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NEW COMPOUND SECTION

Synthesis and Spectral Data of Substituted Acetylenic β -Keto-cyanides

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Different substituted ethyl phenylpropiolates reacted with substituted benzyl cyanides in the presence of sodium ethoxide to give substituted acetylenic β -keto-cyanides. The *o*-methyl and *o*-benzoyl derivatives of the latter were prepared. IR, NMR, and UV spectral data of the above compounds were tabulated and discussed.

In the course of our study on the reactivity of acetylenic esters toward compounds having active methylene groups, we have reported that α -(phenylpropiolyl)benzyl cyanide and 4-methoxy- α -(phenylpropiolyl)benzyl cyanide are the main products obtained from the condensation of ethyl phenylpropiolate with benzyl cyanide and *p*-methoxybenzyl cyanide, respectively (1). We now report similar condensation reactions by use of various substitutions in both reactants. These reactions seem to be of general application since various substituted acetylenic β -keto-cyanides (IIa-k) were obtained following a general modified procedure.

The reaction products were identified and were present in their enol forms (IIla-k) on the basis of spectroscopic evidence (IR, NMR, and UV spectra) (Tables I and II). The NMR values for compounds IIa-k showed complex spin-spin splitting near 2.33–2.82 τ . No signals were observed at lower field which indicated that resonances due to enolic hydrogen overlapped with those due to the aromatic protons. This was concluded from the exchange of one of the protons in this region (as indicated from integration) after shaking the sample with D₂O and the appearance of the HOD signal near 5.3 τ . The presence of the enolic form in the above compounds (IIa-k) was further supported by conversion to their *o*-methyl and *o*-benzoyl derivatives. Methylation of compounds IIa-d with diazomethane gave enol ethers (IVa-d) (Table III); singlets at 5.90–5.92 τ were assigned to the methyl protons of the

ether. In the same manner, compounds were benzoylated with benzoyl chloride to give the derivatives Va-k; these showed absorption in their IR spectra at 1740–1752 cm⁻¹ (C=O stretching of the vinyl aromatic ester) (2) (Table IV).

Generally, the UV spectra of substituted acetylenic β -keto-cyanides and their *o*-methyl and *o*-benzoyl derivatives (Tables II–IV) showed three absorption bands in the range: I, 210–220; II, 230–260 (accompanied by shoulders); and III, 342–354 nm. The relative intensities of bands I and II (which are not well separated in certain cases) depend to a certain extent on the type and position of the aromatic substitution. As

Table I. IR and NMR Spectral Data of Substituted Acetylenic β -Keto-cyanides

Com- pound	IR stretching bands in CHCl ₃			NMR values (τ) in CDCl ₃	
	OH	C \equiv C	C=C		
IIa	2400–3200	2220	1608 ^a	2.67 (m) ^b	All protons
IIb	2400–3400	2215	1608	2.5 (m)	All protons
IIc	2400–3600	2200	1612	2.59 (m)	ArH
				7.62 (s)	ArMe
II d	2400–3570	2200	1613	2.57 (m)	ArH
				7.31 (q)	ArCH ₂
				8.75 (t)	CH ₂ -Me
IIe	2450–3500	2260 (sh)	1600	2.33–2.78	ArH
				7.72 (s)	Ar(CH ₃) ₂
II f	2400–3400	2265	1595	2.5 (m)	All protons
II g	2400–3500	2250	1600	2.43 (m)	All protons
II h	2300–3400	2240	1608	2.37 (m)	All protons
II i	2400–3300	2235	1605	2.82 (m)	All protons
II j	2400–3600	2220	1612	2.33 (m)	All protons
II k	2500–3600	2200	1610	2.51 (m)	ArH
				6.21 (s)	ArOMe

^a IR in nujol. ^b s = singlet; m = multiplet; q = quartet; t = triplet.

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Table II. UV Absorption Bands of Substituted Acetylenic β -Keto-cyanides

Com- pound	EtOH		0.1N NaOH	
	λ_{\max} , nm	log ϵ_{\max}	λ_{\max} , nm	log ϵ_{\max}
IIa	213	4.14	235	4.35
	236	4.18	265 (sh)	4.2
	266 (sh)	4.04	353	4.51
IIb	354	4.32		
	214	4.09	229	4.14
	230	4.09	250	4.08
	250	4.08	347	4.23
	347	4.26		
IIc	211	4.25	220	4.10
	232	4.22	234	4.24
	346	4.41	264 (sh)	4.08
IId			352	4.32
	211	4.02	235	4.27
	234	4.01	265 (sh)	4.11
IIe	348	4.18	353	4.34
	216	4.16	235	4.16
IIf	250	4.07	350	4.12
	344	4.29		
	215	4.4	230	4.14
IIg	260	4.02	262	4.13
	340	4.29	348	4.21
	226	4.04	230	4.21
IIh	248 (sh)	3.97	250	4.16
	263	3.88	260 (sh)	4.13
	342	4.19	348	4.28
	218 (sh)			
IIi	227	4.12	230	4.23
	245	4.1	251 (sh)	4.19
	265 (sh)	3.97	349	4.16
	342	4.3		
IIj	217 (sh)			
	247	4.06	234	4.14
	265	3.96	256	4.19
IIk	344	4.23	349	4.21
	218 (sh)			
	225	3.98	222	4.16
	260	3.88	252	4.05
	342	4.08	356	4.12
IIl	217	4.06	224	4.07
	236	4.11	263	4.02
	255	4.04	348	4.18
	344	4.37		

the addition of sodium hydroxide enhances the intensity of band II, band I absorbs as inflection. In the latter case, the resulting absorption spectra resemble those of the corresponding *o*-methyl derivatives. Moreover, the *o*-benzoyl derivatives showed a similar UV absorption pattern to compound II but with enhancement of the intensity of band III.

Experimental

Infrared spectra were obtained with a Unicam SP 200 spectrophotometer, ^1H NMR spectra with a Varian A-60 D instrument with TMS as internal standard, and UV spectra with a Unicam SP 800 instrument. Compounds were analyzed at the Max Planck Institute, Ruhr, West Germany. Melting points were determined with a Kofler hot-stage apparatus.

Condensation of ethyl arypropionate with arylacetone-triles. General procedure. The reported procedure (1) for the reaction of ethyl phenylpropionate with benzyl cyanide and *p*-methoxybenzyl cyanide was modified and used in this work (Figure 1). Equimolar amounts of ethyl arypropionate (1 mole

Table III. IR, NMR, and UV Spectral Data of *o*-Methylated Acetylenic β -Keto-cyanides

Com- pound	IR bands in CHCl_3 , cm^{-1}		NMR values (τ) in CDCl_3		UV bands, (nm) in EtOH	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
VIa	2200	$\text{C}\equiv\text{C}$	2.41 (m)	ArH	210	4.02
	1600	$\text{C}=\text{C}$	5.9 (s)	C:COMe	228	4.27
VIb	2230	$\text{C}\equiv\text{C}$	2.6 (m)	ArH	343	4.48
	1608	$\text{C}=\text{C}$	5.92 (s)	C:COMe	208	3.86
VIc	2190	$\text{C}\equiv\text{C}$	2.71 (m)	ArH	224	4.14
	1600	$\text{C}=\text{C}$	5.95 (s)	C:COMe	336	4.45
VId	2200	$\text{C}\equiv\text{C}$	7.65 (s)	ArMe	210	4.14
	1600	$\text{C}=\text{C}$	2.6 (m)	ArH	228	4.32
			7.33 (q)	ArCH ₂	242	4.53
			8.75 (t)	CH ₂ Me	210	4.08
					228	4.21
				344	4.49	

Table IV. IR, NMR, and UV Spectral Data of Benzoylated Acetylenic β -Keto-cyanides

Com- pound	IR bands in CHCl_3 , cm^{-1}		NMR values (τ) ^a in CDCl_3		UV bands (nm) in EtOH	
	λ_{\max} , nm	ϵ_{\max}	λ_{\max} , nm	ϵ_{\max}	λ_{\max} , nm	ϵ_{\max}
VIIa	2190	$\text{C}\equiv\text{C}$	2.23	ArH	213	4.23
	1603	$\text{C}=\text{C}$			237	4.40
	1750	$\text{C}=\text{O}$			340	4.48
VIIb	2230	$\text{C}\equiv\text{C}$	2.4	ArH	210	4.02
	1607	$\text{C}=\text{C}$			236	4.31
	1752	$\text{C}=\text{O}$			329	4.37
VIIc	2195	$\text{C}\equiv\text{C}$	2.2	ArH	215	4.39
	1605	$\text{C}=\text{C}$	7.58 (s)	ArMe	239	4.64
	1745	$\text{C}=\text{O}$			335	4.52
VIId	2190	$\text{C}\equiv\text{C}$	2.6 (m)	ArH	209	4.22
	1606	$\text{C}=\text{C}$	7.59 (q)	ArCH ₂	237	4.43
	1748	$\text{C}=\text{O}$	9.02 (t)	CH ₂ Me	337	4.59
VIIe	2200	$\text{C}\equiv\text{C}$	2.22–2.78	ArH		
	1600	$\text{C}=\text{C}$	7.75 (d)	Ar(Me) ₂		
	1750	$\text{C}=\text{O}$				
VIIf	2195	$\text{C}\equiv\text{C}$	2.2–2.66	ArH		
	1595	$\text{C}=\text{C}$				
	1745	$\text{C}=\text{O}$				
VIIg	2200	$\text{C}\equiv\text{C}$	2.23–2.72	ArH		
	1605	$\text{C}=\text{C}$				
	1748	$\text{C}=\text{O}$				
VIIh	2200	$\text{C}\equiv\text{C}$	2.16–2.7	ArH		
	1600	$\text{C}=\text{C}$				
	1745	$\text{C}=\text{O}$				
VIIi	2190	$\text{C}\equiv\text{C}$	2.23–2.76	ArH		
	1605	$\text{C}=\text{C}$				
	1740	$\text{C}=\text{O}$				
VIIj	2195	$\text{C}\equiv\text{C}$	2.18–2.66	ArH		
	1600	$\text{C}=\text{C}$				
	1740	$\text{C}=\text{O}$				
VIIk	2185	$\text{C}\equiv\text{C}$	2.3–2.77	ArH		
	1590	$\text{C}=\text{C}$	6.25 (s)	ArOMe		
	1740	$\text{C}=\text{O}$				

^a ArH, protons appeared as multiplet.

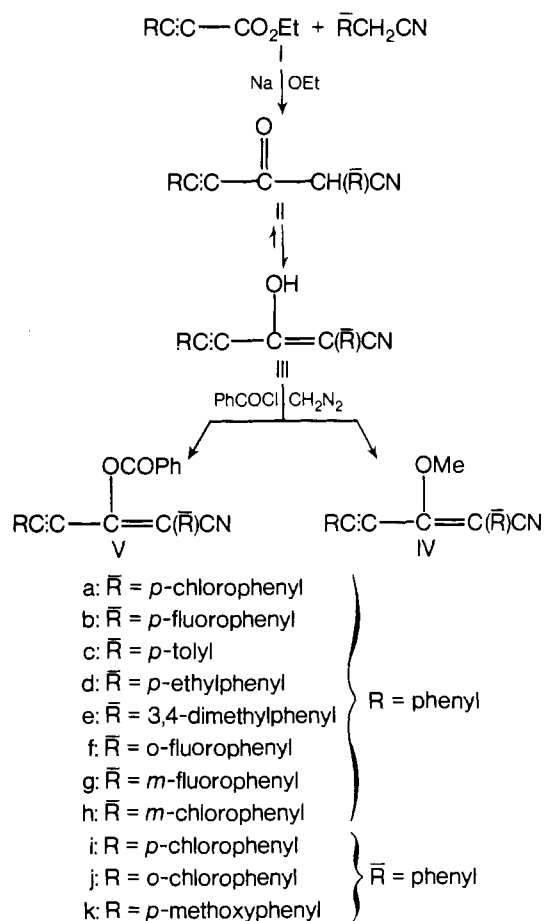


Figure 1. Reactions of ethyl arylpropiolate with different benzyl cyanides

Table V. Results for Acetylenic β -Keto-cyanides^a

Compound ^b	Mp, °C	Yield, %	Formula
IIa	216–217	33.1	C ₁₇ H ₁₀ NOCl
IIb	212–213	15.5	C ₁₇ H ₁₀ NOF
IIc	174–175	44.6	C ₁₈ H ₁₃ NO
IId	144–145	42.7	C ₁₉ H ₁₄ NO
IIe	142	20	C ₁₉ H ₁₅ NO
IIf	188	15.9	C ₁₇ H ₁₀ NOF
IIg	192	13.6	C ₁₇ H ₁₀ NOF
IIh	182	31.8	C ₁₇ H ₁₀ NOCl
IIi	218	21.3	C ₁₇ H ₁₀ NOCl
IIj	170	32	C ₁₇ H ₁₀ NOCl
IIk	120	17.1	C ₁₈ H ₁₃ NO ₂

^a Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. ^b Compounds IIa, b, f, h–k were recrystallized from methanol, and IIc–e, g from benzene.

Table VI. Results for *o*-Methylated β -Keto-cyanides^a

Compound	Mp, °C	Yield, %	Formula
VIa	112	83.3	C ₁₈ H ₁₂ NOCl ^b
VIb	125	95.2	C ₁₈ H ₁₂ NOF ^b
VIc	112	83.2	C ₁₉ H ₁₅ NO ^b
VId	70	95.2	C ₂₀ H ₁₇ NO ^c

^a Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. ^b Compounds recrystallized from methanol. ^c Compound recrystallized from pet-ether (30–40°).

Table VII. Results for *o*-Benzoylated Acetylenic β -Keto-cyanides^a

Compound ^b	Mp, °C	Yield, %	Formula
VIIa	104	65.6	C ₂₄ H ₁₄ NO ₂ Cl
VIIb	78–80	43.5	C ₂₄ H ₁₄ NO ₂ F
VIIc	136	57.1	C ₂₅ H ₁₇ NO ₂
VII d	82	50.7	C ₂₆ H ₁₉ NO ₂
VIIe	92	35	
VII f	85	41	
VII g	94	38	
VII h	101	48	
VII i	67	52	
VII j	78	46	
VII k	108	39	

^a Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. ^b Compounds recrystallized from methanol, except VIIb from pet-ether (30–40°).

equiv.), arylacetonitrile (1 mole equiv.), and sodium ethoxide (1 g-atom equiv.) in dry ether were allowed to stand at room temperature for three days. The reaction mixture, which gradually became deep red, was poured into water and stirred well. Acidification with dilute sulfuric acid and extraction with ether, drying (MgSO₄), and evaporation gave the appropriate acetylenic β -keto-cyanides (Table V) which were present in their enol forms as 3-hydroxy-2,5-diarylpent-2-en-ynenitriles (IIIa–k). In certain cases, an unidentified crude solid compound was obtained as a by-product.

***o*-Methyl and *o*-benzoyl derivatives of compound II.** Compounds IIa–d were methylated by use of diazomethane in ether, and compounds IIa–k were benzoylated by use of benzoyl chloride, following the reported procedures (1) to give 3-methoxy and 3-benzoyloxy-2,5-diarylpent-2-en-ynenitrile (IVa–d and Va–k), respectively (Tables VI and VII).

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