REGIOSELECTIVITY OF REDUCTION OF 2-tert-BUTYL-1-BENZOPYRILIUM PERCHLORATE

K. F. Suzdalev and A. V. Koblik

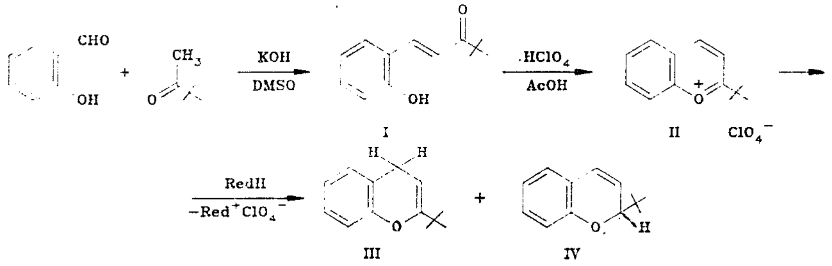
UDC 547.814:542.942.4

The reaction of 2-tert-butyl-1-benzopyrilium perchlorate with various reducing agents leads to a mixture of 2H- and 4H-chromenes. The greatest selectivity (90% 2-tert-butyl-4H-chromene and 10% 2H-isomer) was achieved using 1,3-dimethylbenzimidazoline.

The reduction of 1-benzopyrilium salts has not been studied sufficiently but may become a simple method for the synthesis of 1-benzopyran compounds [1]. The formation of a mixture of 2H- and 4H-chromenes is possible in such transformations. The controlled synthesis of a specific isomer lends importance to the study of the regioselectivity of this reaction.

We have studied the reaction of 2-tert-butyl-1-benzopyrilium perchlorate (II) with various reducing agents in order to synthesize 2-tert-butyl-4H-chromene (III).

Starting salt II is formed in good yield in two steps: 1) alkaline condensation of salicylaldehyde with pinacolin leads to salicylidenepinacolin I and 2) is cyclized by the action of $HClO_4$ to salt II. An attempt to synthesize II in one step from salicylaldehyde and pinacolin by acid condensation [2] proved unsuccessful.



The results of the reduction of perchlorate II are given in Table 1. Regiospecific formation of one of the isomers was not observed. A mixture of 2-tert-butyl-4H-chromene (III) and 2-tert-butyl-2H-chromene (IV) was obtained in all cases. The separation of chromenes III and IV by fractional distillation or thin-layer chromatography presents great difficulties in light of their similar boiling points and R_f values. The contents of isomers III and IV in the mixture were determined by the intensities of their PMR signals.

The reaction with lithium aluminum hydride gives different ratios of isomers III and IV depending on the nature of the solvent, temperature, and amount of reducing agent. The product ratio is often not reproducible. Virtually no regioselectivity is found for the reaction with sodium borohydride.

Bulky reducing agents may be used to shift the ratio of the reaction products toward 4H-isomer III in light of the steric hindrance created by the tert-butyl group at $C_{(2)}$ of the pyrilium cation. However, the use of lithium tris(tert-butoxy)aluminum hydride (see the work of Fieser and Fieser [3], p. 187) leads to the preparation of numerous unidentified products, while chromenes III and IV were not found in the reaction mixture. The best results were obtained in a hydride exchange reaction [4] between 1,3-benzimidazoline V and perchlorate II (the III/IV ratio was 9:1).

M. A. Suslov Rostov State University. Physical and Organic Chemistry Research Institute, Roston-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 313-315, March, 1989. Original article submitted July 31, 1987.

0009-3122/89/2503- 0258$12.50

TABLE 1. Reduction of Salt II

Reducing agent	Amount of reducing agent, mole/mole II	Solvent	T, °C	Yield of chromeme mixture, %	Regioselectivity, %	
					4-H-chromene	2H-chromene IV
$LiAlH_4$	0,4	Et_2O	−80	82	73	27
$LiAlH_4$	1	Et_2O	−80	91	33	67
$LiAlH_4$	0,5	THF	−80	64	64	36
NBH_4	0,8	MeCN	20	66	57	43
$LiAlH(OBut)_3$	1	THF	20	0	—	—
V	1	Hexane	0	92	90	10
VI	1	Hexane	0	89	75	25
VII	1	MeCN	20	75	86	14

The lack of regiospecificity in all these cases is attributed to the circumstance that the hydride exchange reaction proceeds stepwise with the formation of radical species [5, 6]. Okhlobystin et al. [7] have shown that the reduction of 2,4,6-triphenylpyrilium perchlorate by 1,3-dimethyl-2-phenylbenzimidazoline is accompanied by the formation of the triphenylpyranyl radical and benzimidazoline radical-cation. The reduction of salt II proceeds by an analogous mechanism. The 1-benzopyrilyl radical formed in the first step of the one-electron transfer is attacked by a proton [6] or hydrogen atom [7] abstracted from the radical-cation of the reducing agent. In this case, the steric hindrance due to the tert-butyl group does not play a significant role. The regioselectivity using V-VII is a function of the initial orientation of the molecules in the complex formed by salt II and reagent. For compound V this orientation is probably more favorable for the formation of 4H-chromene III.

Thus, the reduction of salt II of imidazoline V proceeds with high regioselectivity and yield is a simple preparative method and may be used for the synthesis of 4H-chromenes from 4-unsubstituted 1-benzopyrilium salts.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-487C spectrometer at 80 MHz with HMDS as the internal standard. The IR spectra were taken on a Specord IR-75 spectrometer in vaseline mull. Benzimidazolines V and VI were obtained according to El'tsov and Girshovich [8] and 2,4-diphenyl-4H-chromene (VII) was obtained according to Löwenbein [9].

The elemental analysis data for I and II for C, H, and Cl corresponded to the calculated values.

Salicylidenepinacolin (I), $C_{13}H_{16}O_2$. A sample of 135 ml (1.11 mole) pinacolin was added to a stirred suspension of 112 g (2 moles) KOH and 300 DMSO. The mixture turns red and considerable heat is evolved; KOH is completely dissolved. The reaction mixture was left overnight and then poured into 1 liter of a mixture of 200 ml concentrated hydrochloric acid with ice. The product separated as an oil, which soon crystallized. The dried product was dissolved in 200 ml hot benzene and 300 ml petroleum ether was added. Upon cooling, the precipitate formed was filtered off. The yield of I was 194 g (86%), mp 126-127°C (from benzene). IR spectrum: 1580 ($C-C_{arom}$), 1675 (C=O), 3345 cm^{-1} (OH). PMR spectrum ($CDCl_3$): 1.13 (9 H, s, CMe_3), 6.60-7.55 (5 H, m, C_6H_4 and 1 olefinic proton), 8.08 (1 H, d, J = 16 Hz, trans-olefinic proton), 8.28 ppm (1 H, s, OH, this signal disappears after deuteration).

2-tert-Butyl-1-benzopyrilium Perchlorate (II), $C_{13}H_{15}ClO_5$. A sample of 28 ml (0.28 mole) 70% perchloric acid was added to a solution of 38.2 g (0.19 mole) salicylidenepinacolin I in 100 ml acetic acid and the mixture was heated at reflux for 30 min. Ths mixture was cooled and diluted with ether. Yellow crystals of salt were filtered off. The yield of II was 47.72 g (89%), mp 163-165°C, IR spectrum: 1090 (ClO_4^-), 1580 (C_6H_4), 1620 cm^{-1} (pyrilium cation).

Reaction of Perchlorate II with Lithium Aluminum Hydride. A sample of 32 g (0.111 mole) 2-tert-butyl-1-benzopyrilium perchlorate (II) was added in portions over 15-20 min to a mixture of 1.7 g (0.045 mole) lithium aluminum hydride and 100 ml absolute ether cooled to −80°C by a mixture of hexane with liquid nitrogen. Then, the mixture was warmed to 0°C over 1 h followed by the consecutive addition of 2 ml water, 4 ml 25% NaOH, and 2 ml water. After filtration to remove the inorganic products, the mixture was distilled in vacuum to give 17.2 g (82%) of the product mixture as a colorless liquid with an unpleasant odor, $C_{13}H_{16}O$, bp 120-122°C (30 hPa), 110°C (16 hPa). IR spectrum (neat): 1240 (C—O—C), 1590 ($C—C_{arom}$), 1685 cm^{-1} (C=C, 4H-chromene).

Reaction of Perchlorate II with 1,3-Dimethylbenzimidazoline (V). A solution of 3 ml (0.02 mole) V in 20 ml hexane was added over 1 h to a suspension of 5.74 g (0.02 mole) salt II in 50 ml hexane cooled to 0°C. The reaction mixture was stirred for an additional 30 min and the precipitate of 1,3-dimethylbenzimidazolium perchlorate was filtered off. The yield of this salt was 4.93 g (100%). The filtrate was distilled in vacuum. The boiling point corresponded to the above experiment. The reaction with benzimidazoline VI was carried out by analogy.

Reaction of Perchlorate II with 2,4-Diphenyl-4H-chromenone (VII). A sample of 5.68 g (0.02 mole) chromene VII was added to a solution of 5.74 g (0.02 mole) salt II in 20 ml dry acetonitrile and the suspension was stirred with a magnetic stirrer. After 30 min, the starting chromene was dissolved and 2,4-diphenyl-1-benzopyrilium perchlorate began to precipitate. Then, 2 h after the reaction onset, the mixture was poured into 400 ml ether. The precipitated 1-benzopyrilium salt was filtered off. The product yield was 7.07 g (93%), mp 214°C (corresponding to the data of Kröhnke and Dickore [10]). The filtrate was distilled to give a mixture of chromenes with the same melting point. The product yield was 2.82 g (75%).

The reaction of perchlorate II with sodium borohydride was carried by analogy to the procedure of Reynolds [1].

LITERATURE CITED

1. G. A. Reynolds and J. A. Van Allan, J. Org. Chem., 32, No. 11, 3616 (1967).
2. H. Decker and R. Fellenberg, Annalen., 364, 32 (1908).
3. L. Fieser and M. Fieser, Reagents for Organic Synthesis [Russian translation], Izd. Mir, Moscow (1970).
4. A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 9, 1171 (1979).
5. A. S. Morkovnik and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 8, 1020 (1980).
6. N. T. Berberova and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 8, 1011 (1984).
7. N. T. Berberova, E. P. Ivakhnenko, A. S. Morkovnik, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 12, 1696 (1979).
8. A. V. El'tsov and M. V. Girshovich, Zh. Org. Khim., 3, 1332 (1967).
9. A. Löwenbein, Berichte, 57, 1517 (1924).
10. F. Kröhnke and K. Dickore, Chem. Ber., 92, 46 (1959).