

# Electron-donating Behaviour of Aliphatic Carboxylic Acids in the Photoreaction with 1,2,4,5-Tetracyanobenzene

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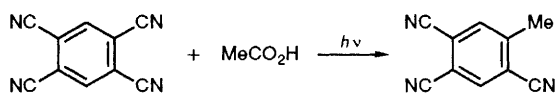
Irradiation of an acetonitrile solution of 1,2,4,5-tetracyanobenzene with aliphatic carboxylic acids gives 2,4,5-tricyanoalkylbenzenes efficiently; electron transfer from the carboxylic acids to the excited tetracyanobenzene is essential.

Photochemical alkylation with aliphatic carboxylic acids is an intriguing method not only in synthetic chemistry but also in mechanistic photochemistry. As a most promising candidate for the alkylation, an electron donor-acceptor (EDA) system is proposed in the photochemical reaction. The EDA-type photodecarboxylation of carboxylic acids has been explored by Davidson<sup>1</sup> and Libman.<sup>2</sup> The carboxylic acids used were limited to the acids having a  $\beta$ -heteroatom or an aromatic ring. No reports have described aliphatic carboxylic acids as having apparently behaved as electron donors in the photoreaction of EDA.

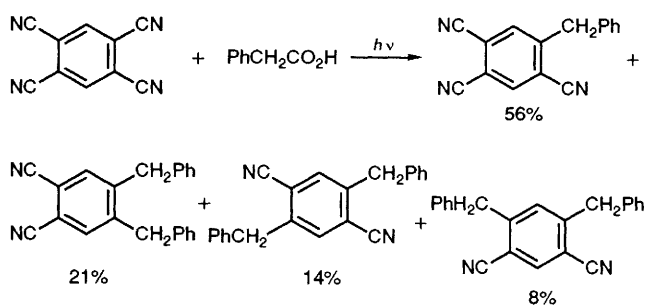
An acetonitrile solution (90 ml) of 1,2,4,5-tetracyanobenzene (TCNB, 1.0 mmol) with acetic acid (100 mmol) was irradiated with a 100 W medium-pressure mercury lamp for 2 h, under bubbling Ar at room temperature. After removal of the unconverted acetic acid with  $\text{Al}_2\text{O}_3$ , 2,4,5-tricyanotoluene (0.55 mmol) was isolated by preparative TLC. The quantum yield of the reaction was 0.1, determined by iron(III) oxalate actinometer, Scheme 1.

The possibility of the reaction of acetonitrile<sup>3</sup> competing with or overwhelming that with acetic acid, can be ruled out since no deuterium was incorporated in the 2,4,5-tricyanotoluene when  $[\text{D}_3]\text{acetonitrile}$  was used in place of acetonitrile. A similar reaction for the other carboxylic acid gave the

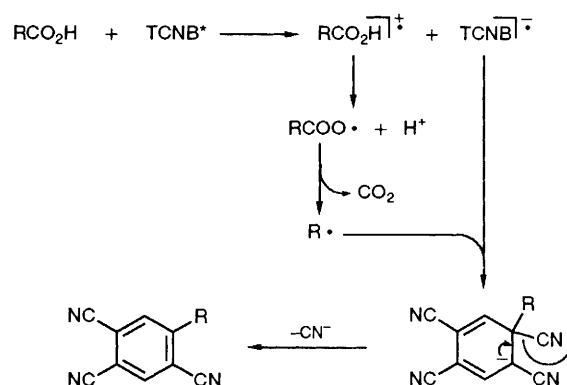
corresponding tricyanoalkylbenzene as well. The fluorescence of tetracyanobenzene was quenched by addition of carboxylic acid and the quenching constant,  $k_q\tau$ , together with the isolated yields and the  $\text{p}K_a$  values<sup>4</sup> of carboxylic acids in water are summarized in Table 1. In the case of phenylacetic acid, the other three kinds of products were also isolated as dibenzylidicyanobenzenes. The high reactivity of phenylacetic acid in this reaction seems to be related to its low value of  $\text{p}K_a$  and highly facile photoinduced-electron-transfer, Scheme 2. Trifluoroacetic acid could also react with the excited TCNB even if the value of  $k_q\tau$  was small, and the similar disubstitution products as observed in the case of phenylacetic acid were obtained. However, the reactivity of the excited TCNB with the aliphatic acid was not entirely determined by the magnitude of the  $k_q\tau$  values of the acid nor by the  $\text{p}K_a$  values. It is unlikely that the carboxylate generated from dissociation of the carboxylic acid is involved, since in acetonitrile even acetic acid shows the extremely high  $\text{p}K_a$  value<sup>5</sup> ( $\text{p}K_a = 22.3$ ). From the above results the alternative reaction mechanism is proposed as follows; single electron transfer from the neutral carboxylic acid to the excited TCNB resulting in the formation of both the anion radical of TCNB and the cation radical of carboxylic acid. The latter feasibly liberates a proton to give the alkyl radical and carbon dioxide. The generated alkyl radical can react with the anion radical of TCNB, followed by the elimination of cyanide anion from the alkylated TCNB anion, as shown in Scheme 3.



Scheme 1



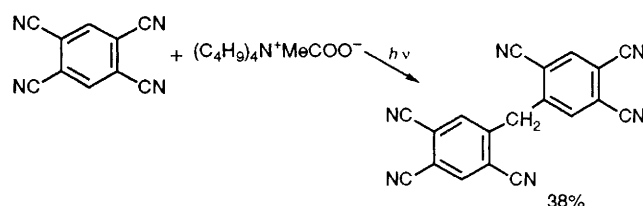
Scheme 2



Scheme 3

Table 1

Carboxylic acids	Isolated yields/%	$k_q\tau$	$\text{p}K_a$
Me	55	1.6	4.56
$\text{MeCH}_2$	22	3.2	4.67
$\text{Me}_2\text{CH}$	92	7.6	4.63
$\text{Me}(\text{CH}_2)_4$	38	12.4	4.63
$\text{Me}_3\text{C}$	73	14.4	5.01
$\text{PhCH}_2$	56	140	4.10
$\text{CF}_3$	11	0.02	0.3



Scheme 4

Concerning this new reaction, the following facts are also found: (i) With tetrabutylammonium acetate the excited TCNB did not give the methylated cyanobenzenes but furnished bis(2,4,5-tricyanophenyl)methane, whereas none of the diphenylmethane was obtained with tetrabutylammonium chloride, Scheme 4. (ii) The photoreaction of TCNB/MeCO<sub>2</sub>H was quenched by adding azoisobutyronitrile, although the reaction was accelerated in addition of small amount of sodium acetate.

The study of the detailed mechanism is now in progress.

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## References

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