

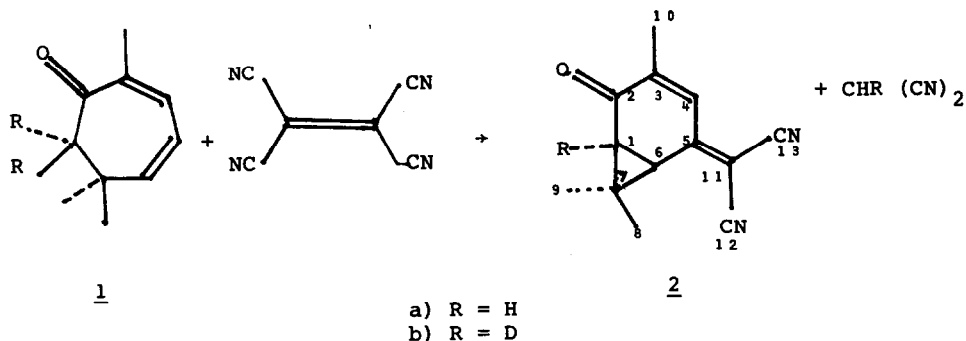
CYCLOPROPANE FORMATION AS A PREREQUISITE FOR TETRACYANOETHYLENE FRAGMENTATION.
AN ACID-CATALYSED REACTION OF EUCARVONE.

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The ability of the cyano group to stabilize negative charge¹ is exceptional. The acidity of the C-H bond in dicyano- and tricyanomethane is well known². Yet, such a property has seldom been exploited as the driving force in a reaction involving tetracyanoethylene (TCNE). Its excellent ability as a dienophile or in other types of cycloadditions³ has superseded other modes of addition and fragmentation. We present such an alternative.

When tetracyanoethylene (1.42×10^{-2} moles) is reacted with eucarvone⁴ (1a) (1.33×10^{-2} moles) in 32 ml. of chloroform, in the presence of 20% CF₃COOH by volume, at 100°C in a sealed glass tube for 16 hours, a yellow crystalline solid is obtained after work-up and purification (m.p. 164-6°C). The yield based on eucarvone is better than 60%. (Equation 1)



Equation 1.

We have determined the structure of this compound as 2a from the following spectroscopic arguments⁵.

In the mass spectrum, the molecular peak, with 75% of the intensity of the base peak at $m/e = 172$, appears at $m/e = 212$. From the high resolution spectrum ($m/e = 212.0954$), the elemental analysis closely matches the molecular formula C₁₃H₁₂N₂O (molecular weight calculated = 212.0949).

The proton magnetic resonance spectrum (Table 1) indicates the presence in compound 2a of 2 diastereotopic methyl groups on a saturated carbon, 1 methyl group on a trigonal carbon coupled with 1 olefinic proton ($J = 1.5\text{Hz}$) and an AB system ($J = 6.7\text{ Hz}$), the lower resonance of which is also coupled with the olefinic proton ($J = 1.5\text{ Hz}$).

In order to identify the various carbons (Table 1), the partially decoupled and fully decoupled ^{13}C spectra were compared. Evidence was obtained for 1 carbonyl group, 1 hydrogen-bearing trigonal carbon, 2 cyano carbons characterized by small intensities (Table 1), due to quadrupolar relaxation by the nitrogen nuclei, 1 trigonal carbon bearing the 2 cyano groups, also with decreased intensity, and 6 saturated carbons, one of which is completely substituted.

Position	1	2	3	4	5	6	7	8	9	10	11	12	13
p.m.r. (CDCl_3)	2.44			7.31		2.74		1.45	1.15	2.07			
$\delta, \pm 0.01$ p.p.m.	d			v^a		d.d ^b		or 1.15 s	or 1.45 s	d			
c.m.r.	38.4	192.3	164.4	133.4	146.7	38.4	34.4	38.4	38.4	38.4	77.7	111.2	112.4
(p.p.m.)	or 34.4		or 146.7		or 164.4	or 34.4		or 34.4	or 34.4	or 34.4		(c) 112.4	or 111.2
relative	28.8					28.8		28.8	28.8	28.8		(c)	(c)
to T.M.S.	16.9					16.9		16.9	16.9	16.9			
± 0.1 p.p.m.)	or 14.9					or 14.9		or 14.9	or 14.9	or 14.9			

Table 1 : Magnetic resonance spectra of compound 2a.

- (a) as defined by P. Laszlo and P. von R. Schleyer, J. Am. Chem. Soc., 86, 1171 (1964).
 (b) due to additional coupling with the olefinic proton : $^4J_{4,6} = 1.5\text{ Hz}$.
 (c) peak identified by its low intensity : ca. 20%, 40% and 50% for the resonances at 77.7, 112.4 and 111.2 p.p.m. respectively, when compared with the peak heights for the other carbons.

The infrared spectrum (CCl_4) shows a conjugated carbonyl (1672 cm^{-1}), an intense absorption for the cyano groups (2228 cm^{-1}), a characteristic doublet for the gem - dimethyl group ($1382, 1370 \text{ cm}^{-1}$), and a sharp medium band at 999 cm^{-1} (KBr pellet) characteristic of carene derivatives.

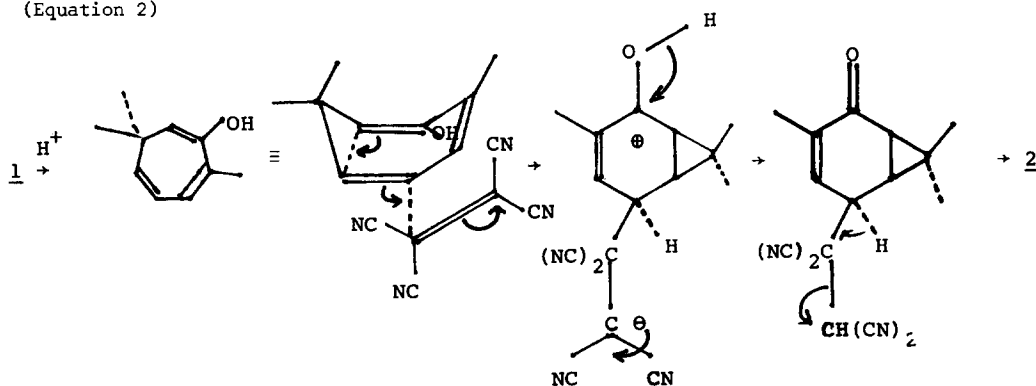
The ultraviolet spectrum ($\lambda_{\text{max}}^{\text{MeOH}} = 322 \text{ nm}$, $\epsilon = 16,000$) indicates increased conjugation relative to 1a.⁶

Formation of a cyclopropane ring during the reaction is demonstrated by the following arguments :

- when eucarvone- d_2 ⁷ (1b) is submitted to the identical reaction, using a $\text{CDCl}_3 - \text{CF}_3\text{COOD}$ solvent mixture, the resonance at $\delta = 2.44$ in the p.m.r. spectrum vanishes, and that at $\delta = 2.74$ becomes a broad singlet;
- the 6.7 Hz coupling between H_1 and H_6 is in the normal range for two cyclopropanic protons in a *cis* relationship;
- the $^1J_{13\text{C-H}}$ couplings for positions 1 and 6 have values of 166 and 167 ± 1 Hz respectively, characteristic of a 3-membered ring⁸.

The base peak in the mass spectrum is observed at $m/e = 172.0631$ ($\text{C}_{10}\text{H}_8\text{N}_2\text{O}$) and corresponds to the loss of methylacetylene⁹. Extrusion of carbon monoxide accounts for the peak at $m/e = 184.0972$.

A plausible mechanism for the formation of 2 involves, stepwise or in a concerted fashion, a cycloheptatriene-norcaradiene-type tautomerism, addition of TCNE, and elimination of $\text{CH}_2(\text{CN})_2$. (Equation 2)



Equation 2.

Under similar experimental conditions, viz. CHCl_3 - CH_3COOD , and in the absence of TCNE, eucarvone 1a readily exchanges the α protons with deuterium, in accord with facile enolisation. Further, there is precedence for the postulated mechanism: Corey and Burke⁴, using basic conditions, added benzaldehyde to eucarvone, and obtained an adduct for which they postulated a structure similar to that of 2¹⁰. Fragmentation of TCNE is not unknown either¹¹. It only requires sufficient acidity of the TCNE-bearing carbon. Further studies on this and related reactions are in progress.

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