

ENE-REACTION BETWEEN ISOPHORONE AND TETRACYANOETHYLENE

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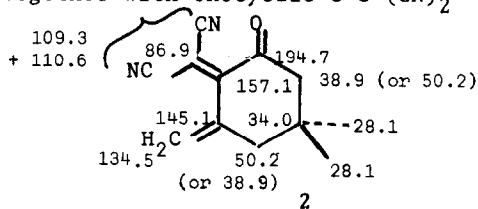
We have shown earlier<sup>1</sup> that an  $\alpha,\beta$ -unsaturated cyclic ketone could react with tetracyanoethylene in acidic medium to yield an addition-fragmentation product, rather than a bicyclic adduct, even though it was potentially enolizable into a planar diene. A complicating feature was the aptitude of the ketone we had selected, eucarvone, to undergo transannular ring closure. We now report that addition-fragmentation again prevails in a simpler system, that of isophorone. The product itself is interesting, it incorporates three adjacent trigonal centers bearing exocyclic double bonds.

Isophorone 1 (0.013 mole) is reacted with tetracyanoethylene (0.013 mole) in a mixture of 10 ml of  $\text{CF}_3\text{COOH}$  and 60 ml of  $\text{CHCl}_3$ , maintained in an evacuated sealed pyrex tube at  $107^\circ\text{C}$  for two hours. After work-up and purification, a yellow crystalline solid (m.p.  $77^\circ\text{C}$ ) is obtained in 10% yield.

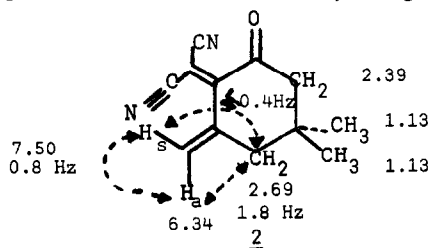
The indicated structure 2 arises from the following spectral arguments<sup>2</sup>:

- (i) an elemental formula  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}$  (calculated mass = 200.0949) is obtained from the high-resolution mass spectrum (observed  $m/e = 200.0934$  for  $\text{M}^+$ );
- (ii) the increase in conjugation displayed in the UV spectrum of 2 ( $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}} = 290 \text{ nm}$ ;  $\epsilon = 30,000$ ;  $\lambda_{\text{max}}^{\text{MeOH}} = 297 \text{ nm}$ ;  $\epsilon = 20,200$ ) relative to that of 1 ( $\lambda_{\text{max}}^{\text{EtOH}} = 236 \text{ nm}$ ;  $\epsilon = 12,300$ )<sup>3</sup>.

- (iii) the presence in the ir spectrum ( $\text{CCl}_4$ ;  $\pm 2 \text{ cm}^{-1}$ ) of absorptions for a conjugated carbonyl (1685), cyano groups (2236), and the scissoring mode for a ring methylene  $\alpha$  to the carbonyl (1412);
- (iv) evidence from the cmr spectrum ( $\text{CDCl}_3$ ;  $\pm 0.1 \text{ ppm}$ ) for the presence of two isochronous methyl carbons, two anisochronous methylene carbons, together with exocyclic  $\text{C}=\text{C}(\text{CN})_2^1$  and  $\text{C}=\text{CH}_2$  groups;

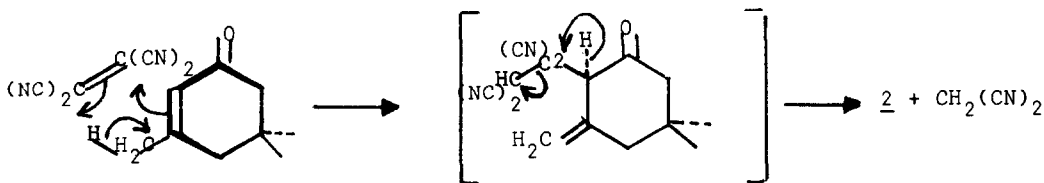


- (v) a substitution pattern characterized by the appearance in the pmr spectrum ( $\text{CDCl}_3$ ;  $\pm 0.01 \text{ ppm}$ ), summarized below, of resonances for the ring methylenes devoid of geminal or vicinal coupling interactions. The pronounced difference (1.16 ppm) between the chemical shifts of the syn and anti =  $\text{CH}_2$  protons is due to proximity of the syn proton with one of the cyano groups.



This substitution pattern is confirmed by the base peak in the mass spectrum at  $m/e = 144$ , arising probably from loss of 1,1-dimethylethylene. Also when 2 is reacted with  $\text{CF}_3\text{COOD}$ , it only exchanges the two protons responsible for the  $\delta = 2.39$  absorption in the pmr spectrum.

A plausible mechanism for the formation of 2 involves an ene reaction<sup>4,5</sup> with subsequent fragmentation of malononitrile :



It is usual for primary allylic C-H bonds to be more readily cleaved in this fashion than secondary ones<sup>4,6</sup>. Ene reactions are indeed acid-catalyzed and occur more readily under pressure<sup>4</sup>. The presence of acid could assist the fragmentation step, in the enolization at C-2 and removal of  $\text{CH}_2(\text{CN})_2$ . The narrow range of experimental conditions (temperature; solvent) required for the conversion of 1 to 2 is consonant with such an addition-fragmentation scheme.

Finally, an apparent paradox is worth mentioning : why is it that 2 is stable under acidic conditions and does not isomerize into the  $\Delta_{3,4}$  molecule with a trisubstituted endocyclic double bond ? The latter system would be subject to considerable angular and torsional strain, in excess of 6.5 kcal/mole according to our semi-empirical calculation<sup>7</sup>.

#### Acknowledgment

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