## Reaction of 2,3,4,5,6-Pentabromobenzyl Bromide with 2,4,6-Triphenylpyranyl

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**Abstract**—The main process in the reaction of 2,4,6-triphenylpyranyl with 2,3,4,5,6-pentabromobenzyl bromide in 2-propanol is electron transfer to give 2,4,6-triphenylpyrylium bromide and 2,3,4,5,6-pentabromobenzyl radical.

2,4,6-Triphenylpyranyl (I) is an electron-rich radical [1]. In the presence of an appropriate acceptor, an 2,4,6-triphenylpyranyl tends to give off an electron, thus being converted into aromatic cation. As an such acceptor we selected 2,3,4,5,6-pentabromobenzyl bromide (II) which possesses a fairly labile bromine atom in the benzylic position and is readily involved in nucleophilic substitution reactions [2, 3]. We pre-

sumed that the C–Br bond in **II** should readily undergo homolytic dissociation with formation of relatively stable pentabromobenzyl radical (**III**) and that compound **II** will react with radical **I** according to scheme (1).

Further transformations of radical **III** may follow several pathways.



The reaction of triphenylpyranyl  $\mathbf{I}$  with pentabromobenzyl bromide  $\mathbf{II}$  was performed with equimolar amounts of the reactants by heating in 2-propanol in a carbon dioxide atmosphere, for triphenylpyranyl is known to react with oxygen to give a mixture of oxidation products [4, 5]. During the first 15 min, the initially purple solution (due to radical **I**) turned light yellow, and a solid precipitated. It was filtered off and analyzed by GLC and TLC. According to the chromatographic data, the product was a mixture of initial

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pentabrombenzyl bromide II, pentabromotoluene VI, 1,2-bis(pentabromophenyl)ethane (V), and two unidentified compounds. Probably, the latter are combination products of pentabromobenzyl and triphenylpyranyl radicals (VII and VIII). The mother liquor contained triphenylpyrylium bromide and acetone (the latter is formed by dehydrogenation of 2-propanol with pentabromobenzyl radical). Evaporation of the mother liquor gave 2,4,6-triphenylpyrylium bromide (IV).

Quantitative analysis of the products revealed some interesting features. The pyranyl radical was consumed completely, while the yield of triphenylpyrylium bromide **IV** was only 65%. Presumably, the remaining part of **I** reacted with the pentabromobenzyl radical **III** formed by reaction (1), leading to compounds **VII** and **VIII**. Insofar as pentabromobenzyl radical **III** is fairly stable, apart from reaction (3), it undergoes dimerization to 1,2-bis(pentabromophenyl)ethane [yield ~15%; reaction (2)] and abstracts hydrogen from the solvent (2-propanol), thus being converted into pentabromotoluene **VI** (yield ~7%).

The reaction of 2,4,6-triphenylpyranyl (I) with 2,3,4,5,6-pentabromobenzyl bromide (II) occurred at a considerably lower rate: the mixture lost its purple color only after heating for 2 h. When the reaction was complete, the precipitate of 2,4,6-triphenylpyrylium bromide (IV) was separated (yield 27.5%), and the mother liquor contained unreacted benzyl bromide (II), 2,3,4,5,6-pentabromotoluene (VI), and compounds VII and VIII (according to the TLC data, the latter were identical to those formed in 2-propanol; Silufol plates, benzene–carbon tetrachloride, 1:1). The quite a low yield of pyrylium bromide (IV) (27.5% of the theoretical amount) must be noted. Assuming that compound IV can be formed only by reaction (1), it becomes clear why the reaction mixture contains a large amount of unreacted pentabromobenzyl bromide (~72.5%). The yield of pentabromotoluene was about 6%, oer reacted pentabromobenzyl bromide. No dimerization product of pentabromobenzyl radical [reaction (2)] was detected in toluene.

Presumably, the observed difference in the behavior of 2,4,6-triphenylpyranyl radical toward pentabromobenzyl bromide in 2-propanol and toluene results from different polarities of these solvents. More polar 2-propanol favors electron transfer from radical I with formation of a more polar species, triphenylpyrylium bromide, while the formation of a polar species in nonpolar toluene is difficult.

## EXPERIMENTAL

The reaction mixtures and products were analyzed by GLC on a Chrom-41 chromatograph equipped with a thermoionic detector and a glass column,  $3000 \times 3$  mm, packed with 3% of OV-17 on Chromaton N-Super (0.16–0.20 mm); carrier gas nitrogen, oven temperature 250°C, injector temperature 300°C. Thinlayer chromatography was performed on Silufol UV-254 plates; spots were visualized under UV light or by treatment with iodine vapor. 2,4,6-Triphenyl-pyranyl dimer was synthesized by the procedure described in [6].

Reaction of 2,4,6-triphenylpyranyl (I) with 2,3,4,5,6-pentabromobenzyl bromide (II) in 2**propanol.** A mixture of 2.6 g of 2,3,4,5,6-pentabromobenzyl bromide and 70 ml 2-propanol was purged with carbon dioxide to remove oxygen, and 1.4 g of 2,4,6-triphenylpyranyl dimers was quickly added. The mixture was heated for 2 h while continuously bubbling carbon dioxide and cooled, and the precipitate was filtered off (2.7 g) and treated with boiling 1-butanol. The residue was 1,2-bis(pentabromophenyl)ethane, yield 0.4 g (9%), grayish crystals, mp 334-337°C. According to the TLC data, the extract contained 2,3,4,5,6-pentabrombenzyl bromide and 2,3,4,5,6pentabromotoluene (Rf 0.60 and 0.78, respectively; eluent petroleum ether) and two unidentified compounds ( $R_f$  0.54 and 0.26; benzene–carbon tetrachloride, 1:1). Evaporation of the mother liquor gave 1.2 g (65%) of 2,4,6- triphenylpyrylium bromide, mp 238-242°C.

Reaction of 2,4,6-triphenylpyranyl (I) with 2,3,4,5,6-pentabromobenzyl bromide (II) in toluene. A mixture of 1.8 g of 2,3,4,5,6-pentabromobenzyl bromide and 24 ml of anhydrous toluene was purged with carbon dioxide to remove oxygen, and 1.0 g of 2,4,6-triphenylpyranyl dimer was quickly added. The mixture was heated for 4 h while continuously bubbling carbon dioxide and cooled, and the precipitate was filtered off. It was 2,4,6-triphenylpyrylium bromide, 0.35 g (28%), mp 238-242°C. Evaporation of the mother liquor gave 2.4 g of yellow oily crystals which, according to the TLC data, were a mixture of 2,3,4,-5,6-pentabromobenzyl bromide, 2,3,4,5,6-pentabromotoluene ( $R_f$  0.60 and 0.78, respectively; eluent petroleum ether) and two unidentified compounds with  $R_f$ 0.54 and 0.26 (benzene-carbon tetrachloride, 1:1).

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