CHEMISTRY LETTERS, pp. 1541-1542, 1989.

# [4+2] Cycloaddition of 3-Cyanocyclopropene with Anthracenes

Katsuhiro SAITO,* Satoru ISOBE, Kazuaki ITO,
Shinzo KAGABU,+ and Kensuke TAKAHASHI
Department of Applied Chemistry, Nagoya Institute of
Technology, Gokiso-cho, Showa-ku, Nagoya 466
+Department of Chemistry, Faculty of Education,
Gifu University, Yanagido, Gifu 501-11

The thermal reactions of 3-cyanocyclopropene with 9-substituted anthracenes afforded [4+2] cycloadducts. The relative rate ratio of the reaction correlated well with the substituent constants.

Cyclopropenes have been applied as efficient dienophiles to Diels-Alder reaction; however, cyclopropenes with functional group at the 3-position seem to have been limitedly employed and their detailed mechanistic studies have been rarely reported.1) We investigated the addition reaction of 3-cyanocyclopropene (2) with 9-substituted anthracenes (3) to clarify the mechanistic aspects through substituent effects. Here the results are discussed.

The generation and cycloaddition of 2 was carried out as follows;2) A mixture of 1 and three-molar equivalents of anthracene (3a) was heated at 200 °C for 24 h to give colorless crystals 4a in 55% yield. The similar reactions using 9-methyl- (3b), 9-chloro- (3c), 9-p-methylbenzoyloxy- (3d), and 9-cyanoanthracene (3e) afforded the corresponding adducts 4b, 4c, 4d, and 4e, in 52, 43, 40, and 10% yields, respectively (Scheme 1).

The IR and NMR spectral data of the cycloadducts are as follows:

4a: mp 259 °C; IR (KBr) 2250 $\text{cm}^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.61 (t, $H_a$), 2.15 (m, $H_b$, $H_c$), 4.54 (d, $H_d$), 7.1-7.4 (m, 8H); $J_{ab}$=3.1 Hz, $J_{bd}$=4.4 Hz.

4b: mp 122 °C; IR (KBr) 2230 $\text{cm}^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.54 (t, $H_a$), 1.80 (dd, $H_c$), 1.98 (s, 3H), 2.14 (m, $H_b$), 4.46 (d, $H_d$), 7.0-7.3 (m, 8H); $J_{ab}$= $J_{ac}$=3.1 Hz, $J_{bc}$=8.0 Hz, $J_{bd}$=4.4 Hz.

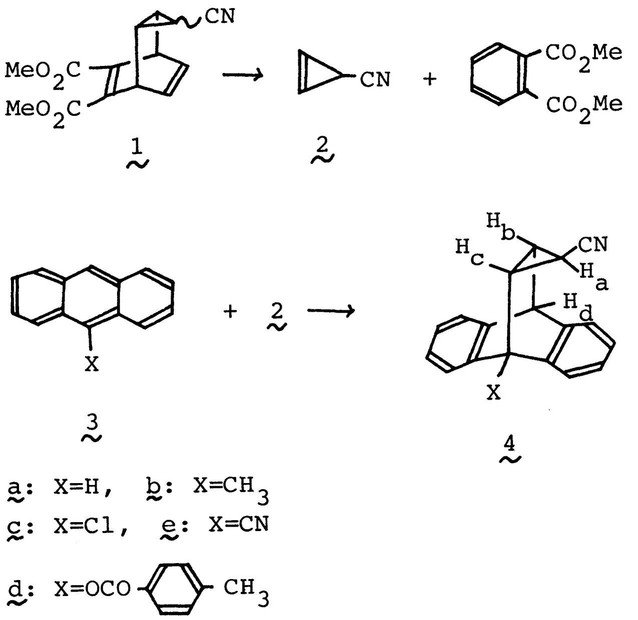
4c: mp 197 °C; IR (KBr) 2240 $\text{cm}^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.84 (t, $H_a$), 2.32 (m, $H_b$), 2.51 (dd, $H_c$), 4.57 (d, $H_d$), 7.1-7.8 (m, 8H); $J_{ab}$=$J_{ac}$=3.1 Hz, $J_{bc}$=8.0 Hz, $J_{bd}$=4.4 Hz.

4d: mp 282 °C; IR (KBr) 2255 $\text{cm}^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.14 (t, $H_a$), 2.40 (m, $H_b$), 2.50 (s, $CH_3$), 2.57 (dd, $H_c$), 4.60 (d $H_d$), 7.1-8.2 (m, 12H); $J_{ab}$=$J_{ac}$=3.1 Hz, $J_{bc}$=8.0 Hz, $J_{bd}$=4.4 Hz.

4e: mp 208 °C; IR (KBr) 2240 $\text{cm}^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.82 (t, $H_a$), 2.32 (m, $H_b$), 2.52 (dd, $H_c$), 4.64 (d, $H_d$), 7.2-7.7 (m, 8H); $J_{ab}$=$J_{ac}$=3.1 Hz, $J_{bc}$=8.0 Hz, $J_{bd}$=4.4 Hz.

The structures of 4 were determined on the basis of their spectral properties and confirmed by resemblance of the NMR spectra with those of the analogous compounds.[3] The coupling constant values (3.1 Hz) between vicinal protons $H_a$ and $H_b/H_c$ on the cyclopropane ring show trans relation of the protons.[4] The anti-configuration of the cyano group is evidenced by the fact that the chemical shifts of $H_a$ are influenced by the substituents on the anthracene moieties.

The relative rate ratios ($k_X/k_H$) of the reaction of 2 with the anthracenes 3a-3e were measured in similar way to our previous method.[5] The ratios of 1.00:2.81:0.62:0.37:0.17 for 3a:3b:3c:3d:3e show a fairly good linear relation of their logarisms ($\log k_X/k_H$) against Hammet's sigma values ( $\sigma_p$) (Fig. 1).[6] The result suggests that 2 adds to anthracenes synchronously with high stereofacial selectivity. The negative $\rho$ -value (-1.41) of the reaction is considered to reflects the interaction between LUMO of 3-cyanocyclopropene and HOMO of anthracenes.[7]



Scheme 1.

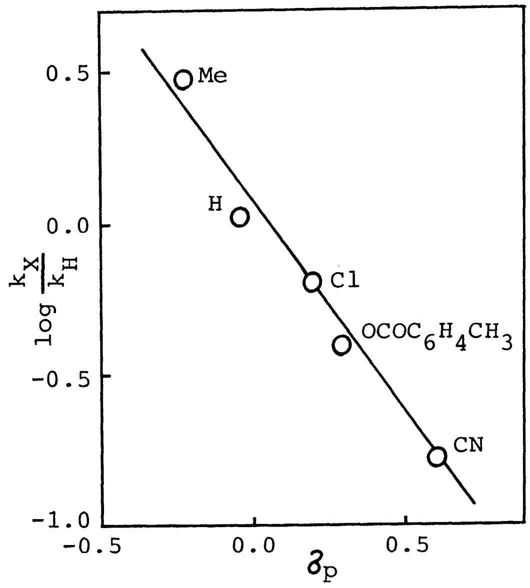


Fig. 1. Correlation of relative rate ratio with Hammet's $\sigma_p$

The authors are indebted to Professor H. Prinzbach for his kind suggestions.

References

1) B. Halton and M. G. Banwell, "The Chemistry of Functional Groups: Cyclopropenes," John Willey, Chichester (1987).
2) G. McMullen, G. Sedelmeier, H. Hildebrand. H. Fritz, and H. Printzbach, Tetrahedron Lett., 1979, 3847.
3) M. J. Goldstein and A. H. Gevirtz, Tetrahedron Lett., 1965, 4417; K. Alder, K. Kaiser, and M. Schumacher, Justus Liebigs Ann. Chem., 602, 80 (1957).
4) K. B. Wiberg, D. E. Birth, and P. H. Schertler, J. Org. Chem., 38, 378 (1973).
5) K. Saito, H. Ishihara, T. Murase, Y. Horie, and E. Maekawa, Bull. Chem. Soc. Jpn., 60, 4317 (1987).
6) H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 79, 1915 (1957).
7) The nearly same $\rho$ -value has been evaluated for the cycloaddition between 1-(p-substituted phenyl)-1,3-butadiene and maleic anhydride.
P. V. Alston and R. M. Ottenbrite, J. Org. Chem., 39, 1584 (1974); J. Sauer and R. Sustmann, Angew. Chem., Int. Ed. Engl., 19, 779 (1980).

(Received May 20, 1989)