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1,2-HOMOHEPTAFULVENE: SYNTHESIS AND CYCLOADDITION

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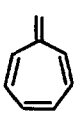
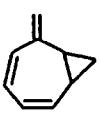
Summary: 1,2-Homoheptafulvene (2) was synthesized and reacted with 4-phenyl-1,2,4-triazoline-3,5-dione to yield [4π + 2π] and [6π + 2σ + 2π] cycloadducts.

Heptafulvene (1) has been synthesized by Doering[1] and later by Zimmerman[2] and by Neuenschwander[3] as an unstable polyolefinic hydrocarbon, and has been know to react with dienophiles to yield [8π + 2π] cycloadducts.[1, 4] However, 1,2-homoheptafulvene (2) is unknown compound although 8,8-disubstituted derivatives such as 8,8-dicyano- and 8,8-diphenyl-1,2-homoheptafulvenes have recently been synthesized.[5]



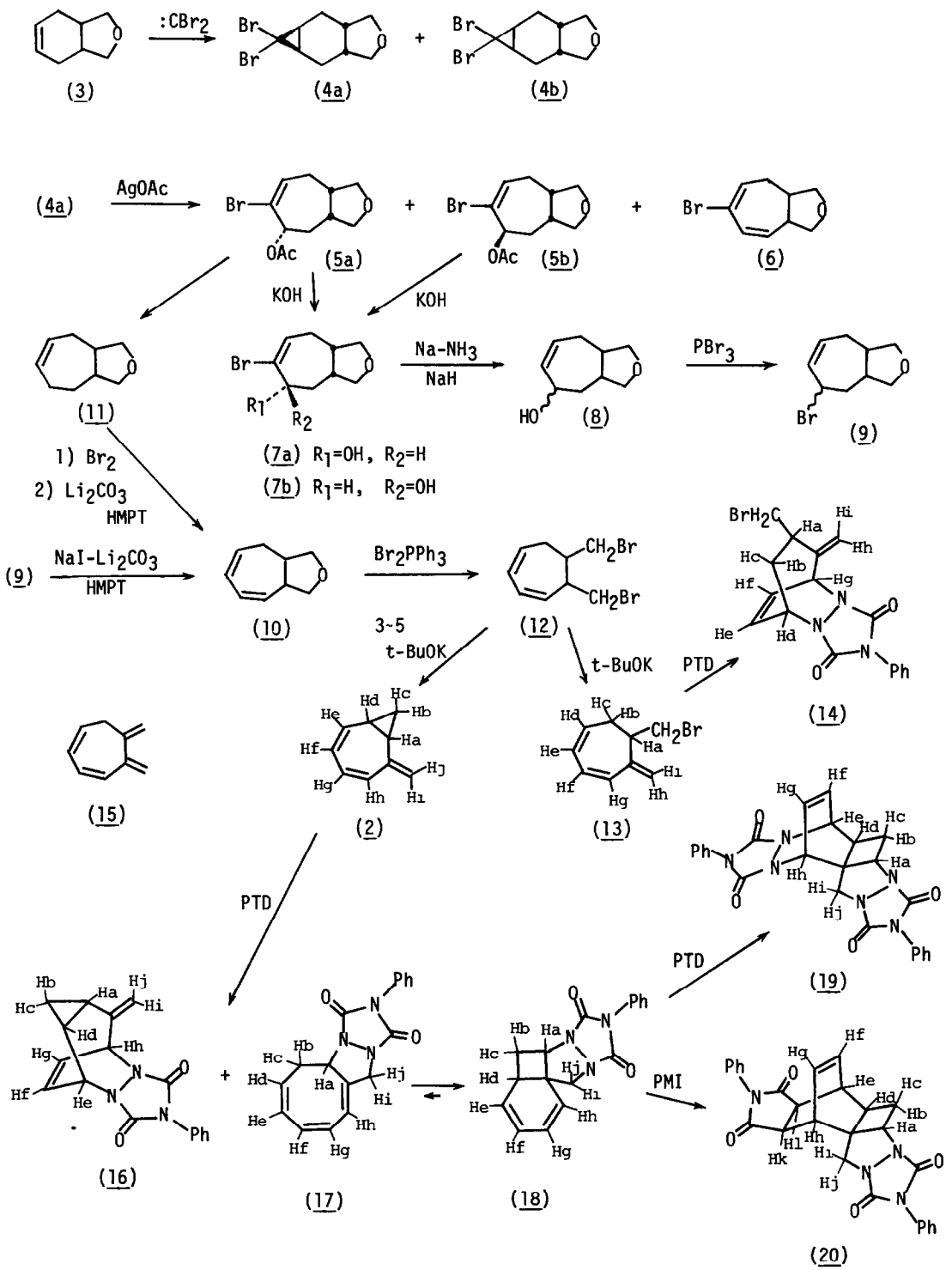
(1)



(2)

We succeeded to synthesize 1,2-homoheptafulvene starting from 8-oxabicyclo[4.3.0]-3-nonene (3), and found that it reacted with dienophile to give cycloadducts by the modes of [4π + 2π] and [6π + 2σ + 2π]. The results are reported in this paper.

The reaction of 3 with large excess of dibromocarbene generated from bromoform and t-BuOK in hexane afforded two stereoisomeric adducts (4a, 70~80%, mp 98.5~100.5°) and (4b, 2%, mp 41.5~42.5°).[6, 7] Treatment of the major adduct (4a) with silver acetate in refluxing acetic acid gave ring enlargement products (5a, 61%, mp 98.5~100.5°), (5b, 36%, mp 65~66°) and (6, 2%, oil).[8] Hydrolyses of 5a and 5b with alcoholic KOH afforded the corresponding bromoalcohols (7a, mp 89~90°) and (7b, mp 64~65°) in 95% yields, respectively. Birch reduction of a mixture of the bromoalcohol with sodium in liquid ammonia in the presence of sodium hydride afforded a


:CBr2
(3)
(4a)
(4b)
AgOAc
(5a)
(5b)
(6)
KOH
KOH
Na-NH3
NaH
PBr3
(11)
(8)
(9)
(7a) R1=OH, R2=H
(7b) R1=H, R2=OH
1) Br2
2) Li2CO3
HMPT
NaI-Li2CO3
HMPT
Br2PPh3
(10)
(12)
3~5
t-BuOK
t-BuOK
PTD
PTD
PTD
PMI
(14)
(15)
(2)
(13)
(19)
(16)
(17)
(18)
(20)

stereoisomeric mixture of alcohol (8, 30~45%, oil bp 85~95°/5 mm), treatment of 8 with PBr_3 in anhydrous ether yielded a bromide (9, 50~70%, mp 58~59°), which was dehydrobrominated with NaI-Li_2CO_3 in HMPT to afford 8-oxabicyclo[5.3.0]-2,4-diene (10, 65~72%, oil bp 92~95°/45 mm).

Compound (10) was also obtained by an alternative route. Thus, Birch reduction of a mixture of 5a and 5b afforded monoene (11, 42%, oil bp 95~105°/45 mm), whose bromination in CCl_4 followed by dehydrobromination with Li_2CO_3 in HMPT afforded the diene (10, 45~50%).

Reaction of 10 with Br_2PPh_3 in chlorobenzene at 90°C gave 5,6-bisbromomethylcyclohepta-1,3-diene (12, 40~50%, oil). Reaction of 12 with equimolar amount of t-BuOK in THF afforded 1-bromomethyl-1,2-dihydroheptafulvene (13, 48%, colorless oil) accompanying a recovery of 12 (19%). The compound (13) reacted with 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) to give [$4\pi + 2\pi$] cycloadduct (14, mp 178~181°).

The dehydrobromination of 12 using 3~5 molar equivalents of t-BuOK in DMSO or THF followed by chromatographic separation on silica gel using pentane as solvent yielded 1,2-homoheptafulvene (2, 54%) as a moderately thermally stable but air sensitive colorless oil, and 1,2-dimethylene-cyclohepta-3,5-diene (15) did not form at all. The structure of 2 was determined by NMR analysis (Table 1) and by cycloaddition with PTD, and furthermore the compound was found to differ from 15 synthesized by other route.[9] Electronic spectrum of 2 shows maxima at 215 nm (ε 3,900) and 299 nm (ε 2,350), and is completely different from that of heptafulvene (1) which shows maxima at 370~580 nm (ε 100~500) with fine structure as well as at around 280 nm (ε ca. 13,000).[1~3]

1,2-Homoheptafulvene (2) reacted with PTD to give 1 : 1 adducts (16, 32%, mp 205~210°(d)) and (17, 20%, mp 123~125°). The compounds (16) and (17) were determined to be [$4\pi + 2\pi$] and [$6\pi + 2\sigma + 2\pi$] cycloadducts, respectively, as shown in scheme by NMR analysis (Table 1). ^{1}H-NMR of 16 shows cyclopropane ring protons at 0.76~1.13 (2H) and 1.58~1.83 ppm (2H). However, the NMR of 17 does not show signals at higher than 2 ppm, and there appears instead a pair of signals at 2.57 and 3.00 ppm with a large coupling of J = 18.5 Hz for the hydrogen atoms which originated from the cyclopropane ring.

A solution of 17 in chloroform or benzene gradually changed to tetracyclic valence isomer (18) although the compound could not be obtained in pure crystalline state. The mixture of 17 and 18, enriched with 18 by standing for a week, reacted with PTD and N-phenylmaleinimide (PMI) to give further [$4\pi + 2\pi$] cycloadducts (19, 66%, mp 201~209°(d)) and (20, 68%, mp 308~309°), respectively.

Spectroscopic data of 2, 13, 14, and 16~20 are shown in Table 1.

Further studies on physical and chemical properties of 2 are now in progress.

Table 1. Spectroscopic Data of 2, 13, 14, and 16~20.

Compounds	Spectroscopic Data [NMR (90 MHz); δ ppm (J in Hz)]
2	IR (CCl_4); 1640, 1595, 1570, 870 cm^{-1}, UV λmax (hexane); 215 nm (ε 3,900), 299 nm (ε 2,350), NMR (CCl_4); 1.2~1.6 (m, Hb,c,d), 2.05 (t,d, J=8, 8, Ha), 4.85 (d, J=2, Hi or Hj), 5.08 (d, J=2, Hj or Hi), 5.3~5.6 (m, olefinic 2H), 5.8~6.2 (m, olefinic 2H)
13	NMR (CCl_4); 2.7~3.1 (m, Ha,b,c), 3.20 (d,d, J=10, 5, CHBr), 3.44 (t, J=10, CHBr), 4.99 (bs, Hh or Hi), 5.03 (bs, Hi or Hh), 5.55~6.0 (m, Hd,e,f), 6.11 (bd, J=11, Hg)
14	NMR ($CDCl_3$); 1.88 (d,d,d, J=12.5, 11, 2, Hb), 2.41 (d,d,d, J=12.5, 6, 6, Hc), 2.72 (m, Ha), 3.61 (m, CH_2Br), 5.11 (d, J=1, Hh or Hi), 5.19 (d, J=1, Hi or Hh), 5.33 (d,d, J= 4.5, 3, Hd), 5.40 (bs, Hg), 6.39 (d,d,m, J=5, 4.5, He,f), 7.2~7.6 (m, aromatic 5H)
16	NMR ($CDCl_3$); 0.76~1.13 (m, Hb,c), 1.58~1.83 (m, Ha,d), 5.07 (bd, J=6.5, He), 5.11 (bs, Hi or Hj), 5.18 (bs, Hj or Hi), 5.39 (m, Hh), 6.04 (d,d,d, J=8.5, 6.5, 1, Hf or Hg), 6.26 (d,d,d, J=8.5, 6.5, 1, Hg or Hf), 7.3~7.6 (m, aromatic 5H)
17	NMR ($CDCl_3$); 2.57 (d,d,d, J=18.5, 11, 4, Hb), 3.00 (d,d,d, J=18.5, 4, 2, Hc), 4.26 (d,d,d, J=14, 2.5, 1, Hi), 4.61 (d,d, J=14, 1.5, Hj), 5.13 (d,d, J=11, 4, Ha), 5.75~6.2 (m, olefinic 5H), 7.2~7.6 (m, aromatic 5H)
18	NMR ($CDCl_3$); 2.65 (m, Hb,c), 3.1 (m, Ha), 3.24 (d, J=10, Hi), 3.95 (d, J=10, Hj), 4.85 (m, Hd), 5.50 (bd, J=9, Hh), 5.55~6.2 (m, He,f,g), 7.2~7.6 (m, aromatic 5H)
19	NMR (Py-d_5); 1.76 (d,t, J=14, 6.5, Hb or Hc), 2.20 (d,d,d, J=14, 9, 4, Hc or Hb), 2.94 (m, Hd), 3.91 (d, J=11, Hi), 4.18 (d, J=11, Hj), 4.25 (d,d, J=6.5, 4, Ha), 5.04 (m, He,h), 6.53 (m, Hf,g), 7.2~7.6 (m, aromatic 10H)
20	NMR (Py-d_5); 1.76 (d,t, J=13.5, 6.7, Hb or Hc), 2.14 (d,d,d, J=13.5, 8.6, 3.6, Hc or Hb), 2.56 (m, Hd), 3.22 (bs, Hk,l), 3.42 (m, He,h), 3.92 (d, J=10, Hi), 4.17 (d, J=10, Hj), 4.25 (d,d, J=6.7, 3.6, Ha), 6.38 (m, Hf,g), 7.25~7.6 (m, aromatic 10H)

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5) M. Oda, private communication.
6) All new compounds gave satisfactory elemental analyses and/or correct mass spectra.
7) The stereochemistry was determined by NMR analysis using shift reagent.
8) The stereochemistry was tentatively assigned by NMR analysis using shift reagent.
9) M. Oda, N. Morita, and T. Asao, to be published.

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