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The Synthesis of the (Diacetylmethyl)tropylium Ion and Its Transformation to the 3-Acetyl-2-methylfurotropylium Ion

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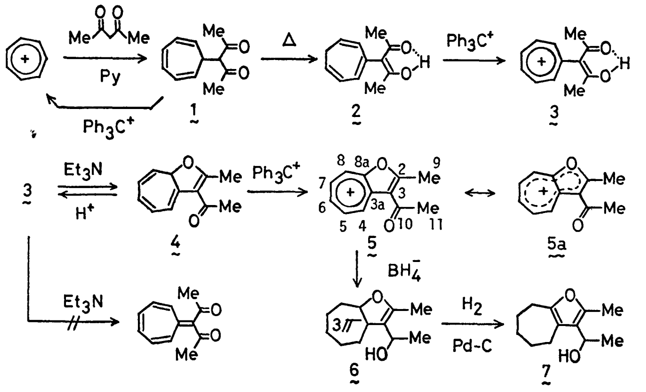
Synopsis. The intramolecularly hydrogen-bonded cation, the (diacetylmethyl)tropylium ion (**3**), has been synthesized. The deprotonation of **3** does not afford 8,8-diacetylheptafulvene, but does give the intramolecularly cyclized cycloheptatriene derivative, which can be transformed to the peripheral ten-π-electron cation, **5**; **5** is characterized by means of ^{13}C NMR spectroscopy.

The deprotonation of substituted tropylium ions is known as the facile method to generate 8-substituted heptafulvenes.[1] Especially, the tropylium ion with an electron-withdrawing group at the α-carbon of the substituent can be regarded as a potential precursor for the stable 8-substituted heptafulvene. Here we wish to report on the synthesis of the (diacetylmethyl)tropylium ion (**3**), the "formal" precursor of 8,8-diacetylheptafulvene, and its transformation to the new ten-π-electron cation, the 3-acetyl-2-methylfurotropylium ion (**5**).

The whole reaction sequence is shown in Scheme 1. The reaction of the trityl cation with the 3-substituted cycloheptatriene, **2**, successfully afforded the **3** cation in a good yield, whereas the reaction with the 7-substituted cycloheptatriene, **1**, was found only to regenerate the unsubstituted tropylium ion in an 81.3% yield. The perchlorate of the **3** cation consists of brownish yellow crystals, stable in air. The IR and NMR spectral data indicated that the diacetylmethyl group of **1** is in the keto form, whereas those of **2** and **3** are in the intramolecularly hydrogen-bonded enol form. The spectrophotometric titration carried out in 23% EtOH indicated the pK_a value for the **3** cation to be 0.72.

As is suggested by the considerable acidity of **3**, a facile deprotonation occurred when **3** was treated with triethylamine in dichloromethane. However, contrary to what was expected, the product (a pale orange oil) was not 8,8-diacetylheptafulvene, but the cycloheptatriene derivative, **4**, that was possibly formed by the intramolecular nucleophilic attack of the enolate anion on the positively charged seven-membered ring.[2] The cyclization product, **4**, is somewhat unstable at room temperature and can be quantitatively reconverted to the **3** cation when treated with proton acids. On the other hand, the hydride abstraction of **4** with the trityl cation gave the perchlorate of the **5** cation as an air-stable, greenish-blue powder.



Scheme 1.

The structure of **5** was confirmed by the chemical transformations (**5**→**6**→**7**) shown in Scheme 1. The hydrogenated product, **7**, exhibited the UV spectrum characteristic of the substituted furans.[3] In the NMR spectrum of **5**, the one-proton multiplet resonating in the lowest field is assigned to H-4, taking into account the diamagnetic anisotropy effect of the acetyl-carbonyl group; therefore, the averaged conformation of the acetyl group appears to be almost coplanar to the molecular plane. The UV-visible spectrum of **5** exhibits the longest wavelength absorption at 634 nm (log ε, 2.46). A comparison of the UV-visible spectrum of **5** with that of 1-acetyl-2-methylazulene[4] suggests the resemblance of the electronic state of **5**, with its furan oxygen donating two unshared 2p electrons to the conjugated π-system, to that of the corresponding azulene derivative. Thus, there seems to be some contribution of the structure, **5a**, to the resonance hybrid of **5**.

Table 1. ^{13}C NMR data for **4** and **5** in CD_3CN

Carbon	δ (ppm from TMS) **4**	δ (ppm from TMS) **5**	Charge density **5**
2	178.7 s	176.9 s	+0.2982
3	116.3 s	122.6 s	−0.0834
3a	138.9 s	149.8 s	+0.1029
4	127.2 d	145.9 d	+0.1358
5	132.7 d	147.2 d	+0.1120
6	123.6 d	151.0 d	+0.1307
7	116.7 d	145.4 d	+0.1162
8	111.0 d	136.9 d	+0.1244
8a	84.7 d	165.2 s	+0.1357
9	17.2 q	17.6 q	—
10	194.0 s	194.3 s	+0.4431
11	31.1 q	31.9 q	—

The ^{13}C NMR spectral data for **5** are shown in Table 1, together with those for the neutral compound, **4**. The signal assignment for **5** was made on the basis of the peak multiplicity observed in the off-resonance spectrum and on that of the charge density obtained by the simple HMO calculation using the following parameters: $h_{\dot{O}}=2.0$, $k_{\dot{O}}=\sqrt{2}$; $h_{\ddot{O}}=2.0$, $k_{\ddot{O}}=0.6$. Each carbon in the seven-membered ring as well as the C-3 in the fused furan ring are shown to be definitely shifted to a lower field upon transformation from **4** to **5**, corresponding to the introduction of the positive charge. Furthermore, it is indicated that the general trend in the π-electron distribution of **5** also resembles that of benzofuran,[5] by a comparison of the ^{13}C chemical shifts observed and reported for these compounds.

Experimental

(Diacetylmethyl)tropylium Perchlorate (3 ClO_4^-). The reaction of tropylium fluoroborate (7.12 g, 40.0 mmol) with acetylacetone (4.00 g, 40.0 mmol) in dry pyridine (80 ml) afforded 7-(diacetylmethyl)cycloheptatriene (**1**)† (7.30 g, 96.0%) as a white powder after a usual work-up; mp 122.1—123.1 °C (from benzene); IR (KBr) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.13 (s, 6, CH_3), 2.83 (dt, 1, H^7), 3.91 (d, 1, $C\underline{H}Ac_2$), 5.10 (dd, 2, $H^{1,6}$), 6.20 (m, 2, $H^{2,5}$), and 6.65 ppm (t, 2, $H^{3,4}$). The cycloheptatriene, **1** (2.18 g, 11.5 mmol), was sealed in an ampoule under a vacuum and heated at 155 °C for 2.5 h. Purification by preparative TLC (benzene–ether (97: 3)/SiO_2) and successive vacuum distillation gave 3-(diacetylmethyl)cycloheptatriene (**2**) (1.12 g, 51.4%) as white crystals; bp 89.5 °C/ 0.3 Torr; IR (KBr) 1600 cm^{-1} (C=O···HO); NMR (CCl_4) δ=2.00 (s, 6, CH_3), 2.33 (t, 2, CH_2), 5.38 (dt, 2, $H^{1,6}$), 5.97 (d, 1, H^2), 6.13 (dd, 1, H^5), 6.45 (d, 1, H^4), and 16.50 ppm (s, 1, OH). A mixture of trityl perchlorate (4.38 g, 12.8 mmol) and **2** (2.42 g, 12.7 mmol) in dry acetonitrile (10 ml) was stirred at room temp for 20 min and at 60 °C for 15 min. The addition of ethyl acetate (50 ml) and ether (20 ml) afforded **3** ClO_4^{-}† (3.14 g, 85.6%); mp 137.1—139.2 °C (dec); UV $\lambda_{\max}^{\text{MeCN-10\%HCl(1:1)}}$ 222 nm (log ε, 4.42), 263 (3.86), 302 (3.68), and 425 (3.68); IR (KBr) 3200—2800 (O–H···O=C), 1598 (C=O···HO), and 1080 cm^{-1} (ClO_4^-); NMR (CF_3COOH) δ=2.23 (s, 6, CH_3) and 9.28 ppm (s, 6, $C_7H_6^+$). The pK_a value was determined by the spectrophotometric method described previously.[6]

*3-Acetyl-2-methylfurotropylium Perchlorate (**5** ClO_4^-).* The reaction of triethylamine (0.399 g, 3.95 mmol) with **3** ClO_4^- (1.00 g, 3.47 mmol) in dichloromethane (80 ml) for 30 min at room temp and a subsequent work-up yielded **4** (0.705 g, 107%); UV $\lambda_{\max}^{\text{MeCN}}$ 229 nm (log ε, 4.22), 286 sh (3.76), and 320 (3.80); IR (neat) 1655 cm^{-1} (conj. C=O); 100 MHz NMR ($CDCl_3$; the numbering is the same as in **5**) δ=2.33 (s, 3, CH_3), 2.41 (s, 3, $COCH_3$), 4.85 (m, 1, >CH–), 5.15 (dd, 1, H^8), 6.00 (ddd, 1, H^7), 6.23 (ddt, 1, H^6), 6.39 (dm, 1, H^4), and 6.58 ppm (ddm, 1, H^5). The reaction of trityl perchlorate (1.43 g, 4.18 mmol) with **4** (0.720 g, 3.81 mmol) in dry acetonitrile (3 ml) for 35 min at room temp gave, after the addition of ethyl acetate and ether, **5** ClO_4^{-}† (0.907 g, 82.9%) as a greenish blue powder; mp 140.0—141.1 °C (dec); UV $\lambda_{\max}^{\text{MeCN}}$ 218 nm (log ε, 4.39), 260 (4.43), 363 (3.85), 590 sh (2.17), and 634 (2.46); IR (KBr) 1660 (conj. C=O) and 1090 cm^{-1} (ClO_4^-); NMR (CF_3COOH) δ=3.00 (s, 3, CH_3), 3.30 (s, 3, $COCH_3$), 9.15 (m, 4, H^{5-8}), and 10.20 ppm (m, 1, H^4).

Reduction of 5. A solution of **5** ClO_4^- (0.848 g, 2.96 mmol) in acetonitrile (50 ml) was added, dropwise, to a stirred suspension of sodium borohydride (0.179 g, 4.73 mmol) in acetonitrile (15 ml). After 1 h at room temp, the orange solution was worked up to give a crude product (0.668 g), from which **6** (0.274 g, 48.7%) was isolated by means of preparative TLC (benzene–ether (4: 1)/SiO_2); IR (neat) 3360 cm^{-1} (OH); NMR (CCl_4) δ=1.37 (br d, 3, CH_3), 2.00 (br s, 1, OH), 2.23 (sx3, 3, ⪢C–CH_3), 3.05 (t, 2, CH_2), 4.73 (qx3, 1, >CH–), and 5.0—6.8 ppm (m, 4, =CH–). Then, **6** (0.151 g, 0.794 mmol) was hydrogenated over palladium–carbon in benzene–ether (3: 1), yielding **7** (0.0671 g, 43.6%) as a colorless oil after purification by preparative TLC (benzene/SiO_2); UV $\lambda_{\max}^{\text{EtOH}}$ 217 nm (log ε, 3.82); IR (neat) 3350 cm^{-1} (OH); NMR (CCl_4) δ=1.25 (d, 3, CH_3), 1.61 (br s, 6, –$(CH_2)_3$–), 2.07 (s, 4, ⪢C–CH_3 +OH), 2.44 (br m, 4, ⪢C–CH_2–), and 4.58 ppm (q, 1, >CH–); MS *m/e* 194 (M^+).

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† Satisfactory analytical results were obtained.