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# THE SYNTHESIS OF 5H-CYCLOHEPT[a]AZULEN-5-ONE AND ITS NOVEL REACTION WITH A SULFUR YLIDE: THE FORMATION OF A NEW HETEROCYCLIC SYSTEM[1)]

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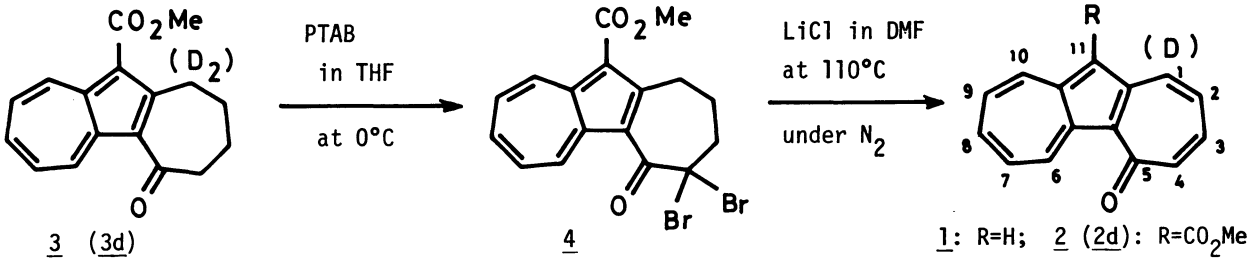
5H-Cyclohept[a]azulen-5-one and its 11-methoxycarbonyl derivative were synthesized. The latter reacted in a novel manner with a sulfur ylide to give a new heterocyclic compound having 5-oxa-5H-dicyclohepta[cd,hi]indene skeleton.

As a new type of nonbenzenoid aromatic compound, cyclohept[a]azulenes and related compounds have been interest in their properties and reactivities based on the tricyclic $C_{2v}$ symmetric carbon skeleton of 7,5,7-ring system.[2)] The present authors have synthesized cyclohept[a]azulenylium ion[3)] which is the most basic compound of this new system, by employing 1,2-pentamethylenazulene.[4)] Among the six possible isomers of cyclohept[a]azulenone (azulenotropone), only 3H-cyclohept-[a]azulen-3-one has been synthesized.[5)] In this communication, we would like to describe the synthesis of 5H-cyclohept[a]azulen-5-one (1) and its 11-methoxycarbonyl derivative (2) and a novel reaction of 2 with sulfur ylide resulting in the formation of a new heterocyclic system having 5-oxa-5H-dicyclohepta[cd,hi]-indene skeleton.

The syntheses of 1 and 2 were carried out by the application of the Jones' tropone synthesis[6)] to a carbonyl compound (3)[7)] as follows. Thus, the bromination of 3 with 3 molar equivalents of phenyltrimethylammonium perbromide (PTAB)

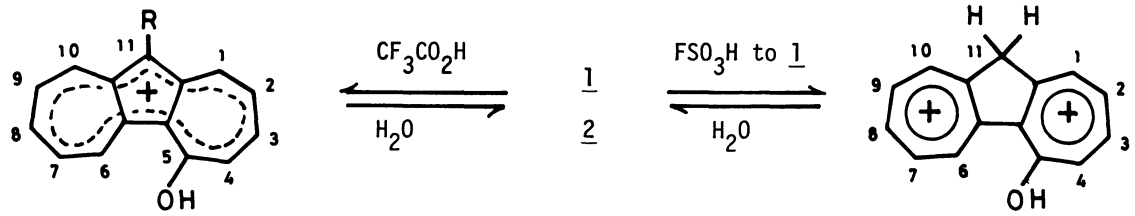



3 (3d) 4 1: R=H; 2 (2d): R=$CO_2$Me

in anhydrous tetrahydrofuran at 0°C gave a dibromo compound (4) [red prisms, mp 121-123°C][8)9)] in 95% yield. The dehydrobromination of 4 by treatment with 6 equivalents of lithium chloride in dimethylformamide at 110°C under a nitrogen atmosphere gave 2 [dark brown needles, mp 140-141°C][10)] in 91% yield. The demethoxycarbonylation of 2 by heating it with 100% phosphoric acid at 95°C yielded 1 [green scales, mp 100-101.5°C][11)] in 97% yield. On the $^1$H-NMR spectra of 1 and 2 in $CDCl_3$, the signal of H-6 was chracteristically observed at low field, 10.35

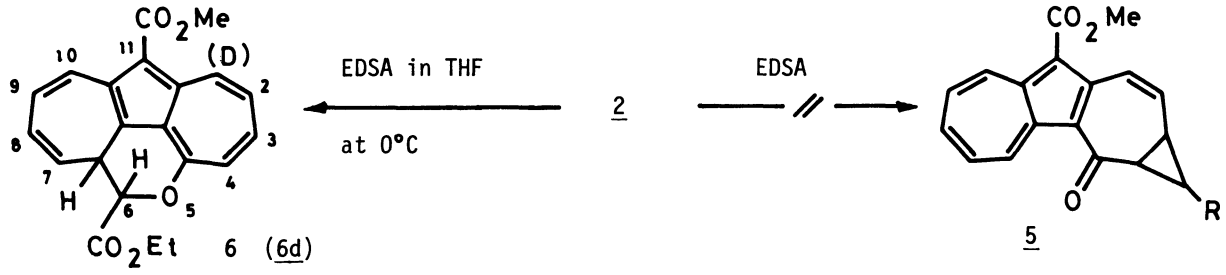
and 10.66 ppm, respectively, by the anisotropy effect of the carbonyl group at 5-position.

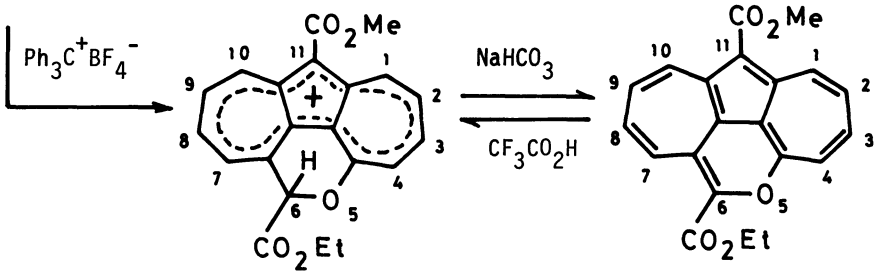
The 5H-cyclohept[a]azulen-5-ones (1, 2) were protonated at the carbonyl oxygen to form cyclohept[a]azulenylium ions (1a, 2a) in $CF_3CO_2H$. Further, the parent compound, 1, was protonated both at the carbonyl oxygen and 11-position in $FSO_3H$ to form a dication (1b). These structures were confirmed by UV and $^1$H-NMR spectra.




1a: R=H; 2a: R=$CO_2$Me 1b

It is well known that tropone[12] and benzo[d]tropone[13] react with sulfur ylides to give 2,3-homotropone derivatives. On the bases of these previous findings, the reaction of 2 with ethyl dimethylsulfurnylidene acetate (EDSA)[14] was tried in expectation of the formation of 3,4-homo derivative (5). However, the homo compound (5) was not formed but an unexpected novel product having a new heterocyclic ring system was formed as a sole product in good yield as follows.



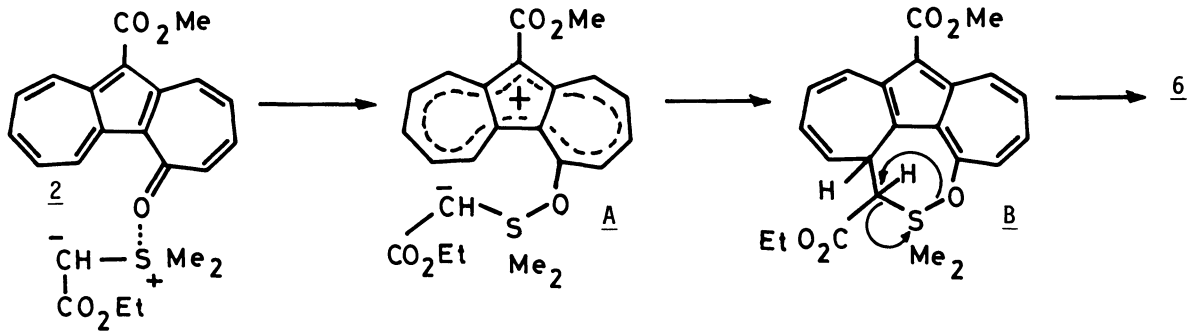




7a: X=$BF_4^-$; 7b: X=$CF_3CO_2^-$ 8

The reaction of 2 with 1.4 equivalents of EDSA in anhydrous tetrahydrofuran at 0°C afforded a crystalline product (6) [reddish violet needles, mp 141-142°C][15] in 98% yield. The IR spectrum of 6 reveals an additional intense band of an ester carbonyl at 1753 $cm^{-1}$ besides the band of the ester group at 11-position (1667 $cm^{-1}$). The $^1$H-NMR spectrum of 6 exhibits no signals which are able to assign to the proton on a cyclopropane ring. The reaction of a deuterated 5H-cyclohept[a]-azulen-5-one (2d)[16] with EDSA under the same conditions gave 6d in 77.8% yield. On the bases of these facts as well as the results on elemental analyses and other spectral data, a new heterocyclic structure, 6-ethoxycarbonyl-11-methoxycarbonyl-6,6a-dihydro-5-oxa-dicyclohepta[cd,hi]indene, was assigned to 6.

The hydride abstraction of 6 with trityl tetrafluoroborate in dichloromethane gave a cation (7a) [reddish brown cryst., mp over 300°C][17] in 99% yield. Treatment of 7a in chlorofrom with sodium hydrogen carbonate solution afforded a new heterocyclic compound, 5-oxa-5H-dicyclohepta[cd,hi]indene derivative (8) [brown prisms, mp 143.5-144°C][18] in 23.7% yield. The compound, 8, was also obtained from 6 by treatment with DDQ followed by neutralization of the resulting cation with sodium hydrogen carbonate in overall 65.3% yield. On the $^1$H-NMR spectrum, the all ring protons of 8 were shifted to higher field in comparison with that of 2. The formation of a cation, 7b, by the protonation of 8 in $CF_3CO_3H$ was confirmed by $^1$H-NMR spectrum.

A probable pathway for the formation of the novel product, 6, is depicted as shown in the Scheme by considering high nucleophilicity of the carbonyl oxygen of 2 and access of the carbonyl oxygen to C-6 position. The positively charged sulfur of the ylide interacts with the carbonyl oxygen to form a cyclohept[a]-azulenylium ion intermediate (A). Then it undergoes a ring closure to form another intermediate (B) followed by elimination of dimethylsulfide from B to give 6.




The reaction of 2 with dimethyloxosulfonium methylide and the reactions of 1 with both sulfur ylides gave no identified products, respectively.

References and Notes

1) Part II of the series of synthetic studies on cyclohept[a]azulene and related compounds, Part I: see ref. 3.
2) R. Fleisher, K. Hafner, J. Wildgruber, P. Hochmann, and T. Zahradnik, Tetrahedron, 24, 5947 (1968).
3) M. Yasunami, T. Amemiya, and K. Takase, Tetrahedron Lett., in press.
4) P. W. Yang, M. Yasunami, and K. Takase, ibid., 1971, 4275.
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6) E. W. Collington and G. Jones, J. Chem. Soc. (C), 1969, 2656.
7) T. Amemiya, M. Yasunami, and K. Takase, Chem. Lett., 1977, 587.
8) All new compounds gave satisfactory results on elemental analyses and spectral data in accord with the assigned structures.
9) IR(KBr): $\nu_{C=O}$ 1695, 1653 cm$^{-1}$; $^1$H-NMR($CDCl_3$, 60 MHz), δ ppm: 1.87-2.37(2H, m, H-2), 2.92-3.15(2H, m, H-1), 3.26(2H, t, J=6.5 Hz, H-3).
10) UV(MeOH): $\lambda_{max}$ 237 nm(log ε 4.46), 268(4.58), 285(4.35), 320(4.26), 335(4.40), 352.5(4.47), 370(4.27), 395(4.13), 440(3.61), 535(2.82), 600(2.55); $\lambda_{max}$ in $CF_3CO_2H$: 263.3(4.37), 282.5(4.18), 332(4.67), 356(4.33), 400(2.89), 441(3.58),

467(4.04), 504(3.36), 542(3.15), 590(2.78); IR(KBr): 1698, 1680, 1580, 1570, 1555, 1522, 1480, 1430, 1415, 1378, 1310, 1288, 1230, 1180, 1160, 1160, 1070, 1048, 1000, 885, 836, 807, 730, 645 $cm^{-1}$; $^{1}$H-NMR($CDCl_3$, 100 MHz), δ ppm, J in Hz: 4.03(s, OMe), 6.84-7.22(3H, m, H-2,3,4), 7.52-8.04(3H, m, H-7,8,9), 8.48-8.72(m, H-1), 9.44(dm, J=10.5, H-10), 10.66(dm, J=9.5, H-6); $^{1}$H-NMR($CF_3CO_2H$, 100 MHz): 4.41(s, OMe), 7.95-8.82(6H, m, H-2,3,4,7,8,9), 9.64-10.22(2H, m, H-1,10), 10.94(dm, J=9.0, H-6).

11) UV(MeOH): $\lambda_{max}$ 229 nm(log ε 4.49), 251.5(4.36), 280(4.23), 288(4.28), 325 (4.45), 338.5(4.59), 355(4.51), 376(4.23), 408(3.68), 440(3.59), 450(3.44), 523(2.81), 558(2.99), 600(3.04), 652(2.78); $\lambda_{max}$ in $CF_3CO_2H$: 284(4.10), 323 (4.60), 335(4.82), 360(4.20), 457(3.76), 487(4.34), 513(3.45), 560(3.25), 612 (3.06), 675(2.55); $\lambda_{max}$ in $FSO_3H$: 345(3.95), 360(4.14), 375(4.18); IR(KBr): 1578, 1561, 1552, 1490, 1445, 1420, 1405, 1395, 1280, 1225, 1052, 813, 738, 540 $cm^{-1}$; $^{1}$H-NMR($CDCl_3$, 100 MHz), δ ppm, J in Hz: 6.45-7.18(3H, m, H-2,3,4), 7.18-7.85(4H, m, H-1,7,8,9), 7.35(s, H-11), 8.36(dm, J=10.0, H-10), 10.35(dm, J=9.5, H-6); $^{1}$H-NMR($CF_3CO_2H$, 100 MHz), δ ppm, J in Hz: 7.72-8.58(6H, m, H-2,3, 4,7,8,9), 8.09(s, H-11), 8.08(dm, J=10.0, H-1), 9.03(dm, J=10.5, H-10), 10.58 (dm, J=10.0, H-6); $^{1}$H-NMR($FSO_3H$, 60 MHz), δ ppm: 5.27(2H, broad s, H-11), 8.10-8.95(9H, m, H-1,2,3,4,6,7,8,9,10).

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13) Y. Sugimura, N. Soma, and Y. Kishida, ibid., 1971, 91.

14) G. B. Payne, J. Org. Chem., 32, 3351 (1967); M. Fieser, L. Fieser, "Reagents for Organic Synthesis" Vol 2, p-196, Wiley-Interscience, New York, 1969.

15) UV(MeOH): $\lambda_{max}$ 226 nm(log ε 4.36), 239(4.39), 278(4.22), 292(4.22), 330(4.41), 366(3.85), 403(3.69), 550(3.03); IR(KBr): 1753, 1677, 1578, 1450, 1390, 1210, 1180, 1160, 1130, 1042, 983, 850, 790, 713, 622 $cm^{-1}$; $^{1}$H-NMR($CDCl_3$, 100 MHz), δ ppm, J in Hz: 1.26(t, J=7.0, $C\underline{H}_3CH_2O$), 3.95(ddd, J=5.5, 3.3, 2.2, H-6a), 3.96(s, OMe), 4.20(q, J=7.0, $CH_3C\underline{H}_2O$), 5.22(d, J=5.5, H-6), 5.65(dd, J=10.3, 3.3, H-7), 6.11(ddd, J=10.3, 6.0, 2.2, H-8), 6.55(dd, J=11.5, 6.0, H-9), 7.11-7.35(2H, m, H-2,4), 7.62(tm, J=10.0, H-3), 7.87(d, J=11.5, H-10), 9.32(dm, J=10.0, H-1); $^{13}$C-NMR($CDCl_3$, 10 MHz), δ ppm: 36.9(d, C-6a), 78.8(d, C-6).

16) This compound was synthesized by the same procedures utilizing a deuterated carbonyl compound (3d).

17) $^{1}$H-NMR($CD_3CN$, 60 MHz), δ ppm, J in Hz: 1.12(t, J=7.0, $C\underline{H}_3CH_2O$), 4.12(s, OMe), 4.15(q, J=7.0, $CH_3C\underline{H}_2O$), 6.98(s, H-6), 7.85-8.45(6H, m, H-2,3,4,7,8,9), 9.68 (dm, J=10.0, H-1 or 10), 9.95(dm, J=10.0, H-10 or 1).

18) UV(MeOH): $\lambda_{max}$ 220 nm(log ε 4.44), 233(4.38), 293(4.71), 325(4.05), 341(4.11), 403(4.14), 470(3.18), 498(2.81), 530(2.33); IR(KBr): 1692, 1683, 1595, 1526, 1462, 1440, 1382, 1330, 1272, 1222, 1214, 1103, 1078, 788, 753 $cm^{-1}$; $^{1}$H-NMR ($CDCl_3$, 100 MHz), δ ppm, J in Hz: 1.25(t, J=7.0, $C\underline{H}_3CH_2O$), 3.73(s, OMe), 4.07 (q, J=7.0, $CH_3C\underline{H}_2O$), 5.01(ddd, J=9.0, 7.5, 1.0, H-8), 5.18(ddd, J=11.0, 7.5, 1.5, H-9), 5.47(d, J=11.5, H-4), 6.78(ddd, J=11.0, 8.5, 0.8, H-2), 6.32(ddd, J=11.5, 8.5, 1.0, H-3), 6.36(dd, J=11.0, 1.0, H-10), 6.60(dm, J=9.0, H-7), 7.80(d, J=11.0, H-1); $^{1}$H-NMR($CF_3CO_2H$, 60 MHz), δ ppm, J in Hz: 1.25(t, J=7.0, $C\underline{H}_3CH_2O$), 4.32(q, J=7.0, $CH_3C\underline{H}_2O$), 4.32(s, OMe), 7.00(s, H-6), 7.97-9.00(6H, m, H-2,3,4,7,8,9), 9.83(dm, J=10.0, H-10), 10.01(dm, J=10.0, H-1).

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