The Reaction of 8-Cyanoheptafulvene with Benzyne

Masaji ODA and Yoshio KITAHARA

Department of Chemistry, Faculty of Science, Tohoku University, Sendai

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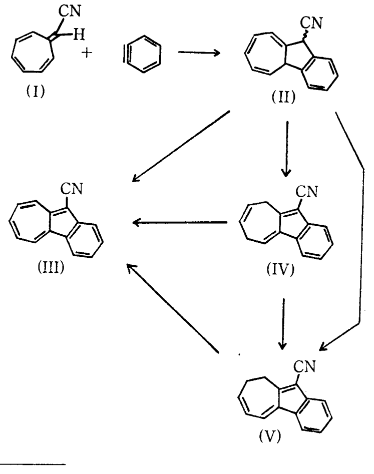
Heptafulvene and 8-monosubstituted heptafulvenes[1-3] undergo 8+2 cycloadditions when dimethyl acetylenedicarboxylate is used as a dienophile leading to azulene derivatives. We wish now to report a similar cycloaddition of 8-cyanoheptafulvene (I) using benzyne.

The refluxing of (I) and benzenediazonium-2-carboxylate[4] (1.2 equiv.) in methylene chloride for 70 min yielded a 1 : 1 addition product (II) in a 36% yield (based on 22% recovered I) on separation by silica-gel chromatography. Although the stereochemistry at C-3 is not yet certain, the sturcture was proved to be a 1,8-cycloaddition product, 1,2-benzo-3-cyano-3,9-dihydroazulene, from the following spectral and chemical evidence; *m/e* 205(M^+); ν_{max} (film) 3050 (w), 3020 (w), 2250 (w), 1610 (w), 750 (s) and 715 (s) cm^{-1}; λ_{max} (cyclohexane)251 (sh, log ε 3.75), 258 (3.80) and 265 nm (sh, 3.76); τ (CCl_4, TMS) 2.50—2.90 (m, 4H, aromatic), 3.38 (m, 3H, H-4∼6), 3.85 (m, 1H, H-7), 4.87 (dd, *J*=9.5 and 4.0 Hz, 1H, H-8), 4.98 (br. s., 1H, H-3) and 6.41 (br., 1H, H-9). On dehydrogenation with *o*-chloranil (refluxing benzene, 15 min), II gave 1,2-benzo-3-cyanoazulene[5] (III), (mp 153—154°C) in a 63% yield.



Compound II is liable to be isomerized to more conjugated systems by the presence of an active hydrogen at C-3. Therefore, on delayed elution from a silica-gel column, II suffered double-bond migration to give mainly 1,2-benzo-3-cyano-4,7-dihydroazulene (IV) as yellow prisms; mp 88—89°C; ν_{max} (KBr), 3040 (w), 2225 (m), 1629 (m) 1603 (w), 1557 (w), 762 (s) 733 (m) and 710 $(m)^{-1}$; λ_{max} (EtOH) 267 (log ε 4.30), 328 (3.71) and 372 nm (sh 3.45); τ (CCl_4, TMS) 2.50—3.00 (m, 5H, aromatic and H-8), 4.06 (m, 2H, H-5 and H-6), 6.51 (d-like, 4.0 Hz, 2H, H-4a and 4b) and 6.85 (t-like, 2H, H-7a and 7b). The IR and NMR spectra indicate the presence of a conjugated cyano group, an isolated double bond (from the chemical shifts and the pattern of the signals), and two kinds of doubly-allylic methylene groups. As is to be expected from the structure of IV, on treatment with triethylamine it suffered further migration of the double bond to give, quantitatively, the most conjugated isomer, 1,2-benzo-3-cyano-4,5-dihydroazulene (V), as orange needles; mp 69—70°C; ν_{max} (KBr) 3050 (w), 3010 (w), 2220 (m), 1632 (w), 1603 (w), 1577 (m), 1551 (m), 768 (s), 759 (s), 729 (s) and 710 (s) cm^{-1}; λ_{max} (EtOH) 216 (log ε 4.42), 259 (4.00), 2.66 (3.97), 295 (3.70) and 377 nm (3.95); τ (CCl_4, TMS) 2.50—3.10 (m, 5H, aromatic and H-8), 3.75 (m, 2H, H-6 and H-7), 7.10 (m, 2H, H-4a and 4b) and 7.58 (m, 2H, H-5a and 5b). In the NMR spectrum, two methylene groups, at C-4 and C-5, are assigned as above by the double resonance technique, the former being affected paramagnetically by the cyano group. Compound (V) was also rightly obtained from II with triethylamine. The dehydrogenation of IV and V also gave III; this fact further supports the above assignments.

Thus, in contrast to the results with tropone,[6] compound (I) afforded exclusively an 8+2 cycloadduct (II), and no trace of a 4+2 cycloadduct.

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