Picryl and 4-Cyano-2,6-dinitrophenyl Derivatives of Acetoacetate Esters

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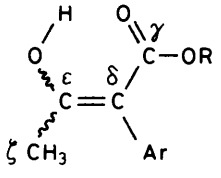
The compounds described in the literature as ethyl 2-picryl-3-oxobutanoate (1) and ethyl 2,2-dipicryl-3-oxobutanoate (2) formed by the action of picryl chloride on ethyl acetoacetate in the presence of base are in fact ethyl 3-hydroxy-2-picrylbut-2-enoate (3a) and ethyl 2-picryl-3-picryloxybut-2-enoate (4a) respectively. A number of analogues of (3a) and (4a), in which picryl moieties have been replaced by the group 4-cyano-2,6-dinitrophenyl, have been synthesised. These compounds have enabled ^{1}H n.m.r. assignments to be made unambiguously.

As part of a continuing study of electron-donor–acceptor (EDA) complexes,[1] we required electron-acceptor molecules containing both aromatic ring protons and exocyclic protons which could be used simultaneously as ^{1}H probes in n.m.r. studies of EDA complexation. For this reason it was originally decided to prepare mono- and di-picryl derivatives of ethyl acetoacetate, *viz.* (1) and (2) respectively. The formation of compounds having these two structures, produced by the action of picryl chloride on ethyl acetoacetate after the addition of sodium ethoxide, had been claimed by Dittrich [2] in 1890. The two products he obtained, m.p. 98 and 205 °C, are readily prepared under the conditions he described. We have also confirmed that acid hydrolysis of the product with m.p. 98 °C yields picrylacetone.[3] However, we now have conclusive evidence that the two products are not (1) and (2) but instead are (3a) and (4a) respectively.

$CH_3COCH(Pic)CO_2Et$ (1)

$CH_3COC(Pic)_2CO_2Et$ (2)

Pic = 2,4,6-trinitrophenyl

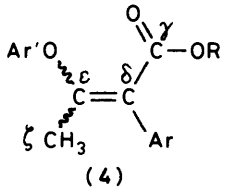


(3)

(3) a; Ar = Pic, R = $\beta\ \alpha$ CH_2CH_3

b; Ar = Pic, R = β CH_3

c; Ar = CDN, R = CH_2CH_3



(4)

(4) a; Ar = Ar' = Pic, R = $\beta\ \alpha$ CH_2CH_3

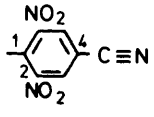
b; Ar = Ar' = Pic, R = β CH_3

c; Ar = Pic, Ar' = CDN, R = CH_2CH_3

d; Ar = CDN, Ar' = Pic, R = CH_2CH_3

e; Ar = Ar' = CDN, R = CH_2CH_3

CDN = 2,6-dinitro-4-cyanophenyl



Results and Discussion

Monopicryl Derivative.—The i.r. spectrum of the solid with m.p. 98 °C supports the end structure (3a) rather than the keto tautomer (1). In particular, there is only one C=O stretching frequency, at the low value of 1 660 cm^{-1}. This is assigned to the carboxy carbonyl intramolecularly hydrogen-bonded to the hydroxy group in the *Z*-isomer of (3a). In this isomer a six-membered ring can be formed by the hydroxy group hydrogen bonding to the carbonyl oxygen of the ethoxycarbonyl group. For comparison, the carbonyl absorption in methyl salicylate is at 1 675 cm^{-1}. ^{1}H N.m.r. evidence suggests that in acetone solution (3a) exists largely as the *Z*-isomer (Table 1). In particular, the somewhat broad, very high frequency (low field) singlet at δ 13.09 is to be noted. On the basis of Dittrich's structure (1) this line would have to be assigned to the proton on C(δ) whereas in (3a) the assignment is to the hydroxylic proton, which group in the *Z*-isomer of (3a) can be intramolecularly hydrogen-bonded as indicated above. Such protons give rise to very low field ^{1}H n.m.r. absorptions. For example, the corresponding line position in a dilute solution of methyl salicylate in carbon tetrachloride is at δ 10.71. In deuterioacetone [$(CD_3)_2CO$] solution there is ^{1}H n.m.r. evidence (Table 1) of small amounts of a second compound which is probably the *E*-isomer. Although the proton of the hydroxy group cannot be involved in intramolecular H-bonding in this isomer, the signal is still at low field: this is reasonable for a hydroxy proton but not for a proton attached to the C(δ) atom in structure (1). Whilst the absorption assigned to the hydroxy proton of the *Z*-isomer in deuterioacetone is concentration independent, the corresponding absorption in the second isomer is concentration dependent, thus further supporting the assignments of these two

Table 1. ^{1}H N.m.r. line positions (δ) for solutions of compounds (3a—c) and (4a—e) at 33 °C, 90 MHz

			δ [b]				
						R [d]	
Compound	Solvent	Isomer [a]	ArH_2	OH [c]	$C(\zeta)H_3$	CH_2	CH_3
(3a)	CD_3COCD_3	*Z*	9.12	13.09	1.86	4.19 (q)	1.11 (t)
		E	8.98	11.34 [e]	2.48	4.02 (q)	1.07 (t)
(3a)	CD_3SOCD_3	*E*	8.99	11.37 [e]	2.47	3.99 (q)	1.06 (t)
		Z	9.14	12.87	1.81	4.16 (q)	1.10 (t)
(3b)	CD_3COCD_3	*Z*	9.10	12.99	1.86	—	3.71
		E	8.98	*f*	2.55	—	3.54
(3c)	CD_3COCD_3	*Z*	8.80	13.06	1.84	4.18 (q)	1.11 (t)
(3c)	CD_3SOCD_3	*E*	8.82	11.46 [e]	2.43	3.97 (q)	1.03 (t)
		Z	8.97	12.80	1.79	4.13 (q)	1.11 (t)
				$Ar'H_2$			
(4a)	CD_3COCD_3	*E*	9.14	9.18	2.57	4.16 (q)	1.11 (t)
(4b)	CD_3COCD_3	*E*	9.14	9.18	2.59	—	3.72
(4c)	CD_3COCD_3	*E*	9.14	8.92	2.57	4.16 (q)	1.11 (t)
(4d)	CD_3COCD_3	*E*	8.90	9.18	2.57	4.20 (q)	1.12 (t)
(4e)	CD_3COCD_3	*E*	8.88	8.92	2.57	4.22 (q)	1.14 (t)

[a] Assignments based on arguments given in text; major isomer given first in each pair. [b] Lines are singlets unless otherwise stated. [c] Somewhat broad sharpened when line corresponding to protons on C(ζ) was irradiated, suggesting weak coupling between these nuclei. [d] For all ethyl groups J = 7 Hz. [e] Concentration dependent. Shifts quoted are for *ca.* 10% w/v solutions. [f] Too weak to measure.

structural isomers. Similar behaviour is observed with other compounds with the general formula (3) (Table 1).

Further evidence that the product with m.p. 98 °C is (3a) and not (1) is obtained from ^{13}C n.m.r. spectroscopy (Table 2). The line in the $^{13}C\{^1H\}$ spectrum which would have to be assigned to C(δ) in structure (1) or in (3a) remains as a singlet when ^{1}H off-resonance decoupling is used. Had the structure been (1), a doublet would have been observed.

By contrast with solutions of (3a) in acetone, in deuteriodimethyl sulphoxide ([$^2H_6$]DMSO) solution the *E*-isomer appears to be dominant (*Z* : *E* *ca.* 1 : 2). This ratio is based on the intensities of the ^{1}H n.m.r. lines due to the protons of the methyl group involving C(ζ) of (3a). The corresponding sets of absorptions from the *Z*- and *E*-isomer are also observed in the corresponding $^{13}C\{^1H\}$ n.m.r. spectrum of (3a) in [$^2H_6$]DMSO (Table 2). Geometrical isomerization, implied by changes in the *Z* : *E* ratio as the solvent is altered, presumably occurs by tautomerism through the keto structure (1).

The ^{1}H shifts of the protons attached to C(3) in deuteriochloroform or deuteriobenzene solutions of (3a), namely δ 1.82 and 1.46, respectively, are close in value to that for the *Z*-isomer of (3a) in acetone (Table 1). We therefore suggest that (3a) exists as this isomer in chloroform and in benzene solution.

Because of our intention to use molecules such as (3a) in n.m.r. studies of EDA complexes,[4] we have also prepared the methyl ester (3b), thus providing all-singlet probes from the ^{1}H n.m.r. spectra. As expected, apart obviously from the absorption due to R, the n.m.r. spectra of (3a) and (3b) are identical (Table 1).

Compound (3c) was synthesised from 4-chloro-3,5-dinitrobenzonitrile (5) and ethyl acetoacetate. Compared with the corresponding reaction involving picryl chloride the reactivity of (5) is low. This is consistent with the observed low reactivity of 4-cyano-2,6-dinitroanisole with methoxide ion to form the 1-methoxy Meisenheimer adduct, compared with the corresponding reaction involving 2,4,6-trinitroanisole,[5] also in the difference in stability of the resulting adducts.[5] Although (3c) was obtained as an impure viscous oil, it gave an acceptable ^{1}H n.m.r. spectrum (Table 1). Comparison of the ^{1}H spectrum (in deuterioacetone) of (3c) with those of the *Z*- and *E*-isomer of (3a), in particular the line positions of the protons on C(δ), indicates that (3c) exists, at least largely, as the *Z*-isomer in this solvent. In [$^2H_6$]DMSO (3c), like (3a), is present primarily as the *E* isomer (Table 1).

Dipicryl Derivative.—At the outset, before any spectroscopic study of the compound of m.p. 205 °C [2] had been made, the fact that significant quantities of the compound are formed when one equivalent of picryl chloride reacts with ethyl acetoacetate in the presence of one equivalent of ethoxide ion seemed surprising if the product had structure (2). Combustion analysis [2] (Found: C, 39.05; H, 2.45; N, 15.3. $C_{18}H_{12}N_6O_{15}$ requires C, 39.15; H, 2.2; N, 15.2%) is consistent with it being a derivative of ethyl acetoacetate in which two hydrogen atoms have been replaced by two picryl groups. Dittrich [2] also obtained a compound, m.p. 80 °C (Found: C, 37.5; H, 2.8; N, 16.3%) by the action of ethanolic potassium ethoxide on the compound of m.p. 205 °C. This compound (m.p. 80 °C) he claimed was ethyl dipicrylacetate ($C_{16}H_{10}N_6O_{14}$ requires C, 37.65; H, 2.0; N, 16.45%), an expected product from the base hydrolysis of (2), thus apparently giving support for structure (2). We have been unable to detect any ethyl dipicrylacetate. However, we have observed the formation of 2,4,6-trinitrophenetole, m.p. 78.5 °C, confirmed by i.r. with an authentic sample. The elemental analysis obtained by Dittrich (see above) fits better with 2,4,6-trinitrophenetole ($C_8H_7N_3O_7$ requires C, 37.35; H, 2.75; N, 16.35%) and there is little doubt that this was in fact the compound he obtained. The spectroscopic evidence below shows conclusively that the ' dipicryl ' product is (4a) and not (2). The formation of 2,4,6-trinitrophenetole is readily explained by the nucleophilic attack of ethoxide ion on the C(1) atom of the picryl group Ar′ in (4a).

The ^{1}H n.m.r. spectrum of the compound of m.p. 205 °C shows two singlets in the aromatic region in acetone solution at 30 °C (Table 1). The difference in shifts is small (0.04 p.p.m.). Originally we thought that this non-equivalence might have arisen through the two picryl groups in (2) being diastereoisotopic through steric congestion at C(δ). At first there appeared to be evidence for this proposal in that, on heating the acetone solution to just below the b.p. of the solvent, the ^{1}H n.m.r. signals of the aromatic protons merged to give a single line. However, steric congestion which might lead to the non-equivalence of the two picryl rings would also imply the

Table 2. ^{13}C N.m.r. δ-values (p.p.m.) for various compounds (3a—c) and (4a—e) in $(CD_3)_2SO$ at 33 °C, 15 MHz

Compd.	Isomer [a]	δ-value [b]														
							Ar				Ar′					
		α	β	γ or ε	δ	ε or γ	ξ	1	2	3	4	1	2	3	4	C≡N
(3a)	*E* [c]	13.84	61.62	169.14	93.49	175.27	19.61	128.28	150.80	122.81	148.14					
	Z [d]	13.84	59.86	164.59	96.59	170.78	19.61	132.17	150.80	122.81	146.61					
(3b)	*Z*	—	51.00 [e]	164.95	95.86	170.84	19.37	131.38	150.38	122.76	146.50					
(4a)	*E*	13.84	61.01	163.62	106.12	165.19	15.91	129.50	149.59 [f]	124.46	147.53	142.61 [f]	143.76 [f]	125.79	144.43 [f]	
(4b)	*E*	—	52.27	164.28	105.70	165.43	15.91	129.19	149.41 [f]	124.51	147.52	142.55 [f]	143.64 [f]	125.79	144.37 [f]	
(4c)	*E*	13.96	63.64	163.80	105.82	165.62	16.03	129.68	149.47 [f]	124.52	147.59	142.25 [f]	144.07 [f]	135.26	111.22 [f]	115.11
(4d) [g]	*E*	14.21	61.74	164.47	108.07	165.56	16.37	130.04	150.99 [f]	133.63	115.17	145.42 [f]	145.40 [f]	126.28	144.49 [f]	115.78
(4e)	*E*	13.90	60.95	163.86	106.12	165.37	15.97	128.70	149.77 [f]	133.44	114.01	142.06 [f]	144.25 [f]	135.14	111.16 [f]	114.01 [h]

[a] See text. [b] Chemical shifts to higher frequency (lower field) from internal $SiMe_4$. For designation of C-atoms, see structures (3) and (4). [c] Major isomer of (3a) in this solvent. [d] Minor isomer of (3a) in this solvent. [e] Methyl ester C-atom. [f] These assignments are tentative. [g] In deuterioacetone. [h] Some line broadening which suggests that the resonances for the C-atoms in the two C≡N groups are not quite coincident.

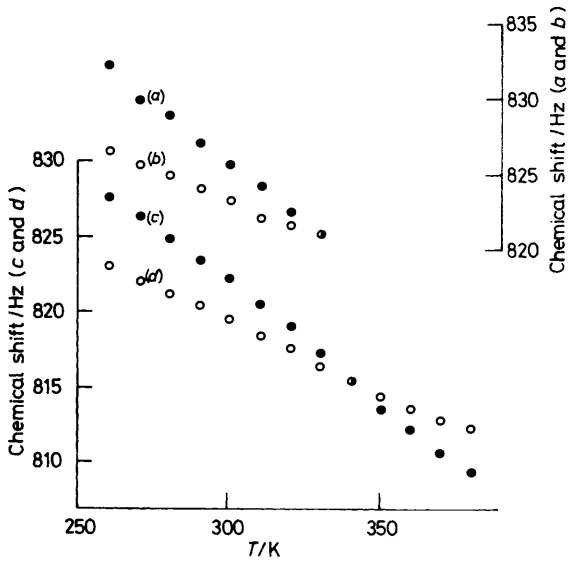


Figure. Temperature dependences for the aromatic 90-MHz ^1H line positions of compound (4a): (*a*) and (*b*) in acetone; (*c*) and (*d*) in heptan-2-one

non-equivalence of the two protons in each of the two rings. Thus, instead of two singlets, two AB systems would have been expected. There is also the strong chemical argument that such a sterically hindered molecule is unlikely to be formed in the first place when only single equivalents of reagents are used. The explanation of the observed coalescence of the two ^1H aromatic signals in acetone as the temperature is raised is that both lines move upfield with increasing temperature and the lower-field line moves faster: the lines happen to coincide at about the b.p. of the solvent (Figure). Confirmation of this explanation is obtained by repeating the experiment using heptan-2-one as solvent. The higher boiling point allows the solution temperature to be increased to 380 K. Over the increased temperature range, the low-field line overtakes the high-field line at *ca.* 340 K (Figure).

Compound (4a) was also prepared by the action of picryl chloride on (3a) in the presence of one equivalent of sodium methoxide.

In terms of structure (4a), the ^1H n.m.r. spectrum in acetone is easily reationalised, although the assignment of the two aromatic lines to the specific picryl groups in (4a) cannot be made from this spectrum alone. In order to make these assignments, compounds (4c), (4d), and (4e) were synthesised. Compound (4c) was made from (3a) and (5). Likewise, (4d) was made from (3c) and picryl chloride. Compound (4e) was formed as a second product in the synthesis of (3c): this parallels the formation of (4a) in the original preparation of (3a).

Correspondences of pairs of lines in the aromatic region of the ^1H n.m.r. spectra of (4a), (4c), and (4d) in deuterioacetone and in deuteriochloroform (Tables 1 and 3) enable the assignments of the two picryl groups Ar and Ar′ in (4a or b) to be made as indicated in Tables 1 and 3. The ^1H n.m.r. assignments of the two corresponding 4-cyano-2,6-dinitrophenyl groups Ar and Ar′ in (4e) may likewise be made by comparison with the n.m.r. spectra of (4c) and (4d) in deuterioacetone. In this solvent the line positions of the protons in a given aromatic substituent are virtually independent of whether the other aromatic substituent is picryl or 4-cyano-2,6-dinitrophenyl. This holds for both Ar and Ar′. This independency of ^1H aromatic line positions is not so closely observed for

Table 3. δ-Values for aromatic protons in the Ar group of compounds (3a—c) and in Ar, Ar′ groups of compounds (4a—e) in deuteriochloroform and in deuteriobenzene at 33 °C, 90 MHz

	δ [a]			
	ArH_2		$Ar'H_2$	
Compound	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
(3a)	8.88	7.79		
(3b)	8.88	7.79		
(3c)	8.48	6.91		
(4a)	9.09	8.21	9.01	7.69
(4b)	9.09	8.20	9.01	7.68
(4c)	9.08	8.26	8.46	6.80
(4d)	8.54	7.27	9.02	7.70
(4e)	8.54	7.26	8.46	6.67

[a] All singlets.

corresponding deuteriobenzene solutions (Table 3) for the reason given below.

Addition of *ca.* 0.04M praseodymium(dpm)$_3$* to solutions of (4a) in deuteriochloroform causes the largest upfield shift for the protons on C(β) (0.425 p.p.m.). This establishes the carbonyl oxygen of the carboxy group as the point of ligand attachment to the shift reagent. The effect of the reagent is next largest on the protons on C(ζ) (0.305 p.p.m.). It is very much smaller for the protons in Ar′ (0.028 p.p.m.). This would appear to establish the geometry of (4a) as the *E*-isomer. The remarkable closeness of δ-values for the various aromatic ^1H lines in various sets of compounds within the group (4a—e), which has been used above as the basis of the assignments of these lines to protons in Ar or Ar′, also provides a strong argument that all within this group have this same geometry. Since no keto–enol tautomerism is possible in compounds with the general structure (4), there is no question of solvent dependence of geometrical isomer population as is the case with compounds of general structure (3).

Arguments similar to those above for the proton spectra have also enabled the ^{13}C lines of the aromatic carbon atoms to be partially assigned in (4a, c, d, and e) (Table 2).

In all the compounds (3a—c) and (4a—e), the ^1H n.m.r. absorptions of the aromatic protons move upfield as the solvent is changed from chloroform to benzene † (Table 3). Two observations are of interest. First, for Ar in the various pairs (3a), (3c); (4a), (4d); and (4c), (4e); and Ar′ in the pairs (4a), (4c) and (4d), (4e); it is the ^1H aromatic signal corresponding to the 4-cyano-2,6-dinitrophenyl moiety, rather than that due to the picryl, which shows the greater ASIS-type shift, although it is expected that picryl would be the better electron acceptor.[5] Secondly, in the series (4a—e), a given aromatic moiety has a larger ASIS-type shift if it is Ar′ than if it is Ar (Table 3). At first sight this appears surprising since it might be expected that Ar, attached to a carbon atom, might be a better electron acceptor than Ar′ attached to oxygen, which atom can back-donate into the ring. However, it is recognised that the ASIS effect may not simply reflect the electron-accepting capacity of the solute, particularly for solutions such as those in the present study where there may be explicit complex formation between solute and the benzene solvent. Indeed, it is the interest in this type of EDA complex formation which prompted the synthesis of this series of compounds (see Introduction).

* dpm is dipavaloylmethanato.

† The change in chemical shift as the solvent is changed from a solvent such as chloroform (or more usually carbon tetrachloride) to an aromatic solvent (usually benzene) is generally called the 'aromatic solvent induced shift' (ASIS) (*e.g.* P. Laszlo, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1967, **3**, 231; E. M. Engler and P. Laszlo, *J. Am. Chem. Soc.*, 1971, **93**, 1317 and references therein).

Experimental

^1H N.m.r. spectra were obtained with either a CW Bruker HX90 (90 MHz) spectrometer or an FT Bruker WP60 (60 MHz) spectrometer. ^{13}C N.m.r. spectra were obtained on the latter spectrometer (15 MHz). All chemical shifts are in p.p.m. positive to higher frequency (lower field) from the appropriate ^1H or ^{13}C signal of internal tetramethylsilane (TMS). I.r. spectra are of Nujol mulls recorded with a Perkin-Elmer 197 spectrometer.

Reaction of Ethyl Acetoacetate with Picryl Chloride.—Ethyl acetoacetate (9.1 g) was added to ethanol (90 ml) in which had been dissolved sodium (1.6 g). Picryl chloride (17.3 g) was added and the mixture was refluxed for 1 h then left for 20 h at room temperature. The insoluble solid was removed by filtration. Recrystallisation from glacial acetic acid yielded *ethyl 2-picryl-3-picryloxybut-2-enoate* (4a) as needles containing three molecules of crystallisation of solvent (as determined by ^1H n.m.r.). The needles were washed with ethanol to give an amorphous off-white product (4.6 g), m.p. 204 °C (Dittrich [2] quotes 205 °C). (Found: C, 39.16, H, 2.15; N, 15.2. $C_{18}H_{12}N_6O_{15}$ requires C, 39.15; H, 2.2; N, 15.2%); $\nu_{max.}$ 1 720 (C=O) and 1 250 (ether). The filtrate of the reaction mixture was evaporated to dryness and the residue recrystallised from ethanol to yield yellow needles of *ethyl 3-hydroxy-2-picrylbut-2-enoate* (3a) (7.7 g), m.p. 98 °C (Dittrich [2] quotes 98 °C); $\nu_{max.}$ 1 660 (C=O) (Found: C, 42.05, 42.7; H, 3.4, 3.5; N, 12.6, 12.2. $C_{12}H_{11}N_3O_9$ requires C, 42.25; H, 3.25; N, 12.3%). Other data are given in the Results and Discussion section.

By replacing the reaction solvent with methanol and by refluxing the base solution after the addition of ethyl acetoacetate for 5 h before the addition of picryl chloride, the corresponding methyl esters were formed. *Methyl 2-picryl-3-picryloxybut-2-enoate* (4b), recrystallised from acetone, m.p. 208 °C (decomp.) (Found: C, 38.0; H, 1.95; N, 15.7. $C_{17}H_{10}N_6O_{15}$ requires C, 37.95; H, 1.85; N, 15.6%); $\nu_{max.}$ 1 725 (C=O) and 1 250 (ether). *Methyl 3-hydroxy-2-picrylbut-2-enoate* (3b), recrystallised from methanol, m.p. 131.5 °C (Found: C, 40.35; H, 2.85; N, 13.05. $C_{11}H_9N_3O_9$ requires C, 40.4; H, 2.75; N, 12.85%); $\nu_{max.}$ 1 655 (C=O).

Reaction of Ethyl Acetoacetate with 4-Chloro-3,5-dinitrobenzonitrile (5).—Ethyl acetoacetate (0.65 g) was added to ethanol (20 ml) in which sodium (0.115 g) had been dissolved. To this solution was added compound (5) (1.15 g). The mixture was refluxed for 2 h then left for 20 h. The solid precipitate was removed and recrystallised from ethanol to give *ethyl 3-(4-cyano-2,6-dinitrophenoxy)-2-(4-cyano-2,6-dinitrophenyl)but-2-enoate* (4e) as an off-white microcrystalline powder (200 mg), decomp. 168 °C (Found: C, 46.7; H, 2.35; N, 16.2. $C_{20}H_{12}N_6O_{11}$ requires C, 46.9; H, 2.35; N, 16.4%); $\nu_{max.}$ 2 240 (C≡N), 1 720 (C=O), and 1 260 (ether). The reaction mixture, after filtration, was extracted with chloroform. On removal of the solvent a very viscous yellow-brown oil was obtained (1 g). Attempts to crystallise this material were unsuccessful and it was used as such for spectroscopic measurements and in the preparation of (4d). The ^1H n.m.r. (Table 1) and i.r. [2 240 (C≡N) and 1 660 (C=O)] data, together with the successful formation of (4d) from it (see below) establish this product as *ethyl 2-(4-cyano-2,6-dinitrophenyl)-3-hydroxybut-2-enoate* (3c).

Addition of 1 equiv. of (5) to an ethanolic solution of

(3a) in the presence of 1 equiv. of sodium ethoxide gave, after recrystallisation from glacial acetic acid and washing the needles with ethanol, *ethyl* 3-(4-*cyano*-2,6-*dinitrophenoxy*)-2-*picrylbut*-2-*enoate* (4c) in 90% yield, m.p. 198 °C (decomp.) (Found: C, 42.85; H, 2.4; N, 15.75. $C_{19}H_{12}N_6O_{13}$ requires C, 42.85; H, 2.25; N, 15.8%. $\nu_{max.}$ 2 240 (C≡N) 1 710 (C=O), and 1 260 (ether).

Reaction of picryl chloride with (3c) under the same conditions gave a low (*ca.* 5%) yield of *ethyl* 2-(4-*cyano*-2,6-*dinitrophenyl*)-3-*picryloxybut*-2-*enoate* (4d), insoluble in hot ethanol, decomp. 162—165 °C (Found: C, 42.65; H, 1.9; N, 15.1%); $\nu_{max.}$ 2 240w (C≡N), 1 710 (C=O), and 1 250 (ether).

Under the same conditions reaction of picryl chloride with (3a) gave (4a), and with (3b) gave (4b).

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