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# The Action of Malononitrile and Ethyl Cyanoacetate on Diphenylcyclopropenone

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**Synopsis.** Diphenylcyclopropenone reacts with malononitrile in the presence of ethanolic sodium methoxide to yield, after acidification, (*E*)-1,1-dicyano-2-hydroxy-3,4-diphenyl-1,3-butadiene (**1a**); an analogous product, ethyl (2*Z*, 4*E*)-2-cyano-3-hydroxy-4,5-diphenyl-2,4-pentadienoate (**1b**), is formed from ethyl cyanoacetate.

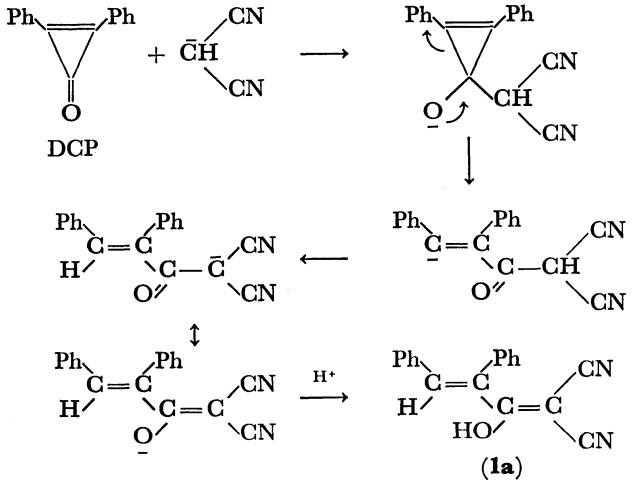
In the young chemistry of cyclopropenones, a leading role has been played by diphenylcyclopropenone (DCP).[1] The synthesis of DCP is considered 'a milestone in theoretical organic chemistry'[2] The 'state of the art' of the cyclopropenones has recently been reviewed.[3,4] The general picture that emerges is the *erratic* behaviour of these microcyclic ketones, particularly in addition reactions.[3] This trend, in which the unpredictable predominates, may be illustrated by the action of malononitrile and ethyl cyanoacetate on DCP.

The reactions of cyclopropenones with malononitrile have previously been employed as a synthetic route to triafulvenes. DCP reacted with malononitrile in boiling acetate anhydride solution to give 4,4-dicyano-1,2-diphenyltriafulvene;[5] aliphatic cyclopropenones condensed analogously.[6-8] The use of β-alanine[9] or boron trifluoride[10] as a catalyst resulted in increased yields.

Likewise, condensation of DCP and ethyl cyanoacetate gave the corresponding triafulvene.[9] In general, basic condensation agents which could cleave the three-membered ring were avoided. An improved procedure employed an active form of DCP. Thus, treatment of 3-ethoxy-1,2-diphenylcyclopropenium tetrafluoroborate and malononitrile with one mole of *N,N*-diethylisopropylamine in dichloromethane solution afforded the dicyanotriafulvene in 85% yield.[11] 3,3-Dichloro-1,2-diphenylcyclopropene reacted directly with malononitrile at 100—120° C without solvent to give the triafulvene in 10% yield.[12] It has been claimed that in the reaction of DCP with malononitrile in pyridine solution seven products were obtained, one of which was tentatively assingned the structure of 3-amino-2-cyano-4,4-diphenyl-2,4-cyclopentadien-1-one (or its 2-amino-3-cyano isomer).[13]

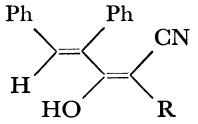
In the present investigation, the reactions of DCP with malononitrile and with ethyl cyanoacetate were studied under basic conditions in protic solutions. We had thought that a Michael addition of the nucleophile (*e.g.*, $\bar{C}H(CN)_2$) to the activated carbon-carbon double bond of the cyclopropenone ring might occur, followed perhaps by a ring enlargement process, leading eventually to a pyridinone derivative. Various nucleophilic addition reactions at the carbon-carbon double bond of cyclopropenones have been effected.[3,4] However, in this case the reactions followed a different course. Treatment of DCP with an ethanolic solution of malononitrile in the presence of sodium methoxide, followed by acidification, gave a high yield of a pale yellow acidic solid, whose analysis and mass spectrum corresponded to that of a 1:1 adduct. The NMR spectrum showed only a multiplet in the aromatic region, but the IR spectrum was more revealing, containing broad OH absorption and strong bands at 2214 and 2209 $cm^{-1}$, indicative of two α,β-unsaturated cyanide groups. We therefore considered that the product was the enolic dinitrile (**1a**) and this structure, together with the *cis*-configuration of the phenyl groups, was readily confirmed by an unambiguous synthesis of the compound from the sodium salt of malonoitrile and (*E*)-2,3-dipheylpropenoyl chloride.[14] The reaction of DCP with ethyl cyanoacetate under the same conditions yielded a colourless adduct, which was insoluble in aqueous alkali; however, the virtual identity of its UV spectrum with that of the previous compound, a positive $FeCl_3$ reaction, and the appearance of intense CN absorption and a sigle carbonyl band at 1655 $cm^{-1}$ (chelated ester) in its IR spectrum suggested that it was the analogue (**1b**), and, indeed, it was also formed by condensation of ethyl sodio-cyanoacetate with the foregoing acid chloride.

The formation of **1a** and **1b** closely resembles the hydrolyses of cyclopropenones with sodium or potassium hydroxide, in which salts of α,β-unsaturated acids are produced.[3] The present reaction presumably involves the addition of the anion of malononitrile (and of ethyl cyanoacetate) to the carbonyl group of DCP, followed by collapse of the intermediate open chain carbanion species (Scheme 1). Protonation




Scheme 1.

would then complete the process. It is interesting to note that the *cis*-configuration of phenyl groups in the substrate (DCP) is retained in the product, in analogy with various basic hydrolyses of cyclopropenones. It may be an indication of the high rate of protonation of the carbanion intermediate. The course of the nucleophilic addition to DCP contrasts with the reaction of malononitrile and 3-ethoxy-1,2-diphenylcyclopropenium tetrafluoroborate in the presence of *two* moles of *N,N*-diisopropylethylamine.[15] In the latter reaction, an addition of the nucleophile to the carbon-carbon doble bond is preferred, and the product is 1,3-diphenyl-3-ethoxy-4,4-dicyano-1,3-butadiene. The reduced cyclopropenium contribution in DCP might have been the determining factor which directed the addition of the nucleophile to the carbonyl rather than to the carbon-carbon double bond. Thermodynamic effects are probably responsible for the ultimate transformation to the conjugated dienols **1a** and **1b**.




**1** **a**; R=CN, **b**; R=$CO_2Et$

## Experimental

Melting points were taken on a "Unimelt" Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 457 and 257 spectrophotometers for Nujol mulls. Ultraviolet spectra were determined with Unicam Model SP 800 and Perkin-Elmer 402 spectrophotometers and NMR spectra with a Perkin-Elmer R 32 instrument at 90 MHz and are reported in ppm relative to $Me_4Si$ as internal standard. The mass spectra of the new compounds, obtained with a Varian Mat-311 spectrometer, contained the appropriate signals representing the molecular ions.

*(E)-1,1-Dicyano-2-hydroxy-3,4-diphenyl-1,3-butadiene (**1a**).* *(a)*: A magnetically stirred solution of sodium methoxide (0.60 g, 11 mmol) in absolute ethanol (100 ml) was treated under anhydrous conditions at room temperature first with malononitrile (0.86 g, 13 mmol) and then with DCP[16] (2.27 g, 11 mmol), whereupon the solution became yellow. After 12 h at room temperature most of the solvent was removed under reduced pressure, concentrated hydrochloric acid and water were added successively to the residue, and the remainder of the ethanol was distilled off. The resulting yellow solid was collected, washed with water, and recrystallised from aqueous ethanol or xylene to give **1a** (2.70 g, 90%) as pale yellow needles, mp 182 °C (decomp); IR 3170 (broad), 2214, 2209, and 1608 $cm^{-1}$; $UV_{max}$ ($CH_3CN$) 259 (log $\varepsilon$ 4.12) and 325 nm (4.06); $UV_{max}$ (cyclohexane) 234, 258, and 338 nm; NMR (DMSO) $\delta$=7.08—7.42 (m).

Found: C, 79.58; H, 4.22; N, 10.57%. Calcd for $C_{18}H_{12}N_2O$: C, 79.40; H, 4.44; N, 10.29%.

*(b)*: A stirred solution of malononitrile (0.61 g, 9.2 mmol) in ethanolic sodium ethoxide, prepared from sodium (0.14 g, 6.1 mmol) and ethanol (50 ml), was slowly treated with (*E*)-2,3-diphenylpropenoyl chloride[14] (1.5 g, 6.1 mmol). After 12 h the solvent was removed under reduced pressure and the residue was stirred with 1 M hydrochloric acid (54 ml); the resulting oil was separated by decantation, washed with water, and dissolved in a small amount of aqueous 5% sodium carbonate. The solution was washed with ether (2×50 ml) and then acidified with 2 M hydrochloric acid; the resulting precipitate was recrystallised from xylene, giving **1a** (0.81 g, 48%), identical (IR spectrum, mp and mixed mp) with the previous product.

*Ethyl (2Z, 4E)-2-Cyano-3-hydroxy-4,5-diphenyl-2,4-pentadienoate (**1b**).* *(a)*: This compound was prepared analogously from ethyl cyanoacetate (1.774 g, 15.7 mmol), DCP (2.55 g, 12.4 mmol), sodium methoxide (0.756 g, 14 mmol), and ethanol (60 ml). After most of the solvent had been removed, dilute hydrochloric acid was added and the resulting oil was separated and crystallised from ethanol or cyclohexane to give **1b** (2.88 g, 73%) as colourless needless, mp 130 °C. IR 2210, 1655, and 1585 $cm^{-1}$; $UV_{max}$ ($CH_3CN$) 265 (log $\varepsilon$ 4.00) and 331 nm (4.18); $UV_{max}$ (cyclohexane) 234 (4.07), 258 (3.96), and 338 nm (4.19); NMR ($CDCl_3$) $\delta$=1.37 (t, $J$=7 Hz, 3H), 4.36 (q, $J$=7 Hz, 2H), 7.04—7.27 (m, 6H), 7.30—7.45 (m, 5H), and 7.57 (s, 1H).

Found: C, 75.28; H, 5.33; N, 4.64; OEt, 13.7%. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39; OEt, 14.1%.

*(b)*: Diphenylpropenoyl chloride (1.5 g, 6.1 mmol) was condensed with ethyl cyanoacetate (1.5 g, 13.2 mmol), as described in (*b*) above, and the solvent was removed after 12 h. The residue was treated with 1 M hydrochloric acid and the resulting oil was washed with water (3×30 ml) and crystallised from ethanol to yield **1b** (0.55 g, 27%), identified by its IR spectrum, mp, and mixed mp.

## References

1) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).
2) W. D. Emmons, *Org. Synth.*, **47**, p. VIII (1967).
3) K. T. Potts and J. S. Baum, *Chem. Rev.*, **74**, 189 (1974).
4) T. Eicher and J. L. Weber, *Top. Curr. Chem.*, **57**, 1 (1975).
5) E. D. Bergmann and I. Agranat, *J. Am. Chem. Soc.*, **86**, 3587 (1964).
6) A. S. Kende and P. T. Izzo, *J. Am. Chem. Soc.*, **86**, 3587 (1964).
7) J. Ciabattoni and E. C. Nathan, III, *J. Am. Chem. Soc.*, **91**, 4766 (1969).
8) I. Belsky, *Israel J. Chem.*, **8**, 769 (1970).
9) S. Andreades, *J. Am. Chem. Soc.*, **87**, 3941 (1965).
10) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Jpn.*, **37**, 1897 (1964).
11) T. Eicher, T. Pfister and N. Krüger, *Org. Prep. Proc. Int.*, **6**, 63 (1974).
12) I. Agranat and R. M. J. Loewenstein, unpublished results.
13) L. G. Wolgemuth, Ph. D. Thesis, University of Michigan, 1964; *Diss. Abstr.*, **25**, 3278 (1964).
14) R. Riemschneider and H. Kampfer, *Monatsh.*, **90**, 518 (1959).
15) T. Eicher and A. Hansen, *Chem. Ber.*, **102**, 319 (1969).
16) R. Breslow and J. Posner, *Org. Synth.*, **47**, 62 (1967).