NUCLEOPHILIC SUBSTITUTION REACTION OF KETO-ALLYLIC SYSTEMS WITH A HETEROCYCLIC RING IN γ-POSITION

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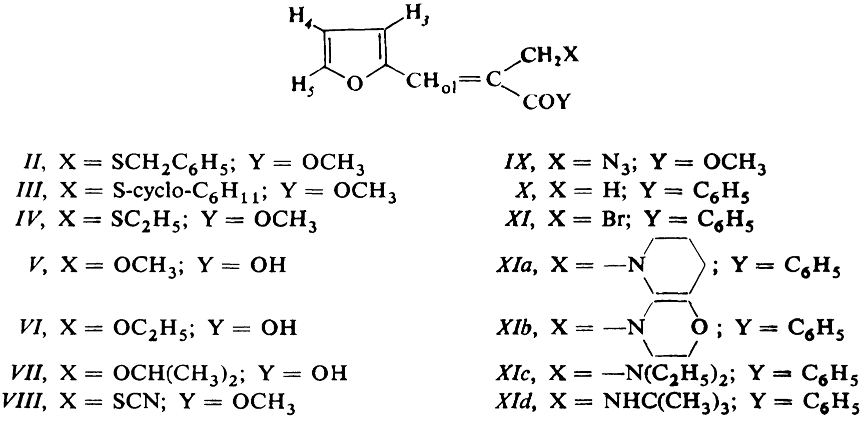
Keto-allylic systems with a heterocyclic ring in γ-position were prepared; these undergo nucleophilic substitution reactions with amines, where a replacement of bromine at the bromomethyl group takes place in contrast to benzene analogues, where the nucleophile attacks the γ-carbon of the keto-allylic system.

The reactions of keto-allylic mobile systems with amines were studied since 1965. As found, 2-bromomethylchalcone[1], 4,4-dimethyl-1,4-dihydro-2-oxonaphthalene[2], 2-benzylidene-3-bromo-1-indanedione[3], methyl 2-bromomethyl-3-phenylpropanoate[4], and 2-bromomethylbenzylidenacetone[5] react in nucleophilic substitution reactions with amines by an S_N2' mechanism to form a C_γ–N bond under a simultaneous break of the C_α-halogen bond. A delocalization of electron density throughout the whole system occurs in a transition state, and the carbonyl group is getting to share a part of the negative charge, which bears the leaving halogen ion. Cyano group acts similarly in reaction of 2-bromomethyl-3-phenylpropenenitrile with amines[6], where products of anomalous bimolecular mechanism were isolated. This system has been denominated as an activated allylic system. Our preceding papers[7,8] verified the effect of a furan and 5-nitrofuran ring in γ-position of the keto-allylic system on the course of nucleophilic displacement reactions. Methyl 2-bromomethyl-3-(2-furyl)propenoate[7] (*I*) and methyl 2-bromomethyl-3-(5-nitro-2-furyl)-propenoate[8] reacted with amines to yield substitution products at the bromomethyl group only. Products without rearrangement were also formed when reacting amines with 2-bromomethyl-3-(5-bromomethyl-2-furyl)propenenitrile[9].

To examine the influence of a heterocyclic ring in γ-position of a keto-allylic system in nucleophilic displacement reactions, compound *I* was treated with further nucleophiles aiming to get a product of allylic rearrangement. Further keto-allylic systems with a furan or thiophene ring were investigated to discover their reaction ability.

Compound *I* gave with sodium phenylmethanethiolate and cyclohexanthiolate, respectively, in acetone exclusively products of bromomethyl substitution (*II*–*IV*). The same products were isolated when reacting thiolates in aqueous methanol. Solvolytic reactions with potassium methoxide, ethoxide or 2-propoxide in the corresponding alcohols afforded 2-alkoxymethyl-3-(2-furyl)propenoic acids, products of substitution at the bromomethyl group, and those of hydrolysis of methoxycarbonyl group (*V*–*VII*). Methyl 2-thiocyanatomethyl-3-(2-furyl)propenoate (*VIII*) and methyl 2-azidomethyl-3-(2-furyl)propenoate, (*IX*), prepared by reaction of sodium thiocyanate, or sodium azide under conditions of interphase catalysis do not undergo, in contrast to like benzene derivatives, a thermal 3,3-, or 1,3-isomerization even at 200°C (ref.[10], see Scheme 1). The product of allylic rearrangement could not be evidenced, nor on action of Lewis acids[11] (aluminium chloride, titan tetrachloride, tin tetrachloride, or trifluoroborane ethereate) in ether.



II, X = $SCH_2C_6H_5$; Y = OCH_3
III, X = S-cyclo-C_6H_{11}; Y = OCH_3
IV, X = SC_2H_5; Y = OCH_3
V, X = OCH_3; Y = OH
VI, X = OC_2H_5; Y = OH
VII, X = $OCH(CH_3)_2$; Y = OH
VIII, X = SCN; Y = OCH_3
IX, X = N_3; Y = OCH_3
X, X = H; Y = C_6H_5
XI, X = Br; Y = C_6H_5
XIa, X = —N ; Y = C_6H_5
XIb, X = —N O ; Y = C_6H_5
XIc, X = $—N(C_2H_5)_2$; Y = C_6H_5
XId, X = $NHC(CH_3)_3$; Y = C_6H_5

SCHEME 1

Following keto-allylic systems were prepared for testing the effect of heterocyclic ring upon the direction of substitution: 1-phenyl-2-bromomethyl-3-(2-furyl)-1-propenone (*XI*) by condensation of propiophenone with 2-furaldehyde and by brominating the methyl group of 1-phenyl-2-methyl-3-(2-furyl)-1-propenone (*X*) with N-bromosuccinimide; 1-phenyl-2-bromomethyl-2-(2-furyl)-1-propenone (*XIII*) by condensation of propiophenone with thienylaldehyde and bromination the methyl group of 1-phenyl-2-methyl-3-(2-thienyl)-1-propenone (*XII*) with N-bromosuccinimide; 1,3-bis(2-thienyl)-2-bromomethylpropenone (*XV*) by condensation of 2-thienylaldehyde with 1-(2-thienyl)-1-propanone followed by bromination of 1,3-bis(2-thienyl)-2-methyl-1-propenone (*XIV*) with N-bromosuccinimide. Methyl 2-bromomethyl-3-(2-thienyl)propenoate (*XVII*) was synhesized by the Perkin reaction of 2-thienyl-

TABLE I

Characteristic data of compounds *II*—*XVII*

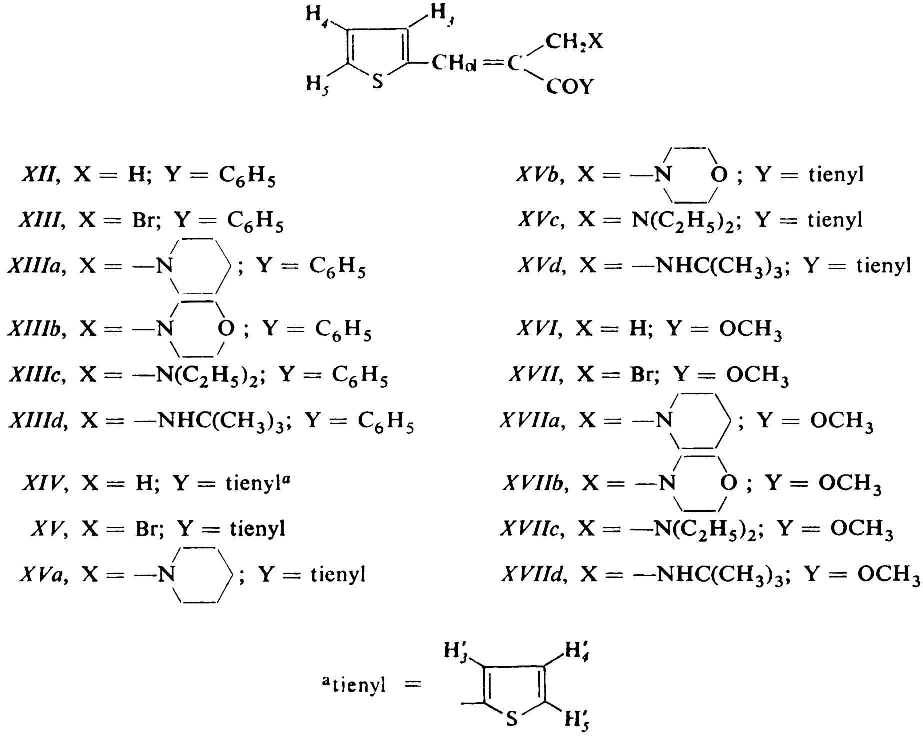
Compound	Formula (M_r)	M.p., °C (yield, %)	Calculated/Found			λ_{max}, nm (log ε)
			% C	% H	% N	
II	$C_{16}H_{16}O_3S$	oil	66·64	5·59	—	305
	(288·4)	(75)	66·57	5·50	—	(3·34)
III	$C_{15}H_{20}O_3S$	oil	64·25	7·18	—	300
	(280·4)	(66)	64·12	7·72		(3·25)
IV	$C_{11}H_{14}O_3S$	oil	58·38	6·23	—	301
	(226·3)	(55)	58·45	6·28		(3·30)
V	$C_9H_{10}O_4$	135	59·33	5·52	—	301
	(182·2)	(82)	59·42	5·61		(3·37)
VI	$C_{10}H_{12}O_4$	57	61·21	6·16	—	307
	(196·2)	(80)	60·95	6·05		(3·36)
VII	$C_{11}H_{14}O_4$	68	62·84	6·71	—	312
	(210·2)	(78)	62·71	6·82		(3·37)
VIII	$C_{10}H_9NO_3S$	oil	53·78	4·06	6·26	310
	(223·3)	(90)	54·00	4·10	6·18	(3·36)
IX	$C_9H_9N_3O_3$	oil	51·66	4·33	20·08	312
	(209·2)	(96)	51·75	4·45	20·05	(3·37)
X	$C_{14}H_{12}O_2$	59 (167/400)^a	74·96	5·39	—	327
	(224·3)	(86)	73·15	5·28		(3·48)
XI	$C_{14}H_{11}BrO_2$	31	55·43	3·65	—	329
	(303·3)	(85)	54·96	3·51		(3·42)
XIa	$C_{19}H_{21}NO_2$	oil	77·26	7·16	4·77	329
	(295·4)	(89)	74·19	7·25	4·75	(3·37)
XIb	$C_{18}H_{19}NO_3$	oil	72·70	6·44	4·71	328
	(297·3)	(87)	69·98	6·48	4·62	(3·35)
XIc	$C_{18}H_{21}NO_2$	oil	76·29	7·46	4·94	330
	(283·4)	(79)	73·12	7·38	4·22	(3·35)
XId	$C_{18}H_{21}NO_2$	oil	76·29	7·46	4·94	329
	(283·4)	(92)	74·14	7·31	4·90	(3·37)
XII	$C_{14}H_{12}OS$	57·5	73·64	5·30	—	327
	(228·3)	(92)	72·91	5·18		(3·05)
XIII	$C_{14}H_{11}BrOS$	39	54·73	3·61	—	332
	(307·2)	(95)	53·85	3·58		(3·09)
XIIIa	$C_{19}H_{21}NOS$	oil	73·27	6·79	4·49	324
	(311·5)	(89)	71·95	6·40	4·38	(3·36)

TABLE I
(*Continued*)

Compound	Formula (M_r)	M.p., °C (yield, %)	Calculated/Found % C	% H	% N	λ_{max}, nm (log ε)
XIIIb	$C_{18}H_{19}NO_2S$	oil	68·98	6·11	4·46	328
	(313·4)	(82)	67·10	5·97	4·50	(3·28)
XIIIc	$C_{18}H_{21}NOS$	oil	72·20	7·40	4·69	326
	(299·4)	(95)	70·03	7·41	4·70	(3·28)
XIIId	$C_{18}H_{21}NOS$	oil	72·20	7·40	4·69	326
	(299·4)	(95)	70·45	7·05	4·36	(3·28)
XIV	$C_{12}H_{10}OS_2$	54/40[a]	61·51	4·30	—	335
	(234·3)	(68)	60·95	4·18		(3·13)
XV	$C_{12}H_9BrOS$	34	46·01	2·89	—	337
	(313·2)	(80)	45·41	2·78		(3·18)
XVa	$C_{17}H_{19}NOS_2$	oil	64·32	5·03	4·41	330
	(317·4)	(78)	62·25	6·15	4·41	(3·20)
XVb	$C_{16}H_{17}NO_2S_2$	oil	60·16	5·36	4·38	331
	(319·4)	(80)	59·11	5·11	4·58	(3·13)
XVc	$C_{16}H_{19}NOS_2$	oil	62·91	6·26	4·58	335
	(305·4)	(71)	61·35	6·15	4·21	(3·20)
XVd	$C_{16}H_{19}NOS_2$	oil	62·91	6·26	4·58	331
	(305·4)	(77)	60·95	6·32	4·30	(3·28)
XVI	$C_9H_{10}O_2S$	92/67[a]	59·29	5·52	—	309
	(182·3)	(58)	58·15	5·47		(3·28)
XVII	$C_9H_9O_2BrS$	40	41·39	3·47	—	303
	(261·1)	(81)	40·72	3·35		(3·30)
XVIIa	$C_{14}H_{19}NO_2S$	46	63·36	7·31	5·27	312
	(265·4)	(65)	62·80	7·05	5·15	(3·78)
XVIIb	$C_{13}H_{17}NO_3S$	39	58·85	6·45	5·27	310
	(265·3)	(67)	57·80	6·40	5·21	(3·20)
XVIIc	$C_{13}H_{19}NO_2S$	oil	61·63	7·55	5·53	312
	(253·4)	(63)	61·10	7·40	5·40	(3·23)
XVIId	$C_{13}H_{19}NO_2S$	oil	61·63	7·55	5·53	311
	(253·4)	(65)	61·00	7·31	5·65	(3·20)

aldehyde with propanoic anhydride, esterification of the carboxyl group and bromination of methyl 2-methyl-3-(2-thienyl)propenoate (*XVI*) with N-bromosuccinimide.

All these compounds are in the sense of Cromwell's notation keto – allylic systems having a heterocyclic ring in γ-position. To verify, whether the nucleophilic displacement reaction follows the S_N2' mechanism, these compounds were reacted with amines as nucleophiles. Amines are the no charge-bearing nucleophiles and therefore, they have a greater chance for S_N2' mechanism than anions, the charge of which is centered to one point. Products of an anomalous substitution resulting from the reaction with amines is due to a primary formation of hydrogen bond between the amine hydrogen and halogen directing the attack to γ-position. The investigation of reaction of keto-allylic systems[1-6] showed that the reaction product does not depend on the basicity of the amine employed, but it depends on its steric construction. All nucleophilic substitutions were performed in a non-polar solvent (pentane) to avoid the S_N1 mechanism to proceed, which piperidine, morpholine, diethylamine, and tert-butylamine. The samples were immediately subjected to ^1H NMR measurement after the respective hydrogen bromides had been filtered off from the mixture and the solvents had been evaporated. No product could be identified as resulting from the anomalous bimolecular mechanism in reactions with these keto – allylic systems (Scheme 2).



SCHEME 2

The UV-spectral monitoring of the reaction excluded the possibility the reaction to proceed by a two-fold S_N2', and no hypsochromic shift of the λ_{max} was observed which would evidence the formation of a product of anomalous substitution.

In contrast to previous examination[1-6] we have ascertained that the respective furan and thiophene rings in γ-position influence the reaction mechanism of keto-allylic systems with amines. This fact can be rationalized as follows: the lone electron pairs of the ring heteroatom prevent the electrostatic repulsive forces from the attack of the nucleophile at γ-carbon of the allylic system; the compounds under study do not have features characteristic of keto-allylic mobile systems. To verify the first assumption, the geometry of the compounds prepared had to be determined; for this purpose ^1H NMR data were of use. Thus, *E*-configuration at the double bond and *s-cis* conformation of the double bond with furan ring[13] was ascribed to methyl 2-methyl-3-(2-furyl)propenoate (*I*) and 1-phenyl-2-methyl-3-(2-furyl) propenone as backed by the long-range coupling constants, by comparison of the experimentally determined chemical shift of the olefinic proton with the calculated one according to Pascual–Matter[12] relationship, and by NOE experiment. The same backing allowed to assign the *E*-configuration and *s-trans* conformation

TABLE II

^1H NMR data (δ. ppm) of methyl 2-X-methyl-3-(2-furyl)-1-propenoates and methyl 2-X-methyl--3-(2-thienyl)-1-propenoates

Compound	H_{01}	H_3	H_4	H_5	CH_2	OCH_3	Other
II	7·58 s	6·77 d	6·4 dd	7·54 d	3·57 s	3·76 s	7·20—7·42 m[a]
III	7·37 s	6·73 d	6·48 dd	7·54 d	3·88 s	3·76 s	1·18—1·99 m[b]
IV	7·48 s	6·74 d	6·46 dd	7·54 d	3·85 s	3·75 s	S—CH_2 = 2·61 q, CH_3 = 1·08 t
V	7·72 s	6·85 d	6·51 dd	7·60 d	4·60 s	—	OCH_3 = 3·46, OH— 11·85
VI	7·72 s	6·85 d	6·50 dd	7·57 d	4·57 d	—	CH_2 = 3·62 q, CH_3 = 1·23 t
VII	7·69 s	6·87 d	6·30 dd	7·56 d	4·58 s	—	CH 3·87 m, CH_3 = 0·61 d
VIII	7·60 s	6·75 d	6·52 dd	7·60 d	4·45 s	3·84 s	—
IX	7·60 s	6·76 d	6·52 dd	7·59 d	4·49 s	3·82 s	—
XVI[c]	7·78 d	7·16 d	6·99 dd	7·39 d	2·13 d	3·68 s	—
XVII	7·91 d	7·43 d	7·14 dd	7·6 m	4·55 s	3·83 s	—
XVIIa	7·88 d	7·35 m	7·0 dd	7·45 m	3·40 s	3·74 s	$N(CH_2)_2$ = 2·4 t, $(CH_2)_3$ = 1·3m
XVIIb	7·99 d	7·47 m	7·03 dd	7·62 m	3·45 s	3·74 s	$N(CH_2)_2$ = 2·48 t, $O(CH)_2)$ = 3·61 t
XVIIc	7·88 d	7·34 m	7·01 dd	7·44 m	3·32 s	3·75 s	CH_2 = 2·54 q, CH_3 = 0·99 t
XVIId	7·90 d	7·35 m	7·0 dd	7·46 m	3·40 s	3·74 s	CH_3 = 0·95 s

[a] Phenyl; [b] xylohexyl; [c] X = H.

TABLE III

^1H NMR data (δ, ppm) of 1-phenyl-2-X-methyl-3-(2-furyl)-1-propenones and 1-phenyl-2-X-methyl-3-(2-thienyl)-1-propenones

Compound	H_{01}	H_3	H_4	H_5	CH_2	H_{arom}	Other
X[a]	6·98 d	6·63 d	6·50 dd	7·53 d	2·32 d	7·41—7·64 m	—
XI	6·94 s	6·77 d	6·51 dd	7·61 d	4·80 s	7·44—7·65 m	—
XIa	6·88 s	6·58 d	6·46 dd	7·44 d	3·85 s	7·44—7·80 m	$N(CH_3)_2$ = 2·45, $(CH_2)_3$ = 1·46
XIb	6·87 s	6·56 d	6·45 dd	7·44 d	3·86 s	7·45—7·80 m	$O(CH_2)_2$ = 3·70 t, $N(CH_2)_2$ = 2·60 t
XIc	6·86 s	6·55 d	6·45 dd	7·44 d	3·88 s	7·47—7·80 m	CH_2 = 2·5 q, CH_3 = 0·96 t
XId	6·96 s	6·71 d	6·97 dd	7·46 d	3·96 s	7·64—7·71 m	CH_3 = 1·21 s
XII[a]	7·36 d	7·18 d	7·06 dd	7·48 m	2·32 d	7·40—7·71 m	—
XIII	7·36 d	7·34 d	7·13 dd	7·64 m	4·71 s	7·41—7·70 m	—
XIIIa	7·39 d	7·28 d	7·09 dd	7·50 m	3·60 s	7·49—7·62 m	$N(CH_2)_2$ = 2·47 t, $(CH_2)_3$ = 1·46
XIIIb	7·46 d	7·28 d	7·06 dd	7·53 m	3·67 s	7·48—7·73 m	$N(CH_2)_2$ = 2·56 t, $O(CH_2)_2$ = 3·65 t
XIIIc	7·43 d	7·28 d	7·04 dd	7·70 m	3·80 m	7·48—7·77 m	CH_2 = 2·56 q, CH_3 = 0·97 t
XIIId	7·33 d	7·17 d	7·05 dd	7·47 m	4·61 s	7·45—7·68 m	CH_3 = 2·90

[a] X = H.

to methyl 2-methyl-3-(2-thienyl)propenoate, 1-phenyl-2-methyl-3-(2-thienyl)propenone, and 1,3-bis(2-thienyl)-2-methylpropenone. Further reactions (bromination of the methyl group and nucleophilic displacement) do not alter the geometry. Inspection of Dreiding models showed that distances between the ring heteroatom and the potential centres of nucleophilic attack (bromomethyl group, γ-carbon of the allylic system) are virtually equal for thiophene derivatives, but different for furan derivatives. Since the reactions with amines gave the same results, the distance factor is not decisive. We presume, therefore, that the substantial factor, causing the keto-allylic systems with furan or thiophene ring in γ-position to react with amines giving products of attack of the bromomethyl group (α-carbon), is the greater mobility of the heterocyclic ring electrons[14,15] in contrast to analogues with a benzene ring in γ-position of the keto-allylic system; these afforded substitution products with amines at the γ-allylic carbon. Nucleophilic displacements at keto-allylic systems with furan, or thiophene ring in γ-position are considered substitution reactions at an *sp*^{3} hybridized carbon atom.

EXPERIMENTAL

The UV spectra were measured with a UV-VIS (Zeiss, Jena) spectrophotometer in 10 mm-cells in ethanol at a $5 \cdot 10^{-5}$ mol l^{-1} concentration (the ε value is given in m^2 mol^{-1}). The ^{1}H NMR spectra of deuteriochloroform solutions (internal reference tetramethylsilane) were recorded with a Tesla BS 487 C spectrometer operating at 80 MHz.

Methyl 2-X-Methyl-3-(2-furyl)propenoates *II*—*IV*

Compound *I* (2·45 g, 10 mmol), sodium phenylmethanethiolate (1·46 g, 10 mmol) and sodium cyclohexanethiolate (1·38 g, 10 mmol), or sodium ethanethiolate (0·84 g, 10 mmol) were refluxed in acetone for 3 h. Sodium bromide was filtered off after cooling, the filtrate was evaporated and the residue was purified on an alumina-packed column (eluent chloroform).

TABLE IV

^{1}H NMR data (δ, ppm) of 1,3-bis(2-thienyl)-2-X-methyl-1-propenones

Compound	H_{01}	H_3	H_4	H_5	H_3	H_4	H_5	CH_2
XIV[a]	7·60 dd	7·24 d	7·08 dd	7·59 d	7·59 d	7·08 dd	7·59 d	2·29 d
XV	7·70 d	7·28 d	7·05 dd	7·62 d	7·60 d	7·09 dd	7·60 d	4·81 s
XVa	7·58 d	7·33 d	7·04 dd	7·49 d	7·63 d	7·11 dd	7·64 d	3·57 s
XVb	7·56 d	7·29 d	7·05 dd	7·48 d	7·61 d	7·07 dd	7·59 d	3·65 s
XVc	7·54 d	7·26 d	7·07 dd	7·42 d	7·61 d	7·07 dd	7·56 d	3·80 s
XVd	7·56 d	7·33 d	7·07 dd	7·46 d	7·65 d	7·04 dd	7·59 d	3·87 s

[a] X = H.

2-Alkoxymethyl-3-(2-furyl)propenoic Acids *V*—*VII*

Potassium methoxide, ethoxide, or 2-propoxide in the respective alcohol was added to compound *I* (1 g, 4·1 mmol) in the respective alcohol (5 ml) and the mixture was heated on a steam bath for 5 h. Potassium bromide was filtered off after cooling and the filtrate was evaporated. The residue was dissolved in a little amount of water, acidified with hydrochloric acid and the precipitate was crystallized from ethanol.

Methyl 2-Thiocyanatomethyl-3-(2-furyl)propenoate (*VIII*) and Methyl 2-Azidomethyl-3-(2-furyl)propenoate (*IX*)

Potassium thiocyanate (30% aqueous solution, 50 ml), or sodium azide (30% aqueous solution, 50 ml) and tetra-n-butylammonium hydroxide (10% aqueous solution, 2 ml) were added to *I* (10 mmol) dissolved in benzene (50 ml). The mixture was stirred at room temperature for 3 h, the organic layer was separated and the aqueous one was extracted with benzene. Benzene solutions were combined, evaporated and purified by chromatography on silica gel (eluent chloroform).

1-Phenyl-2-bromomethyl-3-(2-furyl)-1-propenone (*XI*)

A) *Condensation*: sodium ethoxide (0·1 mol) in ethanol (50 ml) was added to a mixture of propiophenone (0·1 mol) and 2-furaldehyde in ethanol (50 ml) at 0°C. The mixture was left to stand overnight and poured onto crushed ice (400 g). The organic layer was separated and the aqueous one was extracted with benzene. The combined benzene solutions were dried, evaporated and 1-phenyl-2-methyl-3-(2-furyl)-1-propenone (*X*) was distilled under reduced pressure.

B) *Bromination*: A mixture of *X* (50 mmol), N-bromosuccinimide (50 mmol) and α,α'-azobis-(isobutyronitrile) (0·2 g) in tetrachloromethane (200 ml) was refluxed, the excessing succinimide was filtered off after the reaction was through and the solvent was removed *in vacuo*. The product was crystallized from n-heptane.

1-Phenyl-2-methyl-3-(2-thienyl)-1-propenone (*XII*) and 1,3-bis(2-thienyl)-2-methylpropenone (*XIV*) and their bromo analogues *XIII* and *XV* were prepared under the same conditions.

Methyl 2-Bromomethyl-3-(2-thienyl)propenoate (*XVII*)

A mixture consisting of 2-thienylaldehyde (195 g, 1 mol), propionic anhydride (195 g, 1·5 mol) and potassium propionate (120 g, 1·25 mol) was heated at 160°C for 7 h, poured onto crushed ice (2 l), the crude product was filtered off, dried and esterified with methanol in the presence of sulfuric acid. Methyl 2-methyl-3-(2-thienyl)propenoate (*XVI*) was distilled under diminished pressure and brominated with N-bromosuccinimide analogously as with *XI*.

Nucleophilic Displacements with Amines

The respective compound *XI*, *XIII*, *XV*, *XVII* (10 mmol) in pentane (100 ml) was treated with piperidine, morpholine, diethylamine, or tert-butylamine and the mixture was allowed to stand at an ambient temperature for 10 h. The precipitated aminohydrogen bromide was filtered off and the filtrate was evaporated *in vacuo*. The crude reaction product was first subjected to ^{1}H NMR analysis and then purified by column chromatography on a silica gel column (compounds *XIa*—*XId*, *XIIIa*—*XIIId*, *XVa*—*XVd*, and *XVIIa*—*XVIId*).

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