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Preference of an Unusual Pathway in the Formation of 8,8-Dicyano-2,3-benzoheptafulvene from the Reaction of 2,3-Benzotropone with Malononitrile

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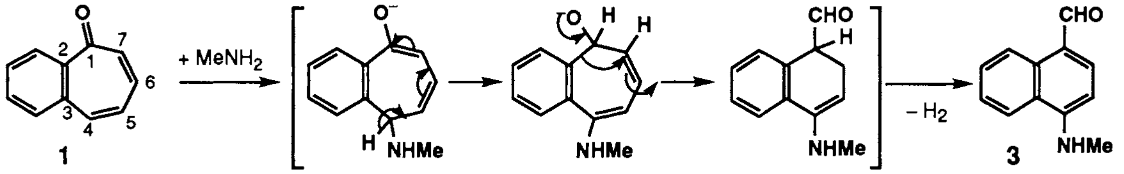
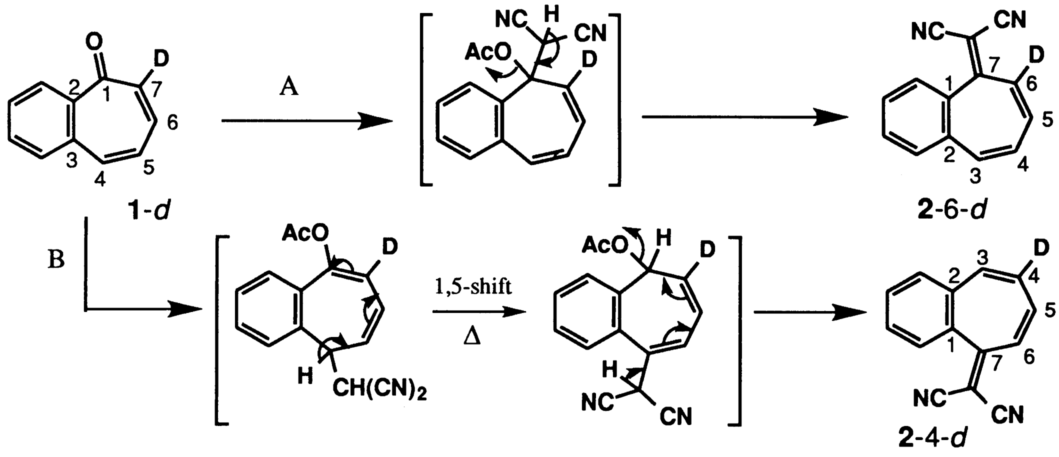
Deuterium tracer experiment clarifies that the condensation reaction of 2,3-benzotropone with malononitrile forms 8,8-dicyano-2,3-benzoheptafulvene via reaction paths involving the preference of an abnormal (Michael type) attack of the nucleophile at the C-4 position to a normal (Knoevenagel type) attack at the C-1 position .

Tropone1) and 2,3-benzotropone2) (**1**) react with malononitrile in refluxing acetic anhydride to give 8,8-dicyanoheptafulvene3) and its 1,2-benzo derivative,4) **2**, respectively. It seems on the surface that these heptafulvenes are formed by the normal attack of the nucleophile at the carbonyl carbon position, since 2,7-dimethyl tropone gives the corresponding 1,6-dimethyl-8,8-dicyanoheptafulve.3b,5) During our recent study on chemical reactivity of 8,8-dicyanoheptafulvene,6) we need to prepare the compound **2**. Based on an SCF-MO calculations7) on the reactivity of **1**, we have become aware that the formation of **2** may result through reaction paths involving the preference of the nucleophile for an abnormal attack at C-4 position to a normal addition at the carbonyl carbon (C-1) position. To examine this idea we tried the reaction of **1** with a nucleophilic reagent.

We have found that oxidative amination of **1** with methylcopperamine sulfate in aqueous methylamine at room temperature affords 4-methylamino-1-naphthalenecarbaldehyde8) (**3**) with a trace amount of 4-methylamino-2,3-benzotropone8) (**4**). These two products show that they are formed by the nucleophilic attack at the C-4 position of the substrate **1** as the following scheme.



From the above experimental fact and MO theoretical result, we expected that the formation of **2** from the reaction between **1** and malononitrile might involve an abnormal attack of the nucleophile at the C-4 position. To make clear the formation pathways of **2**, we performed the deuterium tracer experiment using [7-^{2}H]-2,3-benzotropone9) (**1**-*d*) (isotopic purity: $^{2}H_{1}$, 98.0%; $^{2}H_{0}$, 1.9%, by mass spectrometry) instead of **1** in acetic anhydride10) at 110 °C giving the deuteriated product (isotopic purity: $^{2}H_{1}$, 96.3; $^{2}H_{0}$, 3.6%) as red crystals of mp 154 °C in 36% yield. Spectroscopic analysis showed that the product was a mixture of [6-^{2}H]-8,8-dicyano-1,2-benzoheptafulvene (**2**-6-*d*) and [4-^{2}H]-isomer (**2**-4-*d*) in the ratio of 44:56. The relative percentage were obtained by the integration of ^{1}H NMR signals. This result of deuterium tracer experiment shows that **2** is



produced not only by path A (normal attack of Knoevenagel-type addition), but also by path B (abnormal attack of Michael-type addition followed by thermally allowed sigmatropic 1,5-shift). It should be noticed that the formation of **2**-4-*d* resulting from the preference in the approximate ratio of 3:2 for the abnormal attack of the nucleophile at the C-4 position of **1**-*d* to the normal attack at the carbonyl carbon.[11]

References

1) T. Machiguchi, *Synth. Commun*, **12**, 1021 (1982) and references therein.

2) T. Machiguchi, S. Ebine, and M. Hoshino, *Yuki Gosei Kagaku Kyokai Shi*, **29**, 1077 (1971).

3) a) Y. Kitahara and K. Doi, Japan Kokai, 13071 (1962); *Chem. Abstr.*, **59**, 9914f (1963); b) M. Oda, M. Funamizu, and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **42**, 2386 (1969).

4) Y. Sugimura, K. Iino, H. Kuwano, N. Soma, and Y. Kishida, *Chem. Pharm. Bull.*, **20**, 2515 (1972).

5) It has been known that nucleophilic reactions of tropones take place at the position of C-1, C-2, C-3, or C-7.

6) T. Machiguchi, S. Yamabe, T. Minato, T. Hasegawa, and T. Asao, *J. Am. Chem. Soc.*, **115**, 1669 (1993).

7) π-Electron density, frontier electron density and superdelocalizability [K. Fukui, *Bull. Chem. Soc. Jpn.*, **34**, 230 (1961)], and atom stabilization energy (T. Nakajima, *J. Chem. Phys.*, **1955**, 587) were examined.

8) **3**: Yellow needles, mp 53 °C, IR ν_{max} (KBr) 1634, 1620, and 1590 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.20 (s, 3H), 6.95 (d, 1H, J=8.3 Hz), 7.25 (d, 1H, J=8.3 Hz), 7.10–7.75 (complex m, 3H), 8.32 (dm, 1H, J=8.0 Hz), 8.90 (br s, 1H), and 9.75 (s, 1H). Hydrogenation of the compound **3** over platinium on charcoal led to 4-methylamino-1-naphthylmethanol: colorless liquid, ^1H NMR δ 2.83 (s, 3H), 4.11 (br s, 2H), 4.73 (s, 2H), 7.15 (d, 1H, J=8.3 Hz), 7.41 (d, 1H, J=8.3 Hz), and 7.3–8.2 (complex m, 4H). **4**: Pale yellow oil, M^+ m/z 185.0854 (Calcd for $C_{12}H_{11}NO$, 185.0840), IR ν_{max} (neat) 1656 and 1580 cm^{-1}, ^1H NMR ($CDCl_3$) δ 6.63 (H-5), 7.26 (H-6), 7.25 (H-7) in ABX pattern ($J_{6,7}$=12.0, $J_{5,6}$=8.2, $J_{5,7}$=0.6 Hz).

9) The deuteriated compound **1**-*d* was synthesized starting from 2,3-benzocycloheptanone (Ref. 2) using deuterium oxide (isotopic purity: 99.8%) and anhydrous sodium carbonate.

10) Acetic anhydride was used to promote the dehydration of intermediates in this reaction. The solvent used for the reaction was purified according to a literature method [D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," 2nd ed, Pergamon Press, Oxford (1980), p 77].

11) In our opinion the present result may suggest the possibility that the parent tropone has been received a Michael-type attack of the nucleophile in the formation of 8,8-dicyanoheptafulvene in Ref. 3.

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