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Isolation and Physical Properties of an Electron-Rich 3,4-Diacetoxy-8,8-dimethylheptafulvene

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An electron-rich 3,4-diacetoxy-8,8-dimethylheptafulvene was isolated. The crystal structure shows that the seven-membered ring exists in an "envelope" conformation and the exocyclic C=C bond length is 1.343 Å.

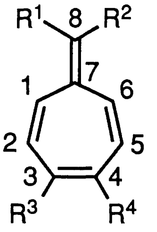
It has been reported that 7-methylenecycloheptatrienes (heptafulvenes) with electron-withdrawing groups at C8 such as 8,8-dicyanoheptafulvene (**1**) are quite stable,[1)] whereas 8-cyano derivative (**2**) is less stable[2)] and the parent heptafulvene (**3**) is unstable.[3)] It is recognized that an electron-withdrawing group enhances the contribution of the cycloheptatrienylium structure to stabilize the molecule. An electron-rich 3-hydroxy-8,8-dimethylheptafulvene (**4**), the extended enol tautomer of nezukone (**5**), has not been isolated in a pure form due to its rapid polymerization.[4)] Thus, since the substituent affects the chemical and physical properties of heptafulvenes, it would be interesting to prepare a heptafulvene with electron-donating substituents. We report here the isolation and characterization of an electron-rich heptafulvene, 3,4-diacetoxy-8,8-dimethylheptafulvene (**6**).

When 5-isopropyltropolone (**7**) was heated at 100 °C with $(n\text{-}Bu)_4NBr$ in acetic anhydride, 2-acetoxy-5-isopropyltropone (**8**) was obtained in 92% yield together with reddish orange prisms (**6**, mp 146-148 °C, gradually decomposed around 140 °C) in 8% yield. Upon further treatment under similar conditions was recovered **8** quantitatively. The NMR spectra of **6** showed it to be C_2 symmetric.[5)]

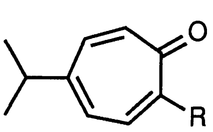
Figure 1 shows the X-ray crystal structure of **6**.[6)] The average bond lengths of the ring are 1.454 Å for a single bond and 1.337 Å for a double bond. A considerable bond alternation was observed. According to the X-ray analysis, the exocyclic C=C bond length (1.422 Å) of **1** is longer than those for typical olefins and this single bond character indicated the contribution of the polar structure.[7)] Contrary to this, the exocyclic C=C bond length of **6** (1.343 Å) is normal as a typical olefin and it suggests that the dimethyl group at C8 is prohibiting the polarization of the π-system.

The exocyclic carbons, C7 and C8, are deviated by 42.34° and 38.90° from the least-squares plane through atoms C1—C6. The seven-membered ring exists in an envelope conformation as represented in cyclopentane. These results are contrasted to those of **1** and **3**, the latter of which is planar from the microwave spectroscopy.[8)]

In conclusion, this constitutes the first isolation of 8-alkyl or 8,8-dialkyl heptafulvene derivatives. Probably, successful isolation of **6** is due to a steric effect of the dimethyl group, which protects an attack of agents.



	R^1	R^2	R^3	R^4
1	CN	CN	H	H
2	CN	H	H	H
3	H	H	H	H
4	Me	Me	OH	H
6	Me	Me	OAc	OAc



5 R = H
7 R = OH
8 R = OAc

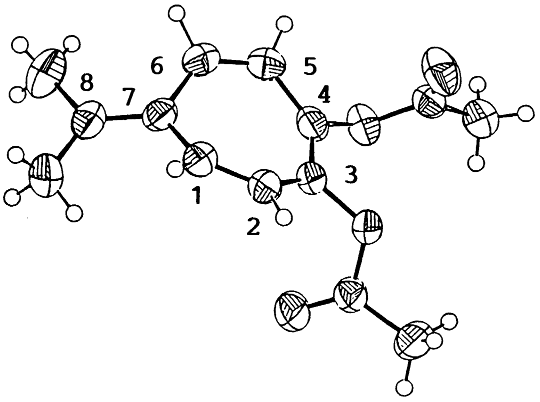


Fig. 1. Crystal Structure of **6**.

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5) ^{1}H NMR δ1.73(6H, s), 2.16(6H, s), 5.56(2H, d, J=11.7 Hz), 6.03(2H, d, J=11.7 Hz); ^{13}C NMR δ20.1(2C), 20.6(2C), 121.3(2C), 127.7, 131.6(2C), 131.6, 140.4(2C), 168.0(2C); IR(KBr) 2920, 1759, 1650, 1620, 1411, 1369, 1184, 1146, 1048, 1008, 890 cm^{-1}; UV(MeOH) λ_{max} 223 nm(ε 22800), 287(10700), 376(160). Found: C, 67.87; H, 6.41%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.
6) Crystal Data: M=248.30, triclinic, space group $P\bar{1}$ with a=7.940(2) Å, b=8.571(1) Å, c=10.215(2) Å, α=105.03(1)°, β=95.56(2)°, γ=94.24(2)°, V=664.7(2) Å^3, Z=2, D_{calcd}=1.24 g/cm^3. Intensity data were collected on a MAC Science MXC18 diffractometer with Cu-$K\alpha$ radiation using a graphite monochrometer at room temperature. A total of 2513 reflections was collected by ω-2θ scan technique up to $2\theta \leq 130°$, among which 2147 unique reflections were used for structure refinement calculations. The structure was solved by Monte-Carlo direct methods based on MULTAN 78 and positions of H were determined by difference Fourier syntheses. Refinement was carried out by full-matrix least squares using F^2. Thermal parameters for C and O were anisotropic and that of H was fixed at 3.66 Å^2. The final conventional R was 0.056 and Rw=0.070 was obtained for $w=1.0/[\sigma^2(F_o)+0.0001(F_o)^2]$. Atomic scattering factors were taken from International Tables for X-Ray Crystallography (Vol. IV).
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