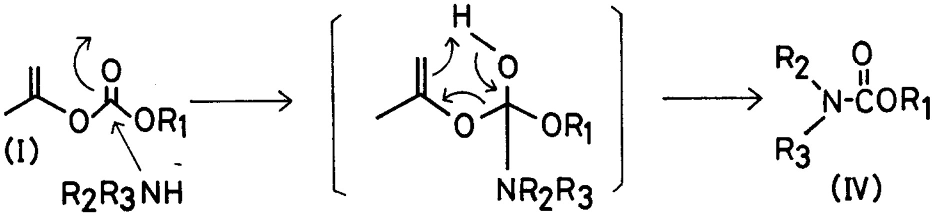
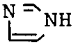


Table II

	R_1	R_2R_3NH	Isolated Yield(%)	$\nu_{max}^{CHCl_3}$ cm^{-1}
IVa	C_2H_5	$C_6H_5CH_2CH_2NH_2$	90	3420, 1700
IVb	C_2H_5	$C_6H_5CH_2NHCH_3$	88	1670
IVc	C_2H_5		95	1660
IVd	CH_3	$C_6H_5CH_2CH_2NH_2$	95	3410, 1700
IVe	CH_3	$C_6H_5CH_2NHCH_3$	83	1670
IVf	CH_3		91	1670
IVg	CH_3		83	1675
IVh	$CH_2CH{=}CH_2$	$C_6H_5CH_2CH_2NH_2$	94	3415, 1700
IVi	$CH_2C_6H_5$	$C_6H_5CH_2CH_2NH_2$	94	3410, 1695
IVj	C_6H_5	$C_6H_5CH_2CH_2NH_2$	83	3410, 1720
IVk	C_2H_5		84	1760
IVl	CH_3		80	1755

and aryl isopropenyl carbonates (Ia-e). The results are shown in Table II. A variety of primary and secondary amines were reacted with (I) at 50-70° for several hr, giving the corresponding N-alkoxy- and N-aryloxycarbonyl compounds (IVa-j) in good yields. In the case of weakly basic amine (IVk,l), a catalytic quantity of p-toluenesulfonic acid or sulfuric acid is required. The advantages of this novel alkoxy- or aryloxycarbonylation using (I) are found in the mild reaction conditions (only the formation of acetone as a by-product), the high yields, the absence of base except for the starting amine in the reaction mixture, and the easiness of procedures.

Aknowledgement

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References and Notes

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