CHEMISTRY LETTERS, pp. 1535-1538, 1981. © The Chemical Society of Japan 1981

THERMAL [1,3] YLIDE REARRANGEMENT AND BASE CATALYZED [2,3] METHYLSULFONIO GROUP MIGRATION OF METHYLSULFONIUM 1-(2,6-DIPHENYL AND 2,3,5,6-TETRAPHENYL-4H-PYRAN-4-YL)-2-OXO-2-PHENYLETHYLIDES

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Thermolyses of dimethylsulfonium 1-(2,6-diphenyl and 2,3,5,6-tetraphenyl-4H-pyran-4-yl)-2-oxo-2-phenylethylides (1 and 3) caused a novel [1,3] ylide rearrangement to give dimethylsulfonium 1-benzoyl-6-oxo-2,6-diphenyl and 2,3,5,6-tetraphenyl-2,4-hexadienylides (6 and 7), respectively. The formations of oxy-thio-acetal derivatives (11 and 12) of 4-pyranylidene from 3 and its methylphenylsulfonium analogue (4) by base treatment are also reported.

It is known that 4H-pyran derivatives show variety of reactions such as elimination or rearrangement of substituents, cyclizations, dehydrations etc.[1] Previously, we synthesized dimethylsulfonium 1-(2,6-diphenyl-4H-pyran-4-yl)-2-oxo-2-phenylethylide (1).[2] Since this compound 1 possesses two reactive moieties, ylide group and 4H-pyran skeleton, it is interesting to compare reactivities of the two functional groups. For this purpose we prepared the same type sulfonium ylides (2,3 and 4).[3] The steric environments of the ylide groups and the hydrogens at the $C_{1'}$ of the diphenyl derivatives (1 and 2) are very different from those of the tetraphenyl derivatives (3 and 4). Therefore, it was expected that the behavior of the formers and the latters toward intramolecular and/or intermolecular reactions would be different. In this report, thermal and base catalyzed reactions of those compounds were investigated from the above point of view, and we would like to present our findings.

Thermal reaction of 1 in refluxing acetonitrile resulted in the formation of dimethylsulfonium 1-benzoyl-6-oxo-2,6-diphenyl-2,4-hexadienylide (6) (as a geometric mixture in 4:1 ratio, mp 95-127°C, 27%), and that of 3 gave rise to corresponding 2,3,5,6-tetraphenyl-2,4-hexadienylide (7) (as a geometric mixture, mp 200°C decomp., 43%) accompanied with a small amount of 2,3,5,6-tetraphenylthioanisole (8) (mp 234°C, 4%). Because heating of 7 in dioxane produced 8 (43%), 8 is the secondary product arising from 7. On the other hand, treatment of 3 in protic solvents such as methanol or ethanol afforded 2-alkoxy-2,3,5,6-tetraphenyl-2H-pyrans (9, mp 166°C, 88%, and 10, mp 154°C, 70%).

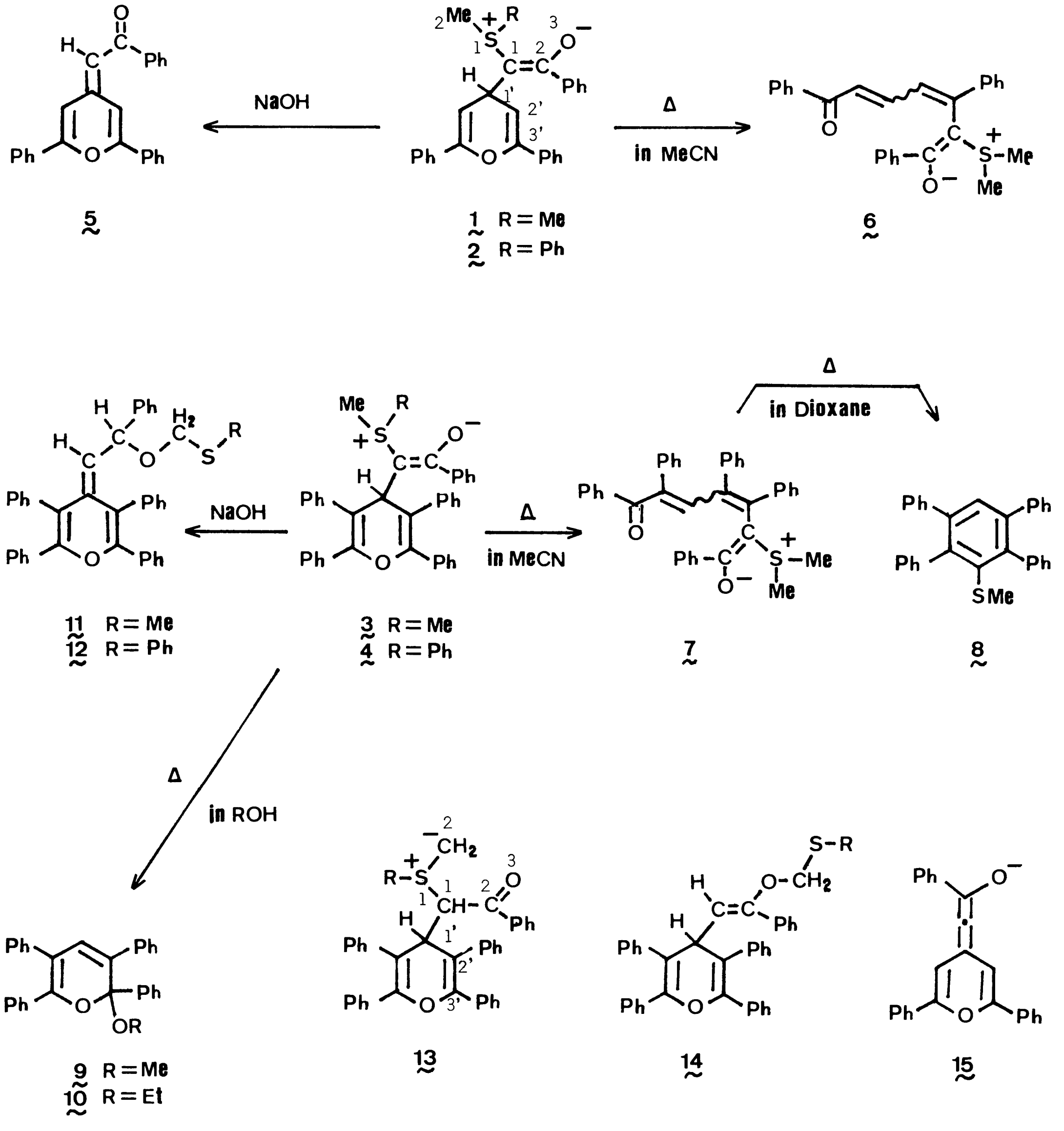
In contrast with the above thermolyses, treatments of 3 or 4 with ethanolic sodium hydroxide resulted in [2,3] migration of the dimethylsulfonio or methylphenylsulfonio group to the carbonyl oxygen to form oxy-thio-acetal compounds (11, mp 162°C, 80%, and 12, mp 168°C, 65%), whereas both 1 and 2 gave 4-benzoylmethylene-2,6-diphenyl-4H-pyran (5)[6] in more than 90% yields by elimination of dimethyl sulfide or thioanisole, respectively.

The structure of all new compounds were deduced by their elemental analyses,[7] spectroscopic properties,[8] and by comparison of their spectral data with those of the analogous compounds. IR spectra of 6 and 7 show the strong carbonyl absorptions at 1640 and 1630 $\mathrm{cm^{-1}}$, and ylide carbonyl bands[5] at 1510 and 1530 $\mathrm{cm^{-1}}$, respectively. In NMR spectra of 6 and 7, the peaks at δ 6.21 and 6.67 of the former and δ 5.7 of the latter can be rationally explained as vinyl protons of the proposed structures, even though a peak of one vinyl proton of the former is superimposed with those of the phenyl protons at δ 6.9-8.0.[8] Raney Ni reduction of 8 affording 1,2,4,5-tetraphenylbenzene[9] established the proposed structure. The formation of 2H-pyran derivatives from pyrylium compounds by reactions with alkoxides has been reported, and spectral data of 9 and 10 are resemble with those of the 2-alkoxy-2H-pyran derivatives.[10] The signals at δ 4.15 of 11 and 4.29 of 12 in their NMR spectra are consistent with the acetal methylene protons, and those at 4.58 and 5.57 of 11 and 4.50 and 5.57 of 12 are assignable as benzyl and vinyl protons. The structure of 11 and 12 can be represented as shown in the scheme.

The formations of 6 and 7 are presumably an intramolecular [1,3] rearrangement of the ylide groups. This type of 1,3-migration of the sulfonium ylide moiety has not been reported. The driving force of the rearrangement should be the formation of more stable hexadienylide derivatives. In the case of the reactions in alcohols, the phenacylide group of 3 picks up a proton from the solvents, subsequent elimination of the dimethylsulfonium phenacylide affords 2,3,5,6-tetraphenylpyrylium, and following attack of the solvent to the formed pyrylium gives 2H-pyran derivatives (9 and 10).

The [2,3] migration of methylsulfonio groups to carbonyl oxygen of α-ketosulfonium ylides has been reported but few.[11] As shown in the scheme, a proton exchange between the S-methyl group and the ylide carbon produces an intermediate (13) by action of base, and following rearrangement of the ylide group to the carbonyl oxygen forms another intermediate (14) as reported by Ratts.[11]

Further migration of the proton at $C_{1'}$ to the benzyl carbon completes the reaction to give the thermally more stable final products (11 and 12). On the other hand, since the hydrogens at $C_{1'}$ of 1 and 2 are not so hindered for attack of base as those of 3 and 4, elimination of dimethyl sulfide or thioanisole occurs readily to give a pyranylidene-enol-allene type intermediate (15) and subsequent ketonization affords the final product 5.



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3. All compounds were prepared from corresponding pyrylium fluoroborates[4] and sulfonium phenacylides[5] by previously reported method.[2]

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7. All new compounds gave satisfactory elemental analyses. However, 6 and 7 contain the solvent of crystallization; acetonitrile for the former and benzene for the latter.

8. Spectral data. 6 [ν (KBr); 1640, 1580, 1555, 1510, 1360, 1315, 1295, 1270, 1165, 1145, 1030, 1015, 980, 775, 760, and 690 cm^{-1}. δ (ppm in $CDCl_3$); 2.98 (Me, 1.2H equi., s, E or Z isomer), 3.09 (Me, 4.8H , s, E or Z isomer), 6.21 (1H, broad d, J=11.5 Hz), 6.67 (1H, broad d, J=15.0 Hz), and 6.9-8.0 (16H, m)]. 7 [ν (KBr); 1630, 1530, 1500, 1470, 1440, 1355, 1290, 1280, 1245, 1080, 1065, 1015, 965, 920, 850, 760, 700, and 680 cm^{-1}. δ (ppm in $CDCl_3$); 2.79 (Me, ~3H, s), 2.86 (Me, ~3H, s), 5.7-5.8 (1H, m), and 6.5-7.8 (25H, m)]. 9 [ν (KBr); 1640, 1600, 1555, 1490, 1445, 1225, 1160, 1095, 1065, 1045, 1030, 1000, 950, 750, and 690 cm^{-1}. δ (ppm in $CDCl_3$); 3.55 (Me, s), 6.92 (1H, s), and 7.1-7.7 (20H, m)]. 11 [ν (KBr); 1675, 1635, 1600, 1485, 1440, 1343, 1270, 1215, 1155, 1015, 1000, 775, 765, and 690 cm^{-1}. δ (ppm in $CDCl_3$); 1.88 (Me, s), 4.15 (2H, s), 4.58 (1H, d, J=10.0 Hz), 5.57 (1H, d, J=10.0 Hz), and 7.2-7.5 (25H, m)]. 12 [ν (KBr); 1660, 1620, 1595, 1480, 1435, 1305, 1255, 1215, 1125, 1065, 1000, 915, 755, and 685 cm^{-1}. δ (ppm in $CDCl_3$); 4.29 (2H, s), 4.50 (1H, d, J=10.0 Hz), 5.57 (1H, d, J=10.0 Hz), and 7.2-7.5 (30H, m)].

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(Received July 24, 1981)