SYNTHESIS OF ETHYL *ortho*-SUBSTITUTED BENZOYLACETATES AND INVESTIGATION OF THE INFLUENCE OF *ortho*-SUBSTITUENTS ON KETO–ENOL TAUTOMERISM AND MS FRAGMENTATION BEHAVIOUR

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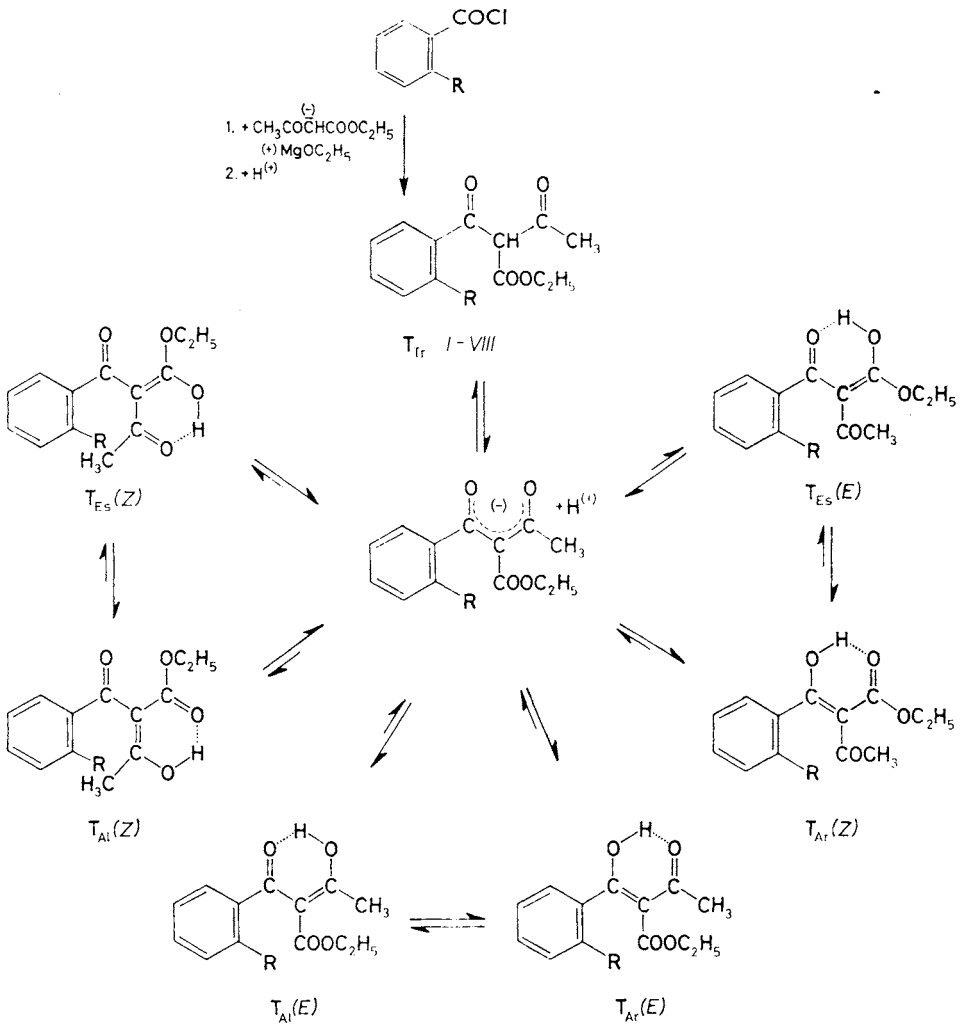
A series of seven ethyl 2-acetyl-(2-substituted benzoyl)acetates *II*— *VIII* was synthesized, together with their parent compound *I*, from the corresponding acid chlorides. The tautomerism of these β-tricarbonyl compounds in tetrachloromethane was studied by ^{1}H NMR spectroscopy and former results concerning this problem were critically evaluated. A further series of seven *ortho*-substituted ethyl benzoylacetates *X*—*XV* and *XVII* was obtained from the corresponding precursors *II*— *VIII*. The keto–enol tautomerism of these β-keto esters was studied by ^{1}H NMR in different solvents and compared with ethyl benzoylacetate *IX* as standard. Differences caused by the *ortho*-substituents are discussed. Investigation of the mass spectrometric fragmentation of the β-keto esters *IX*—*XV* and *XVII* showed both common fragmentation pathways due to the same substance class and typical differences in relative intensities according to the nature of the *ortho*-substituent.

The chemistry of β-ketocarboxylic acids and their derivatives like esters and amides belongs to the areas of organic chemistry which seemed to be well investigated already in the last century. However, the recent literature shows a persisting interest in the β-keto ester chemistry. This concerns new syntheses of β-keto esters[1–7] as well as their further reactions accompanied by loss of the β-keto ester structure like e.g. dealkoxycarbonylations[8–11] or formation of heterocycles[12–15]. The phenomenon of keto–enol tautomerism has been always of special interest. Recently its light-induced variant was reviewed[16] but also the classical physical organic aspects of the problem[17,18] have been under detailed investigation[19–21], leading to successful isolation of the first stable *E*-enols of β-ketocarboxylic acid derivatives[22,23]. Furthermore, the keto and enol tautomers could be separated by low-temperature HPLC[24,25].

In this context, this paper deals with the behaviour of ortho-substituted ethyl benzoylacetates. Ethyl 2-acetyl-(2-substituted benzoyl)acetates *I*—*VIII* were synthesized from the corresponding acid chlorides[26] (Scheme 1). The keto–enol tautomerism of acyclic β-diketoesters was first investigated by Böhme et al.[27] who made use of Meyer's bromine titration method[28] for enol content determination. Further investigations of Forsen and Nilsson[29] confirmed that acyclic β-diketo esters are highly enolized both in the liquid state and in nonpolar solutions. As the β-tri-

carbonyl compounds *I* – *VIII* contain both a β-keto ester and a β-diketone structure, seven tautomers are theoretically possible: one triketo form and six enol forms (Scheme 1).

The tautomers T are denoted using the indices Ar, Al or Es which mean that the enol hydroxyl belongs to the aryl, alkyl or ester part of the molecule, respectively;



I, R = H *II*, R = CH_3 *III*, R = Cl *IV*, R = Br *V*, R = I *VI*, R = OCH_3 *VII*, R = OC_6H_5 *VIII*, R = NO_2

SCHEME 1

the letter in parentheses indicates the configuration at the enolic C—C double bond; T_{Tr} describes the triketo form. The six enol tautomers can be divided into three pairs: $T_{Es}(Z)$ and $T_{Al}(Z)$, $T_{Al}(E)$ and $T_{Ar}(E)$, $T_{Ar}(Z)$ and $T_{Es}(E)$. In each pair an intramolecular very rapid exchange of the enolic proton accompanied by double bond migration should be possible because no rotation of functional groups is required for transition into the other form. This proton exchange will be very fast on the NMR time scale. All other isomerizations leading to members of another pair must include rotation of the functional groups in the anionic state and are therefore slow enough to be observable by the NMR spectroscopy. Therefore, NMR measurements should at most be able to detect three enol forms.

Courtot et al.[30] studied the tautomerism of ethyl 2-acetylbenzoylacetate by means of ^{1}H NMR spectrometry and got evidence of two enol forms. Recently, Romas et al.[31] once again studied tautomerism and stereodynamic behaviour of acyclic β-diketoesters. The ^{1}H NMR spectra of ethyl 2-acetylbenzoylacetates *II*–*VIII* and the parent compound *I* are shown in Table I. All the compounds show an analogous tautomerism. Equilibration of the compounds in tetrachloromethane resulted in a very high degree of enolization. The major part may be ascribed to the enolized β-diketone structural unit, i.e. to the rapidly equilibrating mixture of the tautomers $T_{Ar}(E)$ and $T_{Al}(E)$. The minor part of the enol portion is the enolized β-keto ester unit, indicated by the signal at 13·21 ppm for *I*. This signal suggests an equilibrium between $T_{Ar}(Z)$ and $T_{Es}(E)$ and not $T_{Al}(Z)$ as given by Romas et al.[31], because even using a high field spectrometer no splitting of the methyl signals was observed as would have been expected in the case of $T_{Al}(Z)$ as the result of a long range spin–spin coupling. For the sake of simplicity, we assigned the signal only to the $T_{Ar}(Z)$ form because of low enolization ability of the ester carbonyl group. As seen from Table I, introduction of a bulky *ortho*-substituent leads to an increase of the β-diketone enolization relative to compound *I* and the triketo form completely disappears (Table I).

Conversion of compound *I*–*VII* with ammonium chloride in aqueous ammonia according to Thorp[32] gave the corresponding β-keto esters *IX*–*XV* by splitting off the acetyl group. Because no ethyl acetoacetate appeared in the reaction products it can be concluded that during the cleavage reaction the hydroxide ions selectively attack only the nonenolized carbonyl group of the acetyl substituent (shown for $T_{Ar}(Z)$ in Scheme 2).

However, in nitro compound *VIII* obviously both the carbonyl of the benzoyl and the acetyl groups is attacked in the splitting reaction. The very complex mixture contained e.g. 2-nitrobenzoic acid, ethyl acetoacetate, acetic acid and only traces of ethyl (2-nitrobenzoyl)acetate *XVII* whose separation on a preparative scale would be ineffective. The compound *XVII* was synthesized preferably by conversion of *VIII* (ref.[33]) to 2-nitrobenzoylacetic acid *XVI* according to Needham et al.[34] and subsequent mild esterification of *XVI* to *XVII* (ref.[35]).

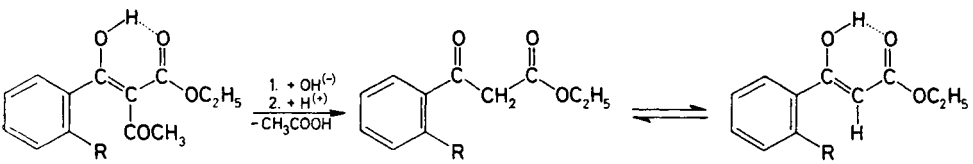
TABLE I

^{1}H NMR spectra of ethyl 2-acetyl-(2-substituted)benzoylacetates *I*–*VIII* and population of tau-

Comp.	2-Substituent	t, 3 H[a] —CH_2CH_3	s, 3 H —$COCH_3$ T_{Tr}	s, 3 H —$COCH_3$ $T_{Ar}(Z)$	s, 3 H —$COCH_3$ $T_{Ar}(E) \rightleftharpoons T_{Ar}(E)$	q, 2 H[a] —CH_2CH_3
I	H	0·79	2·24	2·00	2·33	3·85
II	CH_3[c]	0·60	2·10	2·01	2·33	3·65
III	Cl	0·69	1·90	2·27	2·41	3·76
IV	Br	0·66	2·05	2·25	2·40	3·72
V	I	0·64	2·04	2·28	2·41	3·71
VI	OCH_3[d]	0·70		2·12	2·30	3·70
VII	OC_6H_5	0·75	—	1·60	2·29	3·85
VIII	NO_2	0·69	—	2·38	2·40	3·71

Value for the main tautomer; [b] value for all tautomers; [c] ring—CH_3: 2·26 (s, 3 H) for $T_{Ar}(E) \rightleftharpoons$

The ^{1}H NMR spectra of *IX*–*XV* and *XVII* were recorded in carbon disulfide, carbon tetrachloride, hexadeuteroacetone and tetradeuteromethanol to investigate the keto–enol tautomerism (Scheme 2). Henecka[17] and Mills et al.[21] showed that



$T_{Ar}(Z)$ *IX*, R = H; *X*, R = CH_3; *XI*, R = Cl; *XII*, R = Br; *XIII*, R = I; *XIV*, R = OCH_3; *XV*, R = OC_6H_5; $T_{Ar}(Z)$

SCHEME 2

β-keto esters equilibrate completely only some hours or even weeks (depending on the temperature) after dissolution. We observed that after 24 h at ambient temperature compound *XVII* showed no more variation of the keto–enol ratio in the ^{1}H NMR spectrum.

TABLE I
tomers

s, 1 H —CH T_{Tr}	m[b] arom. H	s, 1 H —C=C—OH $T_{Ar}(Z)$	s, 1 H —C=C—OH $T_{Ar}(E)$ ⇵ $T_{Al}(E)$	Content, % T_{Ar}	 $T_{Ar}(Z)$	 $T_{Ar}(E)$ ⇵ $T_{Al}(E)$
5·32	7·29—7·84	13·21	17·20	2	32	66
5·58	6·75—7·62	13·35	17·39	5	35	60
5·95	6·75—7·62	14·01	17·61	2	24	74
5·85	7·00—7·75	14·11	17·62	2	13	85
5·73	6·75—7·93	14·12	17·62	2	13	85
—	6·62—7·50	13·36	17·69	0	13	87
—	6·50—8·00	13·42	17·50	0	23	77
—	7·00—8·12	14·62	17·52	0	20	80

⇌ $T_{Al}(E)$; [d] ring—OCH_3: 3·60 (s, 3 H) for $T_{Ar}(E)$ ⇌ $T_{Al}(E)$.

The enol content given in Table II decreases significantly on going from a nonpolar solvent to a polar one, as expected if the keto form is the more polar of the two tautomers.

A comparison of the behaviour of the *ortho*-substituted β-keto ester with compound *IX* as standard shows a similar trend in each of the solvents. Halogen substituents cause an increase of the enol content, particularly in polar solvents whereas all other substituents lead to a smaller enolization of the β-keto ester or behave like the standard. Interestingly and unexpectedly, both a strong donor (OCH_3) and a strong acceptor (NO_2) have the same effect. Thus, the tendency to enolize does not seem to be influenced very much by the mesomeric effect of the substituent. However, a comparison of the van der Waals radii of e.g. CH_3 ($2{\cdot}00 \cdot 10^{-10}$ m) with that of Cl, Br or I ($1{\cdot}80$, $1{\cdot}95$ and $2{\cdot}15 \cdot 10^{-10}$ m, respectively) shows that the size of the substituents alone also cannot be responsible for the differences between the methyl- and the halogen-substituted β-keto esters. The matter becomes further complicated because Cl, Br, and I differ from the other substituents by possessing higher than *p*-orbitals which could result in further interactions with the rest of the molecule and finally may lead to a stabilization of the enol form. Thus, our results demonstrate again the complex nature of the *ortho*-effect[36-40].

A comparison of the mass spectrometric behaviour of the β-keto esters (Table III) shows many common features like the same main fragment ions, the fact that the

base peak is formed by benzoyl cations $R—C_6H_4—CO^+$ in all cases and that, due to their acyclic structure, the molecular peaks M^+ always are very weak (or are absent, like in the case of *XVII* where elimination of the NO_2—radical is highly favoured).

However, a change in the nature of the *ortho*-substituent has some typical consequences in the mass spectrum. Thus, in the case of halogen-substituted β-keto esters the intensity of molecular ions is especially low and that of the ion $(M - R)^+$ is significantly higher than all others, the reason in both cases being the enhanced ability of halogens to form a relatively stable radical. Also in the case of the substituted aryl cation $R—C_6H_4^+$, the electronegativity and polarizability of the halogen substituent act in the same direction causing a high relative intensity of this ion in comparison with the methoxy-, phenoxy- or nitro-substituted compound. The very high intensity of ion $m/z = 91$ in the case of *X* is caused by the formation of tropylium ions.

EXPERIMENTAL

The melting points were determined on a Boetius micro hot-stage apparatus and are uncorrected. The ^1H NMR spectra were measured in tetrachloromethane, carbon disulfide, hexadeuteroacetone or tetradeuteromethanol on a TESLA BS 487C spectrometer (80 MHz) at 25°C with tetramethylsilane as internal standard. Chemical shifts are given in the δ-scale. All samples for enol content determination were dissolved (concentration $5 . 10^{-3}$ mol l^{-1}) and stored for 2 weeks prior to the measurement to achieve equilibration. An additional spectrum of *I* was recorded on a Bruker MSL 300 spectrometer at 300·13 MHz in a 20% solution in tetrachloromethane which was allowed to equilibrate for one month. Both the spectra showed identical tautomer population. The mass spectra were recorded on a Varian MAT CH6 spectrometer with electron impact ionisation (70 eV) at an ion source temperature of 200°C (indirect inlet). The

TABLE II

Enol content of ethyl(2-substituted)benzoylacetates (%) in various solvents, determined by ^1H NMR after equilibration (error 5%)

Compound	R	CS_2	CCl_4	$(C^2H_3)_2CO$	$C^2H_3O^2H$
IX	H	31	39	28	21
X	CH_3	31	31	16	15
XI	Cl	57	56	35	27
XII	Br	64	57	33	40
XIII	I	57	58	29	33
XIV	OCH_3	20	17	14	12
XV	OC_6H_5	30	28	18	25
XVII	NO_2	26	33	15	16

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TABLE III

Mass spectrometric fragmentation of ethyl 2-(substituted)benzoylacetates, (% relat. intensity)

Compound	R	M^+	$[M - OEt]^+$	$[M - - EtOH]^+$	$[C_6H_4(R).COCH_3]^+$	$[C_6H_5(R)CO]^+$	$[C_6H_5R]^+$	$[M - R]^+$	$[C_6H_5—CO]^+$
IX	H	2·9	0·9	1·5	0·7	100	50·0	0·1	100
X	CH_3	5·3	5·3	4·5	4·2	100	74·8	4·2	6·2
XI	Cl	0·5	3·8	3·3	2·0	100	22·9	19·7	0·8
XII	Br	0·1	0·9	3·5	2·6	100	29·5	74·4	21·3
XIII	I	0·9	3·2	23·3	7·6	100	33·3	30·2	11·6
XIV	OCH_3	2·5	0·7	0·2	2·1	100	1·4	0·4	8·2
XV	OC_6H_5	5·5	2·5	8·6	17·3	100	4·3	5·5	6·2
XVII	NO_2	—	0·9	4·5	4·2	100	10·3	4·5	13·1

TABLE IV

Characterization and IR spectra of compounds *I*—*XV* and *XVII*

Compound	R	Formula m.w.	Calculated/found			B.p.: °C/kPa or m.p. (C°) (yield, %)	n_D^{20}	IR, cm^{-1} ν(C=O)
			% C	% H	% Het.			
I	H	$C_{13}H_{14}O_4$	66·65	6·02	—	174—176/1·6	1·5393	1 715
		234·2	66·85	6·10	—	(70)		
II	CH_3	$C_{14}H_{16}O_4$	67·73	6·50	—	140—142/0·13	1·5361	1 720
		248·3	67·90	6·75	—	(60)		
III	Cl	$C_{13}H_{13}Cl_4$	58·11	4·88	Cl 13·19	132—134/0·2	1·5490	1 718
		268·7	58·47	5·04	Cl 12·96	(65)		
IV	Br	$C_{13}H_{13}BrO_4$	49·86	4·18	Br 25·52	122—124/0·03	1·5643	1 710
		313·1	50·04	4·36	Br 25·26	(58)		
V	I	$C_{13}H_{13}IO_4$	43·35	3·64	I 35·24	144—146/0·04	1·5930	1 700
		360·1	43·25	3·84	I 35·02	(50)		
VI	OCH_3	$C_{14}H_{16}O_5$	3·63	6·10	—	128—130/0·04	1·5488	1 722
		264·3	63·60	5·89	—	(80)		

VII	OC_6H_5	$C_{19}H_{18}O_5$ 326·3	69·93 69·80	5·56 5·60	— —	57—60 (93)	—	1 670 (KBr)
VIII	NO_2	$C_{13}H_{13}NO_6$ 279·2	55·91 55·61	4·69 4·76	N 5·02 N 5·28	32—33 (63)	—	1 710 (KBr)
IX	H	$C_{11}H_{12}O_3$ 192·2	68·73 68·98	6·29 6·37	— —	136—138/0·5 (75)	1·5323	1 740
X	CH_3	$C_{12}H_{14}O_3$ 206·2	69·88 69·59	6·84 6·64	— —	143—145/1·0 (75)	1·5321	1 742
XI	Cl	$C_{11}H_{11}ClO_3$ 226·6	58·29 58·50	4·89 5·10	Cl 15·64 Cl 15·33	101—103/0·03 (53)	1·5459	1 745
XII	Br	$C_{11}H_{11}BrO_3$ 271·1	48·73 49·05	4·09 4·27	Br 29·48 Br 29·24	131—133/0·05 (72)	1·5518	1 735
XIII	I	$C_{11}H_{11}IO_3$ 318·1	41·53 41·80	3·49 3·68	I 39·89 I 39·59	142—144/0·05 (65)	1·5880	1 735
XIV	OCH_3	$C_{12}H_{14}O_4$ 222·2	64·85 64·80	6·35 6·30	— —	122—124/0·04 (67)	1·5439	1 740
XV	OC_6H_5	$C_{17}H_{16}O_4$ 284·3	71·82 71·99	5·67 5·78	— —	152—154/0·03 (70)	1·5705	1 735
XVII	NO_2	$C_{11}H_{11}NO_5$ 237·2	55·70 55·75	4·67 4·85	N 5·91 N 5·49	28—29 (87 from XVI)	—	1 725 (KBr)

TABLE V

^{1}H NMR spectra of (2-substituted)benzoylacetates *IX*—*XV* and *XVII*

Compound	R	t, 3 H $-CH_2CH_3$	s, 2 H $-COCH_2-$	q, 2 H $-CH_2CH_3$	s, 1 H $-CH=$	m, arom H[a]	s, 1 H $-C(OH)=CH-$	Isomer
IX	H	1·08	3·75	4·00	—	6·88—7·87	—	keto
		1·18	—	4·09	5·50		12·61	enol
X	CH_3[b]	1·08	3·73	4·00	—	6·70—7·62	—	keto
		1·20	—	4·12	5·14		12·44	enol
XI	Cl	1·11	3·85	4·03	—	6·82—7·58	—	keto
		1·22	—	4·14	5·44		12·43	enol
XII	Br	1·12	3·83	4·03	—	6·88—7·58	—	keto
		1·23	—	4·15	5·34		12·28	enol
XIII	I	1·12	3·79	4·03	—	6·63—7·88	—	keto
		1·23	—	4·15	5·20		12·29	enol
XIV	OCH_3[c]	1·08	3·72	3·99	—	6·67—7·80	—	keto
		1·19	—	4·10	5·91		12·66	enol
XV	OC_6H_5	0·95	3·79	3·84	—	6·56—7·91	—	keto
		1·05	—	4·04	5·90		12·65	enol
XVII	NO_2	1·11	3·69	3·99	—	7·25—7·80	—	keto
		1·24	—	4·15	5·27		12·24	enol

[a] Value for both tautomers; [b] ring—CH_3: 2·35 (s, 3 H) for enol form and 2·40 (s, 3 H) for keto form; [c] ring—OCH_3: 3·69 (s 3 H) for both tautomers.

infrared spectra were measured on a UR 20 (Carl Zeiss, Jena) instrument on sample films, unless stated otherwise.

Ethyl 2-Acetyl-(2-substituted) Benzoylacetates *I— VIII*

Magnesium chips (2·4 g, 0·10 mol) were added to dry ethanol (5 ml) and tetrachloromethane (0·5 ml). After the reaction had started a mixture of ethyl acetoacetate (13·0 g, 0·10 mol), dry ethanol (10 ml) and dry toluene (40 ml) was added dropwise at a rate allowing gentle reflux. After all the metal had dissolved a solution of the corresponding acid chloride (0·10 mol) in toluene (10 ml) was slowly added with stirring at −5°C to 0°C, and the stirring was continued for 1 h. After standing overnight the mixture was poured into ice (100 g) and concentrated sulphuric acid (3 ml), the organic phase separated and the aqueous layer extracted twice with 50 ml toluene. The combined organic extracts were washed to neutrality with water and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue fractionated in vacuo or crystallized. For experimental data see Tables I and IV.

Ethyl (2-Substituted) Benzoylacetates *IX—XV*

The corresponding ethyl 2-acetyl-(2-substituted)benzoylacetate (0·10 mol) was added to a solution of sodium hydroxide (4·0 g, 0·10 mol) in water (125 ml) and dissolved under stirring. After addition of ammonium chloride (10·6 g, 0·20 mol) and concentrated ammonia (14 ml) the mixture was stirred for 3 h at 50°C. The crude β-keto ester separated as an oil which was extracted with dichloromethane (3 × 60 ml). The combined extracts were washed to neutrality with water and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue distilled in vacuo. For experimental data see Tables IV and V.

2-Nitrobenzoylacetic Acid (*XVI*)

Cleavage of *VIII* with concentrated sulphuric acid[34] gave *XVI* as colorless needles m.p. 116 to 117°C (benzene) in 57% yield (see also ref.[35]). For $C_9H_7NO_5$ (209·1) calculated: 51·68% C, 3·37% H, 6·70% N; found: 52·01% C, 3·49% H, 6·48% N.

Ethyl 2-Nitrobenzoylacetate (*XVII*)

β-Keto ester *XVII* was synthesized by esterification of the acid *XVI* according to our own procedure[35]. For data see also Tables IV and V.

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