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A NOVEL REACTION OF 5H-CYCLOHEPT[a]AZULEN-5-ONES WITH HALOKETENES: FACILE SYNTHESIS OF DICYCLOHEPTA[cd,gh]PENTALENE

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Summary: 5H-Cyclohept[a]azulen-5-ones were found to react with haloketenes in a novel manner to form some derivatives of dicyclohepta[cd,gh]pentalene.

During the course of our synthetic investigations on cyclohept[a]azulenes and related compounds,[1] 5H-cyclohept[a]azulen-5-one (1) and its 11-methoxycarbonyl derivative (2) have been synthesized in an efficient manner by the use of 1,2-pentamethylenazulene, and indicated synthetical utilities as a versatile intermediate for attractive fully conjugated polycyclic compounds.[2] On the other hand, dicyclohepta[cd,gh]pentalene (3) has been interested as one of the bridged [14]annulenes and synthesized by E. Vogel as the results of excellent continuous investigations on the series of bridged annulenes.[3] In this communication, we would like to report a new facile synthetic method for the dicyclohepta[cd,gh]pentalene skeleton by a novel ring formation reaction of 1 and 2 with haloketenes.

The reaction of 1 or 2 with haloketenes generated *in situ* from corresponding acid chlorides with triethylamine was carried out in a following manner. A solution of 1.2 equivalents of an acid chloride in anhydrous benzene was added dropwise to a refluxing solution of 1 or 2 containing four equivalents of triethylamine in the same solvent, and the reaction mixture was refluxed for an appropriate time under nitrogen atmosphere. The reaction conditions were controlled only by additional refluxing time. After removal of the precipitated triethylamine hydrochloride, the products were isolated by chromatography using a silica-gel column eluted with benzene. The results were summarized in Table 1.

The reaction of 2 with dichloroketene under refluxing for one hour gave a lactone (4) [violet needles, mp 196-198°C],[4,5] whereas under reflux for a long time (11 hr), another crystalline product (5) [yellowish green needles, mp 198-200°C][6] was formed. The compound, 5, was also obtained in 70% yield by heating of a benzene solution of 4 under reflux in the presence of triethylamine.

The ^{1}H-NMR spectral data of 4, together with the results on decoupling

Scheme 1.

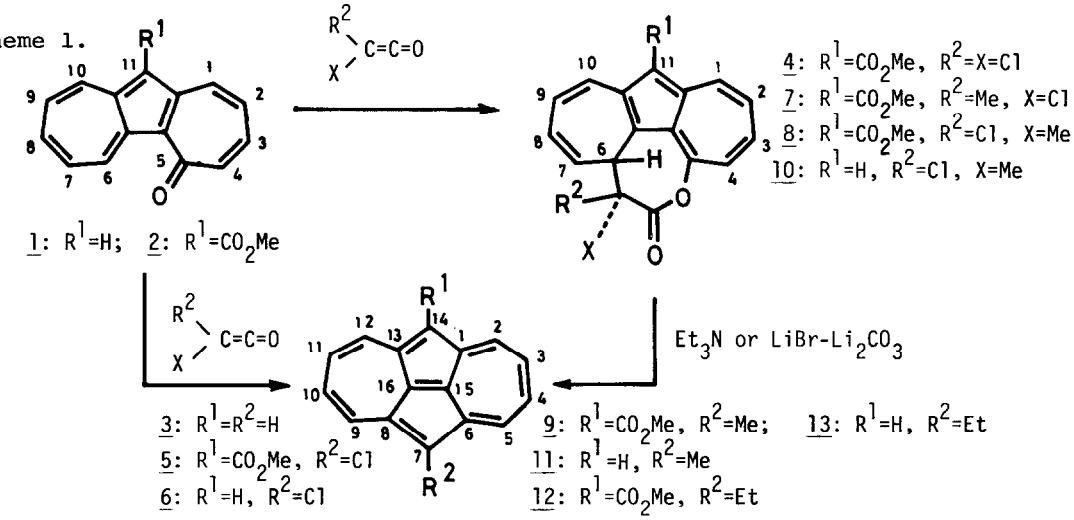


Table 1. Yields of the Products on the Reactions of 1 and 2 with Haloketenes

Substr.	Ketene	Reaction Time	Product: Lactone				Product: Dicyclohepta-pantalene	
2	$Cl_2C=C=O$	1 hr	4	84%				-
		11 hr		-			5	66%
1	$Cl_2C=C=O$	1 hr		-			6	78%
2	Cl-C(Me)=C=O	5 min	7	48.5%	8	48.5%		-
		23 hr	7	5%	8	43%	9	36%
1		9 hr	10[11]	38%			11[12]	19%
2	Br-C(Et)=C=O	98 hr		-			12	31%
1		30 hr		-			13	42%

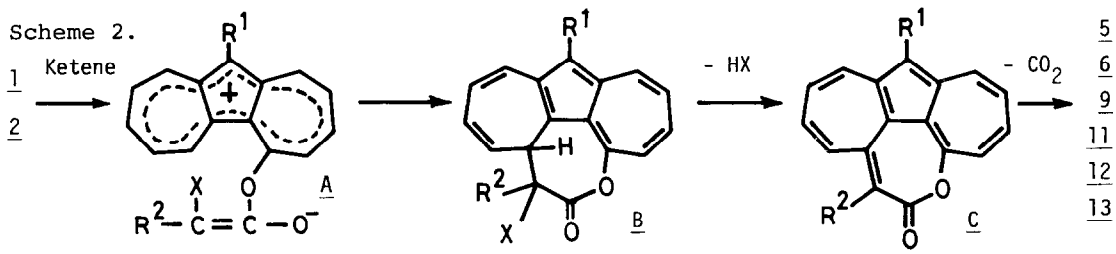
technique, indicated that a methine proton and four olefinic protons aligned in vicinal positions each other. The intence band at 1770 cm^{-1} in the IR spectrum of 4 was reasonable as a seven membered α-halo enol lactone. On the bases of the spectral data, the structure of 4 was assigned as shown in Scheme 1. The UV spectrum of 5 was very similar to that of 3 except an absorption maximum at 640 nm. The ^{13}C-NMR of 5 reveals only nine signals corresponding to the carbon skeleton indicating a symmetrical structure of the compound. On the bases of these observations and other spectral data, the structure of 5 was assigned as 7-chloro-14-methoxycarbonyldicyclohepta[cd,gh]pentalene.

The reaction of 1 with dichloroketene occured most readily as follows. The reaction of 1 with the ketene under reflux for one hour gave directly 7-chlorodicyclohepta[cd,gh]pentalene (6) [greenish brown needles, mp 120-121°C].[7] In this case a lactonic intermediate was not detected.

As shown in Table 1, the compounds, 1 and 2, were also reacted with alkyl haloketenes generated *in situ* in a similar manner to form 7-alkyl derivatives of

3 as follows. Thus, the reaction of 2 with chloromethylketene in a benzene solution under reflux for 5 min afforded two isomeric lactones, 7 [violet cryst., mp 164-165°C][8] and 8 [violet needles, mp 195-197°C].[9] The heating of a benzene solution of 7 for 48 hr in the presence of triethylamine gave 7-methyl-14-methoxycarbonyl compound (9) [green scales, mp 168-169°C],[10] while another lactone, 8, was recovered unchanged on the same treatment. However, the treatment of 8 with lithium bromide-lithium carbonate in dimethylformamide at 120°C for 7 hr afforded 9 in 30% yield. On the bases of these chemical behaviour and the spectral data, the structures of 7 and 8 were assigned as shown in Scheme 1. The reaction of 2 with chloromethylketene under reflux for a long time (23 hr) gave a mixture of 7, 8, and 9. Similarly, the reaction of 1 and 2 with bromoethylketene under reflux for a long time gave 12 [brown prisms, mp 135-136°C][13] and 13 [brownish green plates, mp 173-175°C],[14][15] respectively.

Scheme 2.



A probable pathway for the formation of the above products is depicted in Scheme 2. The electron-deficient carbonyl carbon of ketene interacts with the carbonyl oxygen of 1 or 2 to form a cyclohept[a]azulenylium ion[1] intermediate (A). Then, it undergoes a ring closure to yield the isolable lactonic intermediate (B). The dehydrohalogenation from B leads to an unstable azulenoheptafulvene intermediate (C). The pericyclic ring closure of C followed by decarboxylation yields dicyclohepta[cd,gh]pentalenes.

As mentioned above, the reaction of 5H-cyclohept[a]azulen-5-ones with haloketenes was found to be a useful method for the synthesis of dicyclohepta-[cd,gh]pentalene derivatives. The synthesis of a few derivatives having a functional group at seven membered ring are now in progress. The results will be reported in the near future.

[References and Notes]

1) M. Yasunami, T. Amemiya, and K. Takase, Tetrahedron Lett., in press.
2) M. Yasunami, A. Takagi, and K. Takase, Chemistry Lett., in press.
3) V. H. Reel and E. Vogel, Angew. Chem. Internat. Ed. Engl., 11, 1013 (1972).
4) All new compounds gave satisfactory results of elemental analyses and spectral data in accord with the assinged structures.
5) IR(KBr): 1770, 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$, 200 MHz), δ ppm, J in Hz: 3.41(d, J= 6.0, H-6), 5.83(dd, J=10.0, 6.0, H-7), 6.32(dd, J=10.0, 6.0, H-8), 6.96(dd,

J=11.0, 6.0, H-9), 8.13(d, J=11.0, H-10).

6) UV(MeOH): λmax 289 nm(log ε 5.15), 315(4.05)sh, 368(3.72), 387(3.92), 409 (3.98), 451(3.26)sh, 480(3.75), 640(2.58); IR(KBr): 1690, 1600, 1489, 1452, 1430, 1360, 1314, 1251, 1180, 1130, 789, 745, 665 cm^{-1}; ^{1}H-NMR($CDCl_3$, 90 MHz), δ ppm : 4.61(s, OMe), 8.29(m, H-3,4,10,11), 8.81(m, H-5,9), 9.46(2H, m, H-2,12); ^{13}C-NMR($CDCl_3$, 22.5 MHz), δ ppm: 112.8(s, C-14), 121.8 (s, C-15, 16), 113.5(s, C-7), 128.7(d, C-2, 12), 131.0(d, C-3, 11), 131.5 (d, C-4, 10), 134.2(d, C-5, 9), 139.4(s, C-1, 13), 145.6(s, C-6, 8).

7) UV(MeOH): λmax 240 nm(log ε 4.15), 284(5.13), 310(4.36), 372(3.90), 388 (3.85)sh, 394(5.04), 460(3.25)sh, 490(3.73), 590(2.60); IR(KBr): 1590, 1531, 1444, 1295, 1123, 780, 760, 640 cm^{-1}; ^{1}H-NMR($CDCl_3$, 90 MHz), δ ppm, 8.15(s, H-14), 8.07-8.43(m, H-3,4,10,11), 8.55-8.94(m, H-2,5,9,12).

8) IR(KBr): 1770, 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 1.90(s, Me), 3.20(d, J=6.0, H-6), 4.01(s, OMe), 8.14(d, J=12.0, H-10), 9.52-9.78(m, H-1).

9) IR(KBr): 1750, 1692 cm^{-1}; ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 2.09(s, Me), 2.84(d, J=6.0, H-6), 4.01(s, OMe), 8.18(d, J=12.0, H-10), 9.48-9.73(m, H-1).

10) UV(MeOH): λmax 290 nm(log ε 5.12), 302(4.51)sh, 316(4.07)sh, 350(3.54)sh, 367((3.76), 386(3.92), 407(3.95), 447(3.17), 477(3.65), 640(2.64); IR(KBr): 1675, 1453, 1360, 1180, 1140, 1130, 1010, 788, 660 cm^{-1}; ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 2.74(s, Me), 4.13(s, OMe), 7.62-8.50(m, H-3,4,5,9,10,11), 9.26 (dd, J=10.0, 2.0 Hz, H-2, 12).

11) greenish violet cryst., mp 100°C (dec); ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 2.11 (s, Me), 3.03(dm, J=6.0 Hz, H-6); IR(KBr): 1760, 1580, 1445, 1414, 800 cm^{-1}.

12) brown flakes, mp 130-131°C; UV(MeOH): λmax 283 nm(log ε 5.23), 296(4.58)sh, 310(4.46), 322(3.83)sh, 354(3.71)sh, 370(3.97), 376(3.79)sh, 386(3.93), 391 (4.17), 432(2.90)sh, 460(3.23)sh, 492(3.78); IR(KBr): 1593, 1533, 1450, 1310, 1165, 1042, 780, 646 cm^{-1}; ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 3.14(s, Me), 7.73-8.26(m, H-3,4,10,11), 8.09(s, H-14), 8.36-8.83(m, H-2,5,9,12).

13) UV(MeOH): λmax 283 nm(log ε 5.22), 296(4.56)sh, 310(4.45), 355(3.68)sh, 370 (3.94), 377(3.73)sh, 386(3.92)sh, 391(3.14), 432(2.84)sh, 461(3.18)sh, 490 (3.75), 620(1.95); IR(KBr): 1589, 1530, 1447, 1306, 1158, 1050, 780, 648 cm^{-1}; ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 1.59(t, J=7.5 Hz, Me), 3.78(q, J=7.5 Hz, CH_2), 7.82-8.42(m, H-3,4,10,11), 8.25(s, H-14), 8.54-9.07(m, H-2,5,9,12).

14) UV(MeOH): λmax 290 nm(log ε 5.15), 315(3.04)sh, 368(3.77), 386(3.94), 408 (3.98), 448(3.22), 477(3.69), 660(2.74); IR(KBr): 1685, 1456, 1353, 1135, 1060, 790, 668 cm^{-1}; ^{1}H-NMR($CDCl_3$, 60 MHz), δ ppm: 1.46(t, J=7.5 Hz, Me), 3.48(q, J=7.5 Hz, CH_2), 4.12(s, OMe), 7.75-8.43(m, H-3,4,10,11), 8.61(dd, J=8.0, 2.0 Hz, H-5,9), 9.37(dd, J=8.0, 2.0 Hz, H-2, 12).

15) Recently, X-Ray diffraction analysis of this compound was accomplished supporting the assigned structure: C. Kabuto, K. Fujimori, N. Morita, M. Yasunami, T. Asao, and K. Takase, Acta Crystallographica, in press.

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