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Free Radicals: XXVIII.* Reaction of 2,4,6-Triphenylpyranyl with (Diacetoxy-λ³-iodanyl)benzene

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Abstract—The major product of the reaction of 2,4,6-triphenylpyranyl with (diacetoxy- λ^3 -iodanyl)benzene in acetonitrile and acetone was 2,4,6-triphenylpyrylium acetate. Analogous reaction in isopropyl alcohol resulted in the formation of methane, carbon dioxide, 1,3,5-triphenylpent-2-ene-1,5-dione, 2-benzoyl-3,5-diphenylfuran, 1,3,5-triphenylpenta-2,4-dien-1-one, and a small amount of 2,4,6-triphenylpyrilium acetate.

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Chemistry of peroxy compounds, in particular peroxycarboxylic acids, attracts considerable interest due to their use as radical initiators [2]. At present, the main procedure for the synthesis of acetoxyl radicals is thermal decomposition of peroxy acids. However, decomposition of acetoxyl radical with liberation of carbon dioxide under these conditions is a very fast process, so that a number of authors [3] believe that such radicals cannot exist outside solvent cage. In this connection, search for new methods for generation of acetoxyl radicals seems to be quite important. A probable procedure is that involving electron-rich [4] 2,4,6-triphenylpyranyl (I) as electron donor and (diacetoxy- λ^3 -iodanyl)benzene (II) as acceptor (the latter is widely used as oxidant) [5–7].

We presumed that the reaction of radical I with compound II could give rise to acetoxyl radical IV (Scheme 1) and that the latter could participate in various reactions, including reactions with both radical I and solvent. As solvents we tried acetone, acetonitrile, and propan-2-ol. The reactions in acetone and acetonitrile were carried out at slightly elevated temperature (~35°C) in a carbon dioxide atmosphere, taking into account that 2,4,6-triphenylpyranyl (I) can be oxidized with atmospheric oxygen [8]. The end of the process was determined by disappearance of the red color typical of the initial radical. In fact, pyranyl radical I reacted with (diacetoxy- λ^3 -iodanyl)benzene (II) in acetone and acetonitrile as shown in Scheme 1, and acetoxyl radical thus generated reacted with initial radical I to form pyrylium acetate III. At a I-to-II ratio of 2:1, the major product was pyrylium salt III (80–90%), and the reaction was accompanied by insignificant gas evolution (less than 0.1 mol of a CO₂–CH₄ mixture per mole of compound II).

The reaction of radical **I** with compound **II** with propan-2-ol was performed under carbon dioxide at 60°C. The reaction was accompanied by vigorous gas evolution, and termination of the latter process indicated that the reaction was complete. In this case,



^{*} For communication XXVII, see [1].

pyrylium acetate III was formed in an insignificant amount; therefore, the reaction of triphenylpyranyl I with compound II was studied in more detail at a constant concentration of the former and different concentrations of the latter. At a II-to-I molar ratio of larger than or equal to unity, the reaction solutions lost their red color due to pyranyl I when the reaction was complete (gas evolution ceased), whereas the reaction solutions remained red at II-to-I molar ratio of less than unity.

A solid separated from the solution was identified as 1,3,5-triphenylpent-2-ene-1,5-dione (V). According to the GLC and TLC data, the mother liquor contained triphenylpyrylium acetate (III), acetone, acetic acid, iodobenzene, and a number of products resulting from transformations of 2,4,6-triphenylpyranyl (I); among the latter, we isolated and identified (by IR and ¹H and ¹³C NMR spectra and comparison with authentic samples) 1,3,5-triphenylpent-2-ene-1,5-dione (V), 1,3,5-triphenylpenta-2,4-dien-1-one (VI), and 2-benzoyl-3,5-diphenylfuran (VII).



The amount of liberated gaseous products depends on the ratio of pyranyl I and compound II; it increases in parallel with the amount of I and remains constant when the ratio I: II reaches 1:1. Analogous dependence is observed for acetic acid (Fig. 1). Excess compound II over I after attainment of their equimolar ratio does not affect the amount and composition of the gaseous products (methane and carbon dioxide).** However, the amount of pentenedione V which could be formed only from pyranyl I [8–10] decreases as the reactant ratio increases and remains constant when the reactant ratio becomes equimolar (Fig. 1).

We also examined the reaction of pyranyl radical I with compound II at a reactant ratio of 0.67:1 (mmol/mmol) at different temperatures with a view to



Fig. 1. Dependence of the amounts of acetic acid and 1,3,5-triphenylpent-2-ene-1,5-dione (V) on the reactant ratio II: I ($v_I = 0.667$ mmol).

estimate temperature effect on the product composition (Fig. 2). As follows from the above relations (Fig. 1), the reaction in propan-2-ol is complete at equimolar amounts of the reactants (compounds I and II). Therefore, we concluded that this reaction leads to the formation of compounds III and IV and that compounds V and VII are formed as a result of further transformations of 2,4,6-triphenylpyrylium acetate (III).

While considering solvent effect in the reaction under study, it should be noted that solvents characterized by low viscosity, such as acetone ($\eta = 0.30$ cP) and acetonitrile ($\eta = 0.33$ cP), facilitate escape of acetoxyl (**IV**) from solvent cage, and radical **IV** reacts with pyranyl **I** to produce pyrylium acetate **III**. Quite different pattern is observed with more viscous propan-2-ol ($\eta = 1.77$ cP) as solvent; it may hamper escape of acetoxyl (**IV**) from solvent cage. Acetoxyl radical **IV** can either undergo decarboxylation to give



Fig. 2. Temperature dependences of (1) overall amount of acetic acid and carbon dioxide, (2) overall amount of methane and acetic avid, (3) amount of carbon dioxide, (4) amount of methane, and (5) amount of acetic acid formed in the reaction of 2,4,6-triphenylpyranyl (I) with (diacetoxy- λ^3 -iodanyl)benzene (II) in propan-2-ol; ratio I:II = 0.667:1.

^{**} These compounds are formed as the major products in thermal decomposition of acetyl peroxide in isopropyl alcohol [9].

methyl radical and carbon dioxide or abstract a hydrogen atom from isopropyl alcohol with formation of acetic acid and isopropoxyl radical (VIII). Methyl radical is also capable of abstracting hydrogen from isopropyl alcohol, yielding methane and radical VIII (Scheme 2).

Scheme 2.
AcO'
$$\longrightarrow$$
 Me' + CO₂
AcO' + Me₂CHOH \longrightarrow AcOH + Me₂ĊOH
VIII
Me' + Me₂CHOH \longrightarrow CH₄ + VIII

The reaction direction depends on the temperature (Fig. 2). At low temperature predominant formation of acetic acid is observed, whereas at elevated temperature the main process is decarboxylation of acetoxyl (IV) with formation of methane.

The sum of the mole fractions of methane and acetic acid remains almost constant (~0.65–0.68 mmol) at different temperatures (Fig. 2); therefore, we presumed that both these products originate mainly from radical **IV**. Apart from transformation into pyrylium acetate **III**, triphenylpyranyl **I** can be involved in other reactions. In particular, isopropoxyl (**VIII**) can reduce pyranyl radical **I** to 1,3,5-triphenylpenta-2,4-dien-1-one (**VI**) which is also formed via reduction of pyrylium salts [11] (Scheme 3).



Pyrylium acetate III (which was expected to be the major product of the reaction of radical I with compound II in propan-2-ol) was formed in a very small amount, and its yield decreased as the temperature rose: \sim 7% at 35°C, \sim 4% at 40°C, \sim 2% at 50°C, and \sim 1% at 60°C. These data may be rationalized only assuming ready reaction of pyrylium salts with nucleophiles [10–13]; the latter may be acetate ion and iso-

propyl alcohol. The major product of reactions with nucleophiles is usually 1,3,5-triphenylpent-2-ene-1,5dione (V) [10, 12, 13]. For instance, compound V was formed together with VI and VII in the reaction of 2,4,6-triphenylpyrylium tetrachloroferrate with sodium nitrite in isopropyl alcohol [13], and the yield of V changed from 14 to 60%, depending on the conditions. The same compound was formed in analogous reactions performed using different alcohols as solvents [13]. 2-Benzoyl-3,5-diphenylfuran (VII) is likely to be formed as a result of mild oxidation of V [13]. Structurally related 2-acetyl-3,5-dimethylfuran was obtained by oxidation of 2,4,6-trimethylpyrylium perchlorate with hydrogen peroxide [14].

EXPERIMENTAL

Gas chromatographic analysis was performed on Chrom-42 and Kristall LYuKS 2000 chromatographs equipped, respectively, with nitrogen phosphorus and flame ionization detectors; glass columns, 3000×3.5 and 1500×3.5 mm; stationary phase 3% of OV-17 on Chromaton N-Super (0.16–0.20 mm); oven temperature 40, 170, and 250°C; injector temperature 100, 240, and 300°C; carrier gas nitrogen, flow rate 40 ml× min⁻¹. The ¹H and ¹³C NMR spectra were recorded from solutions in CD₂Cl₂ on a Bruker AMX-400 spectrometer at 400 and 100 MHz, respectively. TLC analysis was performed on Silufol UV-254 plates using toluene, petroleum ether, benzene, chloroform, or CCl₄–benzene (1:1) as eluent; spots were detected by treatment with iodine vapor and UV irradiation.

Compounds I [15] and II [16] were synthesized by known methods. Authentic samples of V, VI, and VII were prepared as described in [17, 12, 18], respectively. Solvents were purified according to standard procedures [19].

Reaction of 2,4,6-triphenylpyranyl (I) with (diacetoxy- λ^3 -iodanyl)benzene (II). The reaction was carried out in a setup analogous to the Zerewitinoff– Hölscher setup for microdetermination of active hydrogen [20]. One arm of the setup was charged with a mixture of compounds I and II at a required ratio, an the other arm was charged with 5 ml of the corresponding solvent. The reaction vessel was adjusted to 35°C (with acetone or acetonitrile as solvent) or 60°C (propan-2-ol), and dry carbon dioxide was bubbled through the solvent over a period of 30 min. The solvent was then transferred into the arm containing the reactants. When the reaction was complete (red color disappeared), the volume of the evolved gas was measured, and carbon dioxide was absorbed by alkali. The remaining gaseous product was methane.

Analysis of the reaction mixture (in acetone or acetonitrile) by GLC showed the presence of acetic acid (9 and 7%, respectively). The mole fraction of acetic acid was calculated with respect to iodobenzene whose yield was arbitrarily assumed to be 100%. After evaporation of the reaction mixture, the residue was almost pure 2,4,6-triphenylpyrylium acetate (III; 87 and 90%, respectively).

When the reaction was carried out in propan-2-ol, the mixture was kept for 24 h on exposure to air, and the precipitate of 1,3,5-triphenylpenta-2,4-dien-1-one (VI) was filtered off. The filtrate contained (GLC) iodobenzene, acetic acid, and acetone. The fraction of acetic acid was calculated with respect to iodobenzene whose yield was arbitrarily assumed to be 100%. The filtrate was evaporated to dryness, and the residue was treated with diethyl ether. The undissolved material was 2,4,6-triphenylpyrylium acetate (III). The ether extract was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel (40-100 µm) using benzene as eluent. We isolated three fractions: 1,3,5-triphenylpent-2-ene-1,5-dione (V), mp 120–122°C [12], R_f 0.45; 1,3,5-triphenylpenta-2,4-dien-1-one (VI), mp 124-126°C [17], $R_{\rm f}$ 0.60; and 2-benzoyl-3,4-diphenylfuran (VII), mp 117°C [18], $R_{\rm f} = 0.70$.

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