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SYNTHESIS AND SOME PROPERTIES OF 8,8'-DIHEPTAFULVENYL KETONE

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8,8'-Diheptafulvenyl ketone has been synthesized, and its uv, ir, and nmr spectra were demonstrated, from which it can be concluded that a dipolar structure would largely contribute for the ground state. Some chemical properties of the compound has also been studied.

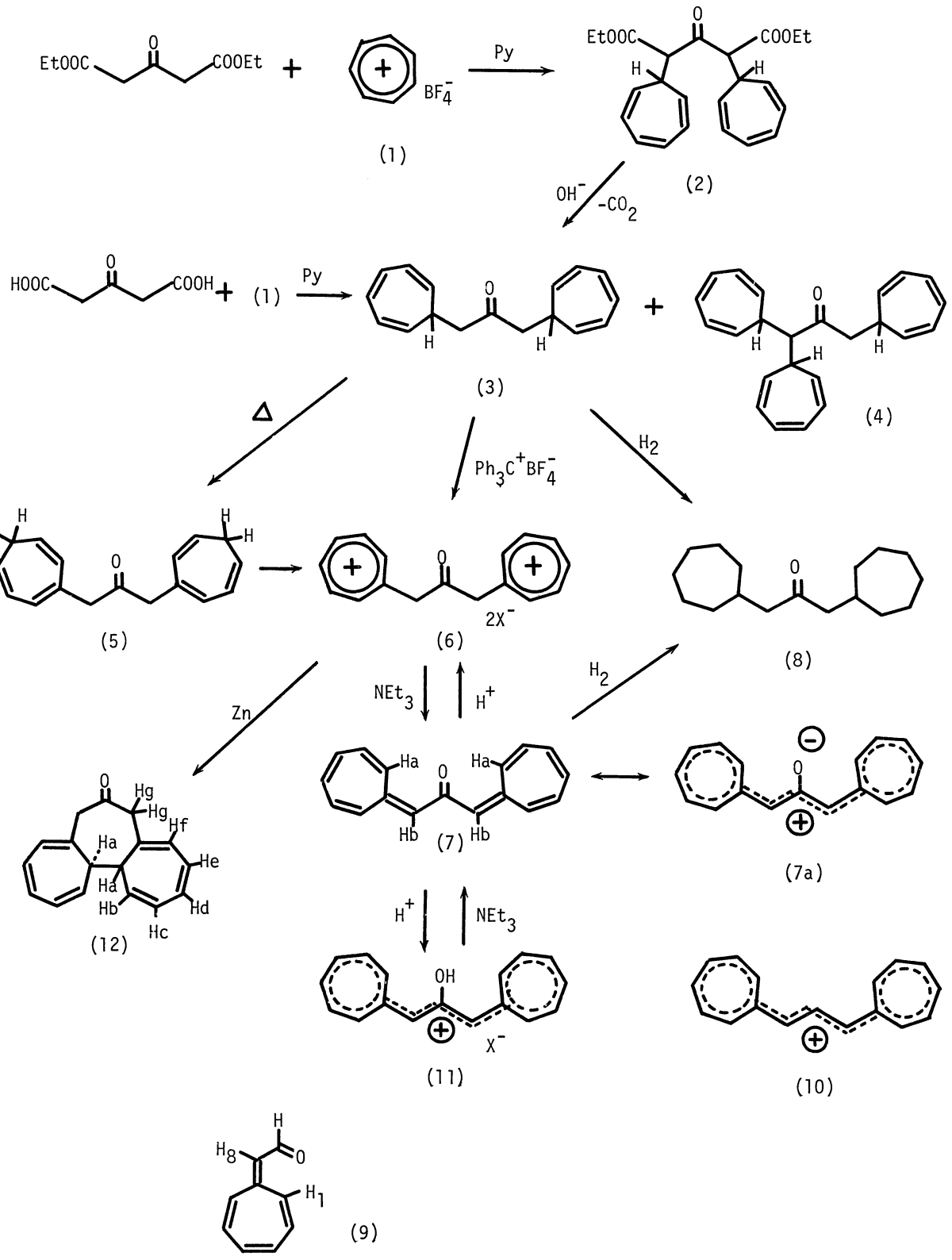
As a part of the investigation of the difulvenyl derivatives,[1] we synthesized 8,8'-diheptafulvenyl ketone, and studied some of its chemical properties, the results of which will be reported herein.

Reaction of two equivalents of tropylium tetrafluoroborate (1) with diethyl acetonedicarboxylatein pyridine afforded an oily diethyl 1,3-bis(cycloheptatrienyl)acetonedicarboxylate (2),[2] in 74% yield. Alkaline hydrolysis of (2) in aqueous ethanol yielded 1,3-bis(cycloheptatrienyl)acetone (3), m.p. 85~86°C, involving decarboxylation, in quantitative yield. The compound (3) was also obtained (21.6%) in one step by the reaction of (1) with acetonedicarboxylic acid in pyridine accompanied with 15.3% of 1,1,3-tris(cycloheptatrienyl)acetone (4), m.p. 86~87°C.

The compound (3) exhibits M^+ 238 (mass spect.), ir (KBr) 1700 cm^{-1}, and nmr (in $CDCl_3$) δ 2.9 ppm (4H, d, J = 4.0 Hz, methylene protons), and 2.45 (2H, m, methine protons of cycloheptatrienyl group). The compound (4) exhibits M^+ 328 (mass spect.), ir (KBr) 1700 cm^{-1}, and nmr (in $CDCl_3$) δ 3.25 ppm (1H, t, J = 4.0 Hz, -CO-C<u>H</u>-), 2.9 (2H, d, J = 4.0 Hz, -CO-C<u>H_2</u>-), and 2.1~2.6 (3H, m, methine protons of cycloheptatrienyl groups).

Heating of (3) in refluxing xylene yielded a thermally isomerized mixture which mainly consists of a compound (5). Treatment of (5) with triphenylmethyl tetrafluoroborate in CH_2Cl_2 afforded an unstable pale brown solid (6) in a good yield, which was also obtained in 87% yield directly from (3) by the similar hydride abstraction.

The compound (6) shows nmr signals (in CF_3COOH) at δ 8.9 ppm (s) and 5.1 (s) in the ratio of


EtOOC
COOEt
Py
BF_4^-
(1)
(2)
OH^-
$-CO_2$
HOOC
COOH
(3)
(4)
Δ
$Ph_3C^+BF_4^-$
H_2
(5)
(6)
$2X^-$
(8)
NEt_3
H^+
Zn
Ha
Hb
Hc
Hd
He
Hf
Hg
(7)
(7a)
OH
X^-
(11)
(10)
(12)
(9)

3 : 1 indicating the structure of ditropylium dication derivative shown in the scheme. The compound rapidly changed to an unidentified violet solid upon standing in air. The diluted solution of the dication in CH_2Cl_2 was treated with triethylamine, and the product was purified by chromatography on neutral alumina to give an unstable reddish needles (7), m.p. 115~116°C. Catalytic hydrogenation of the compound (7) in the presence of Adam's catalyst afforded perhydro ketone (8) which was identical with the reduction product of the compound (3). Therefore, the compound (7) was found to be 8,8'-diheptafulvenyl ketone, and this is also supported by the following spectroscopic data. Nmr (in $CDCl_3$): δ 8.35 ppm (2H, m, Ha), 6.35 (10H, br. s), and 5.7 (2H, s, Hb), which suggests that Ha are strongly deshielded by anisotropy of carbonyl group. Ir (KBr): 2950(w), 1680(w), 1625(m), 1510(s, νC=O), 1430(m), 1250(m), and 1110(s) cm^{-1} (Fig. 1), which indicates that the carbonyl group is strongly polarized by a contribution of dipolar resonance form (7a). While, it has been reported that 8-formylheptafulvene (9), which has a similar structural moiety with diheptafulvenyl ketone, shows nmr (in $CDCl_3$) at δ 7.63 (H-1), 6.18 (other ring protons) and 5.36 (H-8), and ir (neat) at 1648(m), 1633(s), 1542(s), 1513(s), and 1200(m) cm^{-1}.[3]

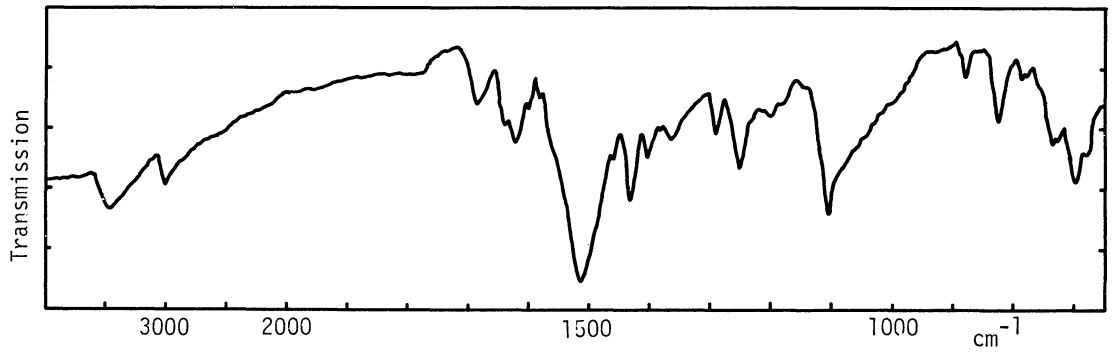


Fig. 1. Infrared spectrum of (7). (KBr disk)

The reddish solution of (7) was immediately changed to green upon addition of one drop of acid (e.g. HBF_4), and the color is reversibly returned to red by the addition of an amine.

The absorption curve (Fig. 2) of (7) in CH_3CN exhibits a maximum at 450 nm (logε 4.00), however, when one drop of HBF_4 was added to the solution, the curve exhibits two maxima at 443 nm (logε 3.58), and 610 (3.58), and is a similar to that of trimethine ditropylium cation (10) reported by Hafner et al.[4] Therefore, it is clear that the compound (7) easily undergoes a protonation at the carbonyl oxygen to form a hydroxy monocation (11). However, it is found that the compound (7) changes to dication (6) ($X^-=CF_3COO^-$) in trifluoroacetic acid solution, because of the color of the solution is reddish and the nmr of (7) in trifluoroacetic acid is almost the same with that of (6) ($X^-=BF_4^-$) in the same solvent.[5]

When the dication (6) ($X^-=BF_4^-$) was treated with zinc in aqueous acetonitrile, an oily compound

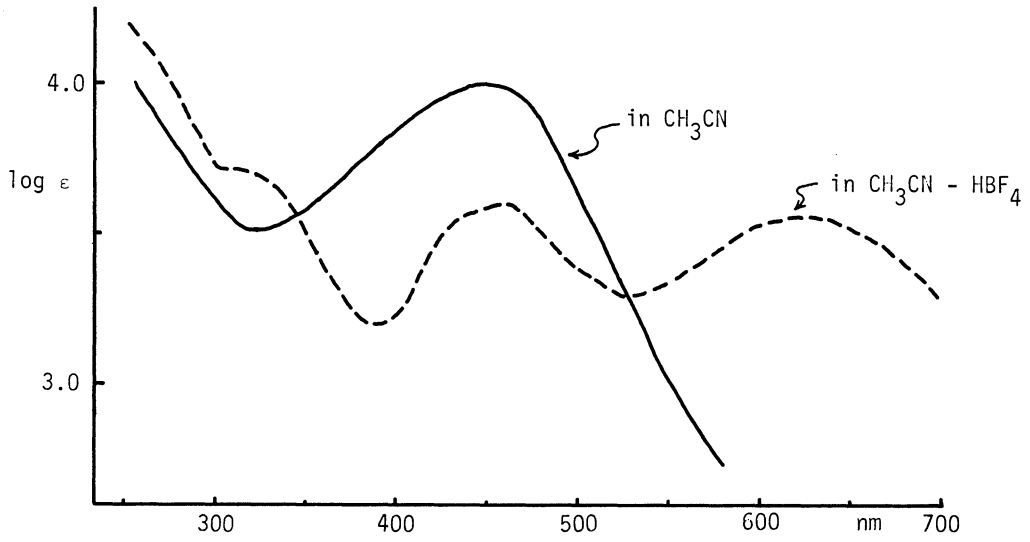


Fig. 2. Electronic spectra of (7).

(12) was obtained in a good yield. The compound (12) was found to be ditropyl derivative shown in the scheme by the following data : M^+ 236, ir (neat) 1710 and 710 cm^{-1}, and nmr (in $CDCl_3$) δ 6.6 ppm (4H, m, Hd and He), 6.25 (4H, m, Hc and Hf), 5.45 (2H, d,d, J = 9.0, 5.0 Hz, Hb), 3.45 (4H, s, Hg), and 2.45 (2H, d, J = 5.0 Hz, Ha). Attempted oxidation of (12) with triphenylmethyl tetrafluoroborate, bromine or NBS for an expectation of formation of a heptafulvalene derivative was not achieved.

References

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1) Cf. T. Otomo, M. Oda, and Y. Kitahara, Chem. Commun., 114 (1971); M. Oda, K. Tamate, and Y. Kitahara, ibid., 347 (1971).

2) All new compounds gave satisfactory elemental analyses.

3) M. Oda and Y. Kitahara, Chem. Commun., 352 (1969); Chem. & Ind., 920 (1969).

4) K. Hafner, H. W. Riedel, and M. Danielisz, Angew. Chem., 75, 344 (1963).

5) The protonations of (7) to (11) and to (6) is considered to occur successively. However, because of an unstability of the compound (7) and of time dependent reactions of (7) were observed in the acidic solution, mechanism of the protonation of (7) to (11) and (6), and determination of $_pK_R^+$ values of (11) and (6) are not studied yet.

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