Preparation and characterization of mixed anhydrides of *O*-allylbenzohydroximic acid

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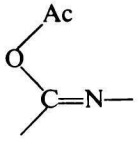
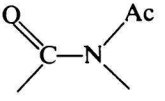
Mixed anhydrides of *O*-allylbenzohydroximic acid were prepared by acylation of *O*-allylbenzohydroxamic acid in pyridine using a number of acylating agents: acetyl, benzoyl, *p*-nitrobenzoyl, anisoyl, *p*-toluenesulfonyl chlorides. The structure elucidation of the resulting mixed anhydrides was performed by chemical and spectroscopic methods. Attempts to rearrange several mixed anhydrides by heating in dioxane were not successful.

In connection with our study of 1,3-acyl migration from O to N atom in isoimides, search was made for the isoimides which would be stable during the reaction conditions. Unfortunately most isoimides *A* are unstable and they undergo rapid 1,3-acyl migration to afford imides *B*.

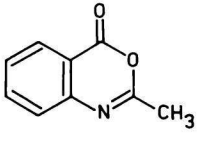


A

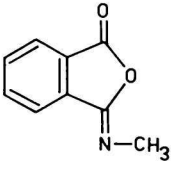


B

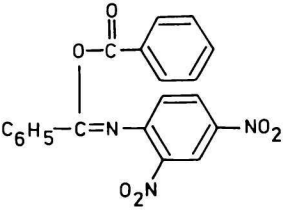
As early as 1915 *Mumm et al.* [1] predicted such facile 1,3-rearrangement in isoimides. But this rearrangement could not be studied intensively due to the fact that stable isoimides were not available. The exceptions are few cyclic compounds such as *I* and *II* in which the carbonyl group is sterically inaccessible to nucleophilic attack by the imino nitrogen [2, 3].



I

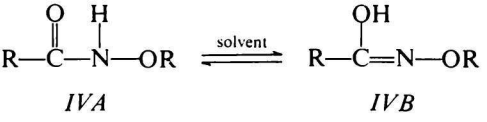


II



III

In the acyclic system, only *N*-(2,4-dinitrophenyl)benzimidoyl benzoate (*III*) was found by *Curtin* and *Miller* [4] to be stable enough to be isolated. The stability of *III* was attributed to the reduced nucleophilicity of imino nitrogen due to the presence of electron withdrawing the nitro group in benzene ring attached to imino nitrogen. *O*-Alkylhydroxamic acid (*IVA*) in solution easily tautomerizes to *O*-alkylhydroximic acid (*IVB*) which upon acylation may afford isoimides in which imino nitrogen is attached to the electronegative oxygen atom which may cause their stability. This consideration prompted us to select *O*-allylbenzohydroxamic acid as the starting material for the preparation of isoimides.



IVA *IVB*

Ward et al. [5] studied acetylation of the potassium and silver salts of several *O*-alkylhydroxamic acids and reported on the formation of both *O*- and *N*-acetylated products. *Hegarty et al.* [6] also prepared a number of *O*-acetylated products from silver salts of *O*-benzylbenzohydroxamic acid and announced that *O*-acetylated products were formed exclusively as (*Z*)-isomers. *Challis et al.* [7] effected acetylation of a number of *O*-benzylarylcarbohydroxamic acids by using acetic anhydride and pyridine in organic solvents and reported that acetylation proceeds by the primary formation of (*Z*)-acetic *O*-benzylhydroximic anhydride which rearranged to the more stable *O*-benzyl-*N*-acetylbenzohydroxamate isomers. *Misra et al.* [8] have studied acylation of *O*-benzylbenzohydroxamic acid using various acyl and sulfonyl halides in dioxane in the presence of Et_3N and claimed that (*Z*)-isomers of the *O*-acylated products are preferentially formed which are stable during the reaction conditions. Earlier, *Misra et al.* [9, 10] studied aromatic sulfonylation of several sodium *O*-alkylarylcarbohydroxamates and reported that in benzene medium, only *O*-tosylated products were formed as major products in a yield exceeding 80 %. From NMR spectroscopic evidence, they indicated that *O*-tosylated products were formed as (*Z*)- and (*E*)-isomers which could not be separated by them nor could they assign correct configuration to these isomers.

In the present study, we report on acylation of *O*-allylbenzohydroxamic acid using acetyl, benzoyl, *p*-nitrobenzoyl, anisoyl, and *p*-toluenesulfonyl chlorides as acylating agents in the presence of pyridine as solvent. The resulting mixed anhydrides have been characterized by chemical and spectroscopic methods.

Experimental

Melting points are uncorrected. The petroleum ether had a boiling temperature range of 60—80 °C. The purity of the compounds was checked by TLC, the column was packed with silica gel G using benzene—ethyl acetate ($\varphi_r = 3:7$) as eluant. IR spectra were recorded in a spectrophotometer Infra Cord Model 337 (Perkin—Elmer) using KBr pellets, UV spectra on Spectronic 20 (Bausch—Lamb), ^{1}H NMR spectra in $CDCl_3$ or $CDCl_3 + F_3CCOOH$ on an instrument FT-100 (Jeol) using TMS as an internal standard.

Potassium benzohydroxamate was prepared by the modified method of *Jeanrenaud* [11]. *O*-Allylbenzohydroxamate was prepared by following the method of *Cooley et al.* [12]. The product yield after recrystallization from a mixture of ether—petroleum ether was 52 %, m.p. = 63—64 °C. For $C_{10}H_{11}NO_2$ w_i(calc.): 67.79 % C, 6.21 % H, 7.90 % N; w_i(found): 67.95 % C, 6.13 % H, 7.75 % N. IR spectrum (nujol), $\tilde{\nu}/cm^{-1}$: 1655 ν(CONH). UV spectrum (MeOH), λ_{max}/nm ($\varepsilon/(m^2\,mol^{-1})$): 360 (712). ^{1}H NMR spectrum ($CDCl_3$), δ: 4.5 (d, 2H, OCH_2), 6.2 (m, 1H, =CH), 5.5 (d, 2H, $=CH_2$), 7.15—7.60 (m, H_{arom}).

p-Nitrobenzoic O-allylbenzohydroximic anhydride (*Va*)

O-Allylbenzohydroxamic acid (0.01 mol) in pyridine (30—35 cm^3) was treated with *p*-nitrobenzoyl chloride (0.01 mol) and the reaction mixture was stirred under reflux for 24 h. The progress of the reaction was monitored by TLC and after completion of the reaction, excess of pyridine was removed by distillation and the residue washed with water ($4 \times 50\,cm^3$). The residue dissolved in ether (50 cm^3) and dried over anhydrous sodium sulfate. The ethereal solution upon cooling to 5 °C gave a crystalline product *Va* which was recrystallized from benzene in a yield of 59 %, m.p. = 244—245 °C. For $C_{17}H_{13}N_2O_5$ w_i(calc.): 62.76 % C, 3.92 % H, 8.55 % N; w_i(found): 62.70 % C, 4.02 % H, 8.60 % N. IR spectrum, $\tilde{\nu}/cm^{-1}$: 1620 ν(C=N), 1700 ν(O—C(O)), 1360 ν(C—NO_2), 1115 ν(C—O—C). UV spectrum (MeOH), λ_{max}/nm ($\varepsilon/(m^2\,mol^{-1})$): 400 (940). ^{1}H NMR spectrum ($CDCl_3$), δ: 5.5 (d, 2H, $=CH_2$), 3.6 (d, 2H, OCH_2), 6.2 (m, 1H, =CH), 8.5 (m, H_{arom}).

The above compound *Va* was also prepared by using benzene as solvent and pyridine, triethylamine, sodium methoxide as bases. Since the yields of the mixed anhydrides were very low in these cases (Table 1), all the other mixed anhydrides *Vb*—*Vd* were prepared by using pyridine both as a solvent and a base. The physical and spectroscopic data of the mixed anhydrides are presented in Tables 1—3.

Acetic O-allylbenzohydroximic anhydride (*Ve*)

O-Allylbenzohydroxamic acid (0.01 mol) in benzene (25—50 cm^3) was treated with acetyl chloride (0.01 mol) followed by addition of pyridine (7—10 cm^3). The reaction mixture was stirred at room temperature for 72 h and then poured into an ice bath. The

Table 1

Physical data of the mixed anhydrides *V*

Compound	Solvent	Base	Yield/%	M.p./°C
Va	Pyridine	Pyridine	59	244—245
	Benzene	Pyridine	48	244—245
	Benzene	Et_3N	45	244—245
	Benzene	NaOMe	20	244—245
Vb	Pyridine	Pyridine	50	120—121
Vc	Pyridine	Pyridine	45	52
Vd	Pyridine	Pyridine	42	225—226
Ve	Benzene	Pyridine	50	54—55

Table 2

IR spectral data of the mixed anhydrides *V*

Compound	$\tilde{\nu}/cm^{-1}$					
	ν(C=N)	ν(O—C(O))	ν(C—O—C)	ν(C—NO_2)	ν(O—$S(O)_2$)	ν($S(O)_2$)
Va	1620	1700	1115	1360		
Vb	1620	1700				
Vc	1590				1160	1320
Vd	1610	1695	1030			
Ve	1590	1660	1165			

Table 3

^{1}H NMR spectral data of the mixed anhydrides *V*

Compound	Chemical shift δ
Va	5.5 (d, 2H, =CH_2), 3.6 (d, 2H, OCH_2), 6.2 (m, 1H, =CH), 8.5 (m, H_{arom})
Vb	5.65 (d, 2H, CH_2), 3.6 (d, 2H, OCH_2), 6.2 (m, 1H, =CH), 7.15—7.6 (m, H_{arom})
Vc	4.9 (s, 2H, OCH_2), 5.5 (d, 2H, =CH_2), 6.2 (m, 1H, =CH), 7.03—8.13 (m, H_{arom})
Vd	5.25 (d, 2H, =CH_2), 3.7 (s, 3H, OCH_3), 3.6 (d, 2H, OCH_2), 7.25—8.2 (m, H_{arom})
Ve	5.1 (d, 2H, =CH_2), 3.6 (d, 2H, OCH_2), 2.1—2.35 (s, 3H, OCH_3), 7.25—8.2 (m, H_{arom})

benzene layer was extracted successively with saturated $NaHCO_3$ ($2 \times 50\,cm^3$), 1 % HCl ($2 \times 50\,cm^3$), and water ($2 \times 50\,cm^3$) and dried over anhydrous sodium sulfate. Upon removal of solvent under reduced pressure, a crude product was isolated which was recrystallized from a mixture of ether—petroleum ether to give the product in a yield of 50 %. The spectroscopic data of this compound (*Ve*) are presented in Tables 2 and 3.

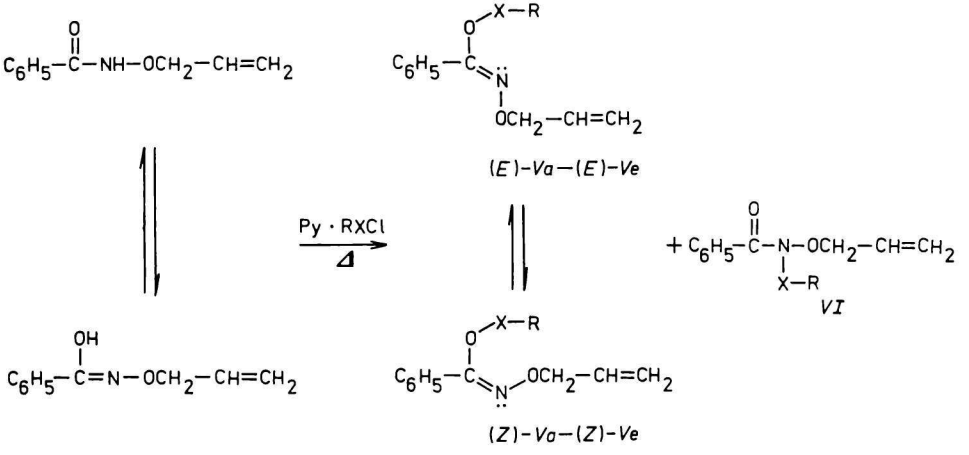
Acid hydrolysis of Va

6 M-HCl was added to 0.2 g of *Va* and the reaction mixture heated for 1 h when a crystalline precipitate (0.05 g, 25 %) appeared, m.p. = 170—173 °C. The IR spectra of the product were identical with an authentic sample of allyloxyammonium chloride.

Results and discussion

Allylbenzohydroxamate was prepared by treatment of potassium benzohydroxamate with allyl chloride in basic medium. The principal drawback of this method is that it is time-consuming but the selectivity is high and only monoallylated product was obtained. Very small amount of dialkylated product was formed. Acylation of *O*-allylbenzohydroxamate was carried out by refluxing pyridine solution in the presence of acyl halides. The reaction was monitored by TLC and was stopped, when, only single spot corresponding to the product was observed. When acylation was effected in solvents other than pyridine using different bases, the yield of *O*-acylated product was found to be less (Table 1). Hence acylation was carried out by using pyridine both as a solvent and a base.

Acylation may give rise to *O*-acylated (*Z*)-*V* or (*E*)-*V* and *N*-acylated products *VI* (Scheme 1).



Scheme 1

The infrared spectrum of the product obtained from the reaction between *O*-allylbenzohydroxamic acid and *p*-nitrobenzoyl chloride showed a band at $\tilde{\nu} = 1760—1770\,cm^{-1}$ attributed to ester grouping (—OC(O)—) and this indicates that the product has isoimide structure (*Z*)-*Va* or (*E*)-*Va*. Vinyl acetate and isourea [13, 14] derivatives also show carbonyl vibrations in this region. Further in the IR spectrum of the product another band was observed in the region of $\tilde{\nu} = 1590—1600\,cm^{-1}$ assigned to ν(C=N). *N*-Acylated product *VI* would have shown a band in the region of $\tilde{\nu} = 1670—1700\,cm^{-1}$; in ^{1}H NMR spectrum, δ: 5.5 (d, 2H, $=CH_2$), 3.6 (d, 2H, OCH_2) and 8.5 (m, H_{arom}). All the other products also showed identical spectral behaviour.

It is therefore concluded that acylation of *O*-allylbenzohydroxamic acid afforded compounds having mixed anhydride structures. Further, hydrolysis of the *p*-nitrobenzoic *O*-allylbenzohydroximic anhydride (*Va*) with hydrochloric acid under mild conditions afforded a product which showed identical TLC spot and IR spectrum as that of *O*-allylbenzohydroxamic acid. Results of the hydrolysis support the fact that the acylated product is best represented by the mixed anhydride structure. The *N*-acylated product upon treatment with HCl may also afford *O*-allylbenzohydroxamic acid but in this case the cleavage of amide bond would require much more drastic conditions. On the basis of chemical degradation studies and spectral evidence, it may be concluded that acylation affords *O*-acylated product in major amounts. Another question concerning the configuration of mixed anhydrides remains to be settled. The mixed anhydrides can exist as (*Z*)-*V* and (*E*)-*V* isomers. Compound *Va* in pyridine was heated at 70 °C for 4 h and there was no change in the TLC spot and IR spectrum. This indicates that the *O*-acylated product formed is stable towards heat and the mixed anhydrides have the (*Z*)-configuration [6, 8] in which the acyloxy group and lone electron pair of nitrogen atom are *trans*.

In the ^{1}H NMR spectrum the upfield shift of OCH_2 protons in *Va* ($\delta = 3.6$) as compared to protons in *O*-allylbenzohydroxamic acid ($\delta = 4.5$) is possible only when *Va* has (*Z*)-configuration.

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