REACTIONS OF ETHYL 4-BROMO-3-(2-FURYL)-2-BUTENOATE WITH NITROGEN NUCLEOPHILES*

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Nucleophilic substitution reactions of ethyl 4-bromo-3-(2-furyl)-2-butenoate with nitrogen nucleophiles are described. UV, IR, and ^{1}H-NMR spectra of the prepared substances have been interpreted.

We have previously described[1] preparation of ethyl 4-bromo-3-(2-furyl)-2-butenoate and its reactions with sulphur nucleophiles. In the present work we describe nucleophilic substitution reactions of the starting ester with primary, secondary and tertiary amines. Allylic halides react with amines to form allylic amines or quarternary ammonium salts. Primary allylic halides react with primary, secondary and tertiary amines in the usual manner, in most cases *via* S_N2 mechanism, to give normal substitution products. Secondary allylic halides react with secondary amines predominantly *via* S_N2' mechanism[2,3].

Following presumably the S_N2 mechanism[4], S_N reactions of ethyl 4-bromo-3-(2-furyl)-2-butenoate with secondary and tertiary amines give products of normal substitution. Reactions of the ester with primary amines give five-membered ring products.

The most intense bands in the IR spectra of compounds under investigation are those of the stretching of the carbonyl group. In the spectra of compounds *I*–*XI* these bands appear at 1715–1705 cm^{-1} (ref.[5]). The α,β-unsaturated lactames *XII*–*XIV* show the carbonyl absorption band within 1680–1665 cm^{-1}. The bands at 1624–1604 cm^{-1} were assigned to the ethylenic C=C stretching. The medium intensity band at ~1300 and the sharp band at 1030 cm^{-1} are, respectively, those of asymmetric and symmetric stretchings of C—O—C group. To the out-of-plane bend of the furan ring was assigned the band at 880 cm^{-1}. The electron absorption spectra of all compounds studied show an absorption band centered at 210 – 220 nm. corresponding to $\pi-\pi^*$ electron transitions of the furan ring, the maximum of which is almost unaffected by the change of substituents. The other, more intense band at ~300 nm is that of $\pi-\pi^*$ electron transitions of the overall conjugated furylacrylic system. The structures of synthesized substances were confirmed by ^{1}H-NMR

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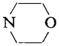
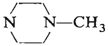
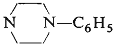
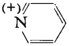
spectroscopy. Chemical shifts characteristic of selected substances are in Table II. The trisubstituted ethylene derivatives can exist as geometrical *E* and *Z* isomers. The identification of the individual isomers was based on the comparison of calculated

TABLE I

Ethyl 4-X-3-(2-Furyl)-2-butenoates

Compound	X	Formula (mol.w.)	M.p., °C[a] (yield, %)[a]	Calculated/Found[a]		
				% N	% C	% H
I	$N(CH_3)_2$	$C_{12}H_{17}NO_3$ (223·3)	144—145 (78·6)	4·33 4·53	63·20 63·41	5·26 5·11
II	$N(C_2H_5)_2$	$C_{14}H_{21}NO_3$ (251·3)	147—149 (79·2)	3·98 4·09	47·90 47·69	5·98 5·80
III	$N(CH_3)C_6H_5$	$C_{17}H_{19}NO_3$ (285·3)	123—124 (68·3)	3·63 3·72	53·02 52·81	4·93 4·81
IV		$C_{14}H_{19}NO_3$ (249·3)	136—137 (81·0)	4·01 4·06	48·17 48·40	5·44 5·52
V		$C_{15}H_{21}NO_3$ (263·3)	130—132 (78·5)	3·85 3·78	49·62 49·53	5·78 5·59
VI		$C_{14}H_{19}NO_4$ (265·3)	174—176 (76·7)	3·83 4·08	46·06 45·81	5·20 5·09
VII		$C_{15}H_{22}N_2O_3$ (278·3)	203—204 (73·4)	7·41 7·36	47·65 47·33	5·82 5·69
VIII		$C_{20}H_{24}N_2O_3$ (340·4)	175—176 (71·2)	6·36 6·19	54·57 54·50	5·45 5·28
IX		$C_{15}H_{16}NO_3$ (258·3)	138—139 (67·6)	3·92 3·96	50·32 50·03	4·47 4·24
X	$\overset{(+)}{N}(C_2H_5)_3$	$C_{16}H_{26}NO_3$ (280·2)	184—185 (62·0)	3·69 3·78	50·57 50·42	6·84 6·70
XI	$\overset{(+)}{N}(CH_3)_2C_6H_5$	$C_{18}H_{22}NO_3$ (300·2)	165—166 (48·8)	3·51 3·63	54·05 53·79	5·50 5·37
XII[b]	C_6H_5	$C_{14}H_{11}NO_2$ (225·2)	135—136 (58·6)	6·22 6·08	74·66 74·30	4·88 4·57
XIII[b]	$CH(CH_3)_2$	$C_{14}H_{11}NO_2$ (191·2)	133—134 (47·3)	7·33 7·41	69·10 68·92	6·80 6·71
XIV[b]	cyclohexyl	$C_{14}H_{17}NO_2$ (231·3)	121—122 (52·1)	6·06 6·67	72·72 72·48	7·35 7·12

[a] Data for *I*—*XI* obtained on perchlorates; [b] 1-X-4-(2-furyl)-2,5-dihydropyrrole-2-one.

and observed chemical shifts for olefinic protons. The calculations were done using the additive formula[6] and increments corresponding to the aromatic system of the furan ring. In this way, it has been found that compounds *I*–*XI* exist as *E* isomers, which can be explained, firstly, by the *E*-isomeric purity of the starting ethyl 4-bromo-3-(2-furyl)-2-butenoate and, secondly, by the conditions applied in the performed S_N reactions under which no isomerization had taken place.

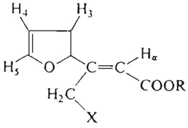
EXPERIMENTAL

Ethyl 4-X-3-(2-Furyl)-2-butenoates

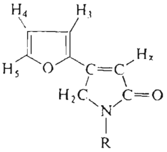
A) The respective secondary amine (0·02 mol) was added to a solution of ethyl 4-bromo-3-(2-furyl)-2-butenoate (0·01 mol) in ether (50 ml). The mixture was stirred at room temperature and then refluxed, for 1 h each. After cooling, the separated amine hydrobromide was

TABLE II

^{1}H-NMR Data (δ, ppm; J, Hz) for the Studied Substances



I–*IX*



XII, *XIV*

Compound	H_α s[a]	H_3 d	H_4 dd	H_5 d	CH_2 s	R	
						CH_2 q	CH_3 t
I	6·47	6·92	6·39	7·41	3·86	4·21	1·31
II	6·46	7·00	6·39	7·37	3·90	4·19	1·27
IV	6·42	6·90	6·38	7·38	3·96	4·16	1·28
V	6·45	6·96	6·38	7·37	3·79	4·16	1·26
VI	6·48	6·90	6·40	7·42	3·85	4·20	1·29
VII	5·47	6·91	6·43	7·40	3·84	4·21	1·31
IX[b]	6·57	7·22	6·65	7·77	6·00	4·19	1·25
XII	6·29	6·70	6·49	7·51	4·63	—	—
XIV	6·23	6·62	6·47	7·48	4·25	—	—

[a] s Singlet, d doublet, t triplet, q quartet, $J_{3,4} = 3·5$; $J_{4,5} = 1·7$; $J_{CH_2,CH_3} = 7·0$ Hz; [b] measured in hexadeuteriodimethyl sulphoxide.

filtered and the crude product was purified by chromatography. The thus obtained, unstable derivative was treated with perchloric acid and the formed salt was purified by crystallization from methanol.

B) An acetone solution of the respective tertiary amine (0·02 mol) was added to ethereal solution of ethyl 4-bromo-3-(2-furyl)-2-butenoate (0·01 mol), the mixture was refluxed for 3 h, and the mixture was left at room temperature to allow the reaction to come to completion. The precipitated product was converted to a perchlorate and the latter crystallized from methanol (Table I).

Reactions with Primary Amines

The respective primary amine (0·02 mol) was added to an ethereal solution of the starting ester (0·01 mol). The mixture was refluxed for 3 h and then left for 6 h at ambient temperature. The separated amine hydrobromide was filtered and the filtrate was concentrated. The crude product was purified by chromatography and the isolated substance was crystallized from chloroform.

Spectral Measurements

The ^{1}H-NMR spectra for solutions in deuterio chloroform or hexadeuteriodimethyl sulphoxide were measured with a Tesla BS 487C spectrometer using tetramethylsilane as the internal standard, see Table II. The IR spectra (KBr technique, 1 mg samples/300 mg KBr) were measured in the range of 3 700—400 cm^{-1} with a UR-20 spectrometer (Zeiss, Jena) which was calibrated against a polystyrene foil of 25 µm thickness. The UV spectra were recorded with a UV VIS (Zeiss, Jena) apparatus in methanol at a 5—7 . 10^{-5} mol/l concentration. Spectra of *I*—*XI* were taken after their conversion to the corresponding perchlorates.

I: UV data (λ_{max}, nm, (log ε)): 213 (3·94), 316 (4·33); IR data (ν, cm^{-1}): 882, 1 028, 1 305, 1 618, 1 706, 3 140.

II: UV data: 211 (3·75), 316 (4·33); IR data: 887, 1 028, 1 297, 1 623, 1 713, 3 139.

III: UV data: 211 (4·26), 3·04 (4·31); IR data: 883, 1 027, 1 300, 1 617, 1 705, 3 132.

IV: UV data: 211 (3·86), 315 (4·35); IR data: 879, 1 026, 1 296, 1 617, 1 705, 3 140.

V: UV data: 212 (3·81), 315 (4·26); IR data: 878, 1 031, 1 297, 1 616, 1 706, 3 136.

VI: UV data: 211 (3·82), 313 (4·40); IR data: 877, 1 032, 1 298, 1 616, 1 707, 3 135.

VII: UV data: 211 (3·99), 307 (4·32); IR data: 879, 1 031, 1 302, 1 620, 1 707, 3 137.

VIII: UV data: 212 (4·24), 315 (4·43); IR data; 881, 1 030, 1 302, 1 618, 1 706, 3 135.

IX: UV data: 215 (4·15), 317 (4·36); IR data: 878, 1 032, 1 309, 1 624, 1 712.

X: UV data: 212 (4·15), 316 (4·38); IR data: 877, 1 033, 1 621, 1 711.

XI: UV data: 216 (4·17), 318 (4·37); IR data: 878, 1 030, 1 622, 1 710.

XII: UV data: 213 (4·07), 320 (4·29); IR data: 882, 1 031, 1 299, 1 602, 1 681.

XIII: UV data: 211 (4·79), 301 (4·25); IR data: 789, 1 022, 1 303, 1 604, 1 678.

XIV: UV data: 211 (3·89), 299 (4·38); IR data: 880, 1 020, 1 302, 1 605, 1 676.

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