

SYNTHESES OF CONDENSED HEPTAFLUVENE AND 3H-BENZ[c,d]AZULEN-3-ONE DERIVATIVES

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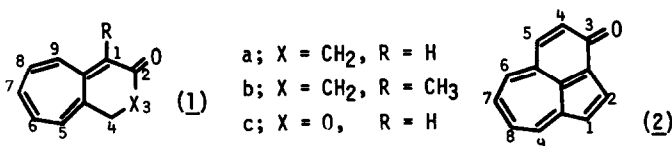
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Many studies on the heptafulvene have appeared, in spite of the most of which were concerning the monocyclic ones.² Heptafulvenes condensed at 1- and 8-positions such as 1 are interested in the following two points: 1) restriction of a rotation around 1,9a-bond may rise a stability of the heptafulvene system, 2) the compound can be led to polycyclic compounds such as 3H-benz[c,d]azulen-3-one (2) by cycloaddition with dienophiles at 1,9-position.³ The compound (2) is interested in the field of non-benzenoid aromatic compound as an isomeric phenalenone although several derivatives have been synthesized.⁴

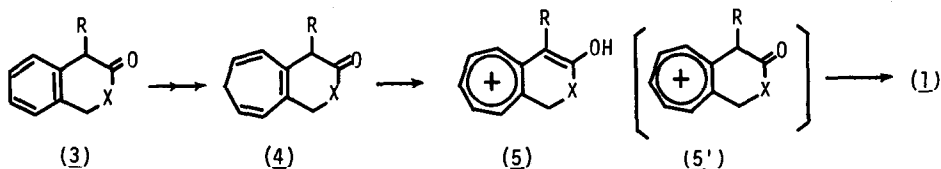


We have synthesized the compounds (1) as moderately stable compounds and have also derived to the derivative of 2, the results will be reported in this paper.

2H-3,4-Dihydrobenzocycloheptatriene-2-one (1a) was synthesized as follows. Ring expansion of β -tetralone ethylene ketal with carbene produced from diazomethane and cuprous chloride followed by hydrolysis of ketal with acid gave tetramethylenecycloheptatrienone (4a). Since the compound (4a) could not be separated from unreacted β -tetralone (3a), the mixture was submitted to hydride abstraction with triphenylmethyl tetrafluoroborate to give a tropylium ion (5a), which could be separated from β -tetralone. The spectroscopic evidence of 5a, ir showed no carbonyl band and nmr in CF₃COOH showed a olefinic signal at δ 6.47 ppm, indicates the compound exists as an enol form (5a) rather than a keto form (5'a). Deprotonation of 5a with triethylamine in methylene chloride at 0°C and subsequent purification by column

chromatography on silica gel afforded 1a in 45% yield from 5a, which is stable on standing in the air at room temperature for several days.

The facts that the chemical shift of seven membered ring protons of 1a in CDCl_3 , δ 6.32 ppm, showed down field shift of 0.14 ppm from that of 8-acetylheptafulvene,⁵ and that the compound (1a) is much more stable than 8-acetylheptafulvene, must be attributable to a coplanarity of seven membered ring and carbonyl group.

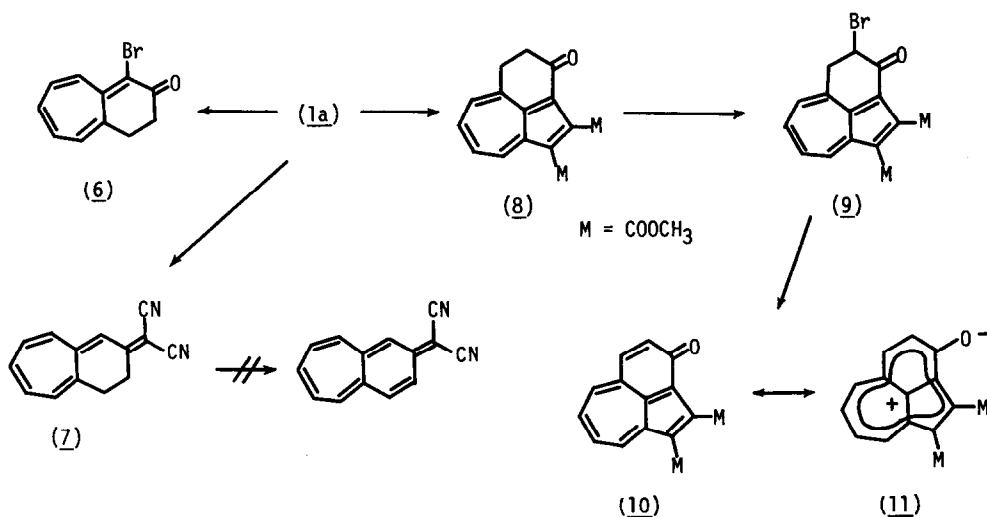


1-Methyl derivative (1b) and 2H-3,4-dihydro-3-oxabenzocycloheptatriene-2-one (1c) were synthesized by the similar procedure for 1a starting from 1-methyl- β -tetralone (3b) and 4,5-benzo-3,6-dihydro-2-pyrone (3c), respectively. The compound (1b) is unstable, whereas 1c is fairly stable in the air at room temperature. Uv spectra of 1a-c show maxima around 360 nm and tailing to visible region similar to those of 8-acetyl-,⁵ 8-formyl-⁶ and 8-ethoxycarbonyl-heptafulvenes.⁶

The compound (1a) easily undergo bromination with NBS to give unstable 1-bromo derivative (6), and 1a also reacted with malononitrile in the presence of triethylamine in methylene chloride to yield dicyanomethylene derivative (7).⁷ However, dehydrogenation of 7 leading to a fully conjugated system resulted in the formation of resinous products. The reaction of 1a with dimethyl acetylenedicarboxylate in refluxing xylene afforded an azulene derivative (8) in low yield which must be formed by the initial [8 + 2] cycloadduct followed by dehydrogenation. Bromination of 8 with NBS yielded an unstable monobromide (9) whose dehydrobromination with triethylamine afforded a fully conjugated compound, dimethyl 3H-benz[c,d]azulen-3-one-1,2-dicarboxylate (10)

Ir of the compounds (8) and (10) show carbonyl bands of C-3 position at 1660 and 1620 cm^{-1} , respectively, which indicate a dipolar structure. (11) would largely contribute to the compound (10).

Physical properties of the products are shown in Table 1.



References and Footnotes

- 1) Present Address: Department of Chemistry, College of General Education, Tohoku University, Kawauchi, Sendai 980 Japan.
- 2) Hydroxy and benzo derivatives of 2 have been synthesized from azulenes; W. K. Gibson, D. Leaver, J. E. Roff and C. W. Cumming, *Chem. Commun.*, 214 (1967); T. Abe, T. Morita and K. Takase, *Tetrahedron Letters*, 4755 (1973); 3621 (1974).
- 3) Cf. Recent Reviews; Y. Kitahara and M. Oda, "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," *The Jerusalem Symposia on Quantum Chem. and Biochem.*, III, Jerusalem 1971; F. Pietra, *Chem. Rev.*, 73, 293 (1973); T. Nozoe and I. Murata, *MTP Intern. Rev. of Sci., Org. Chem.*, Ser. I, Vol. 3, Edit. by H. Zollinger, p. 201 (1973), Butterworths, London.
- 4) Cycloaddition of heptafulvenes has been studied; W. von E. Doering and D. W. Willy, *Tetrahedron*, 11, 183 (1960); M. Oda, H. Tani and Y. Kitahara, *Chem. Commun.*, 739 (1969); M. Oda and Y. Kitahara, *Bull. Chem. Soc. Japan*, 43, 1920 (1970); *Synthesis*, 367 (1971).
- 5) K. Hafner, *Angew. Chem.*, 75, 1041 (1963); *Angew. Chem. Intern. Edit.*, 3, 165 (1964); M. Oda and Y. Kitahara, unpublished result.
- 6) M. Oda and Y. Kitahara, *Chem. & Ind.*, 920 (1969).
- 7) Uv spectra of 7 is similar to 8-(β,β -dicyanovinyl)heptafulvene; C. Jutz, *Chem. Ber.*, 97, 2050 (1964).

Table 1. Physical properties of the products.

Compound	Color mp(°C)	Uv λ_{\max} (log ϵ)	Nmr δ ppm (J in Hz)	molecular ion at m/e
<u>5a</u>	brown solid 80-81	[a] 239(4.25) 298(3.65) 374(3.35) 430(3.30)	[d] 2.96(t, 2H) 3.53(t, 2H) 6.47 (s, 1H) 7.29(m, 1H) 8.02 (m, 5H)	
<u>5c</u>	greenish yellow solid 106-107	[a] 233(4.50) 285(sh 3.60) 290(3.65) 300(sh 3.45)	[d] 4.65(s, 2H) 6.00(s, 2H) 9.15 (s, 5H)	
<u>1a</u>	red cryst. 50-51	[b] 231(4.12) 370(4.13)	[e] 2.37-2.44(m, 2H) 2.72-2.77 (m, 2H) 5.58(s, 1H) 6.32 (m, 5H)	158
<u>1b</u>	red oil	[b] 240(4.03) 365(4.29)	[e] 1.80(Me) 2.60(m, 4H) 6.35 (m, 5H)	172
<u>1c</u>	red needles 109-110	[b] 355(4.35)	[e] 4.77(s, 2H) 5.42(s, 1H) 6.38 (m, 5H)	160
<u>6</u>	red oil	[b] 382*	[e] 2.72(m, 4H) 6.51(m, 4H) 7.01 (m, 1H)	
<u>7</u>	dark red solid 139-140	[b] 252(3.94) 276(4.06) 283(sh 4.04) 463 (4.48)	[e] 2.73(m, 4H) 6.39(s, 1H) 6.58 (m, 5H)	206
<u>8</u>	purple needles 187	[b] 243(4.60) 285(4.62) 300(4.53) 308(4.54) 338(3.99) 368(4.01) 510(3.23)	[e] 2.90(m, 4H) 3.95(Me) 4.10 (Me) 7.85(m, 4H)	298
<u>10</u>	blue needles 153-154	[c] 286(4.43) 295(4.39) 355(3.64) 374(3.83) 395(3.83) 580(3.12)	[e] 3.90(Me) 4.08(Me) 6.88(d J= 9.8 1H) 7.62(d J=9.8 1H) 8.06(m, 3H) 9.73 (m, 1H)	296

[a] in conc. H_2SO_4 , [b] in CH_2Cl_2 , [c] in CH_3CN , [d] in CF_3COOH , [e] in $CDCl_3$

* Accurate intensity could not be measured because of its instability.