Reaction of 5-phenylpenta-2,4-dienoic acid with benzene in trifluoromethanesulfonic acid

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The reaction of 5-phenylpenta-2,4-dienoic acid with benzene in CF_3SO_3H, depending on the reaction conditions, gives three products, namely, 5,5-diphenylpent-2-enoic acid and tetralone and indanone derivatives. These carbocyclic compounds are formed through the addition of two benzene molecules to the starting diene acid and subsequent intramolecular acylation.

Key words: dienoic acids, 5-phenylpenta-2,4-dienoic acid, indanones, 3,4-dihydronaphthalen-1(2*H*)-ones, 5,5-diphenylpent-2-enoic acid, trifluoromethanesulfonic acid, carbocations, superelectrophilic activation.

Superelectrophilic activation of organic compounds under the action of various strong Brønsted and Lewis acids or acidic zeolites is one of the most efficient organic methods.[1,2] This activation promotes the generation of multiply charged cations in low nucleophilic media, in which they can react with poor nucleophiles, for example, with arenes.[2] Some of the best studied objects in this area are alkenes, the protonation of which in superacids or coordination with strong Lewis acids gives alkyl cations, which would undergo further transformations.[3—14] Despite the large amount of data on the superelectrophilic activation of alkenes, the transformations of conjugated dienes under these conditions remain poorly studied. The 1,3-butadiene systems conjugated with various acceptor substituents contain several basic centers, such as acceptor heteroatoms and carbon atoms of multiple bonds. Their protonation gives cationic species with several electrophilic sites capable of reacting in different directions.

The purpose of the present work is to study the reactions of 5-phenylpenta-2,4-dienoic acid **1** with benzene in Brønsted superacids (CF_3SO_3H, FSO_3H) or under the action of strong Lewis acids AlX_3 (X = Cl, Br).

We found that in trifluoromethanesulfonic acid (TfOH), depending on the conditions, the reaction of phenyl diene **1** with benzene gives diphenylalkene **2**, tetralone **3**, and indanone **4** (Scheme 1, Table 1).

The structures of compounds **3** and **4** was confirmed by X-ray diffraction analysis (Fig. 1). Carrying out this reaction in the TfOH—CH_2Cl_2 system (Tf = F_3CSO_2) at 0 °C for 1 h gives products **2—4** in a 55% total yield with the incomplete conversion of substrate **1** (see Table 1, entry *1*). Raising the temperature to ambient and prolongation the reaction to 1—5 h leads to a significant growth in the yields of compounds **2—4**, with the yield of diphenyl diene **2** decreasing from 14% to 6% as the reaction time increases from 1 to 5 h (entries *2—4*). Lowering the acidity of the reaction medium by adding pyridine to TfOH slows down the reaction, and at room temperature it requires 24 h to achieve a complete conversion of starting compound **1** (entries *5* and *6*). Indanone **4** is not formed in the system with the lowest acidity (TfOH/pyridine = = 4 : 1 v/v) (entry *6*). The reactions under the action of aluminum halides (entry *8*) or in the stronger than TfOH fluorosulfonic acid FSO_3H at −78 °C (entry *7*) lead to complex mixtures of products.

The formation of compounds **2—4** indicates that cationic species with several electrophilic sites are generated from diene acid **1** in TfOH. A plausible mechanism of these transformations is presented in Scheme 2. The initial protonation of the carboxy group of acid **1** gives cation **A**, which can be further protonated at the C=C double bonds under superacidic conditions similarly to the O,C-diprotonation of conjugated enones.[5] In this case, in species **A** different double bonds can be protonated: at the C(2) atom to generate dication **B** or at the C(4) atom to generate dication **F**. The reaction of the latter with benzene gives

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Scheme 1

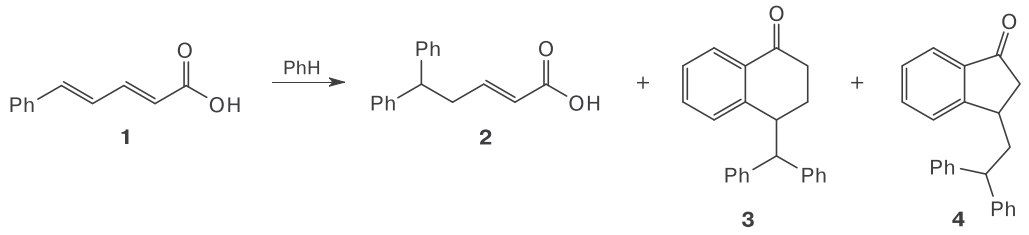


Table 1. Reactions of 5-phenylpenta-2,4-dienoic acid **1** with benzene in various acidic systems leading to compounds **2**, **3**, and **4**

Entry	Reaction conditions			Product yields (%)		
	Medium	T/°C	τ/h	**2**	**3**	**4**
1	TfOH, CH_2Cl_2	0	1	13	21	21
2	TfOH	20	1	14	46	32
3	TfOH	20	2	12	48	26
4	TfOH	20	5	6	51	27
5	TfOH—pyridine (5 : 1 v/v)	20	24	13	41	30
6	TfOH—pyridine (4 : 1 v/v)	20	24	59	31	—
7	FSO_3H	−78	1	A complex mixture of compounds		
8	AlX_3 (X = Cl, Br)	20	1	A complex mixture of compounds		

species **G**, the deprotonation of which in a low acidic system TfOH—pyridine leads to diphenylalkene **2**. Further protonation in the superacid TfOH of the C=C bond in cation **G** gives species **H**, the reaction of which with benzene leads to cation **I**. Subsequent intramolecular acylation finalizes the formation of indanone **4**. In an alternative direction, dication **B** reacts with benzene (a resonance form **B′**) to form cation **C**, which through intermediates **D** and **E** is converted into reaction product **3**.

Based on this reaction scheme, it can be assumed that indanone **3** and tetralone **4** are formed *via* different pathways (see Scheme 2). The bifurcation of the reaction directions occurs at the stage of formation of dications **B** and **F**. In the first case, the hydrophenylation takes place at the C(2) and C(5) positions of the pentadienone system of the starting compound **1** (generation of species **C**), while in the second case, the hydrophenylation occurs at the C(4)=C(5) bond of compound **1** (generation of species **G**). In this case, diphenylpentenoic acid **2** lies in the path of formation of indanone **4**. However, indanone **4** is not formed in the system with the lowest acidity TfOH—pyridine (4 : 1 v/v) (see Table 1, entry *6*). Apparently, this

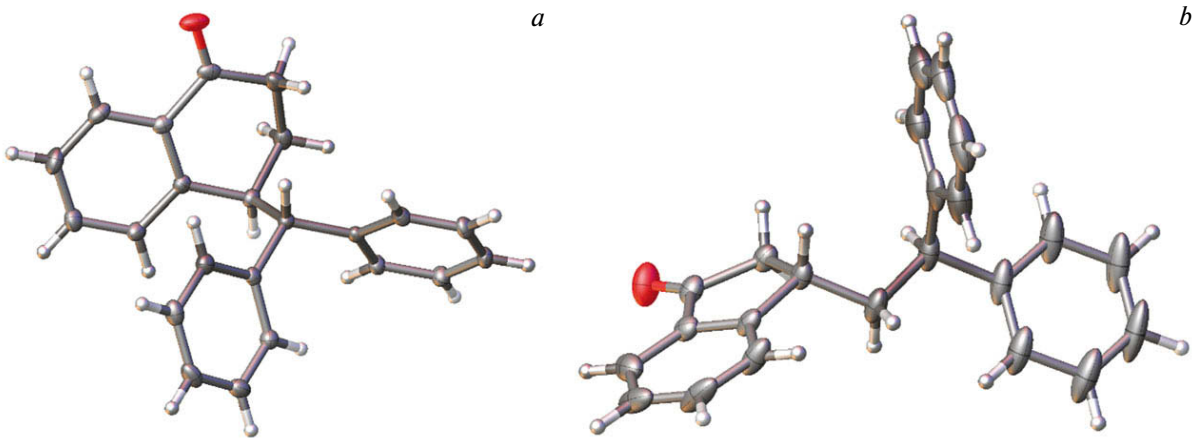
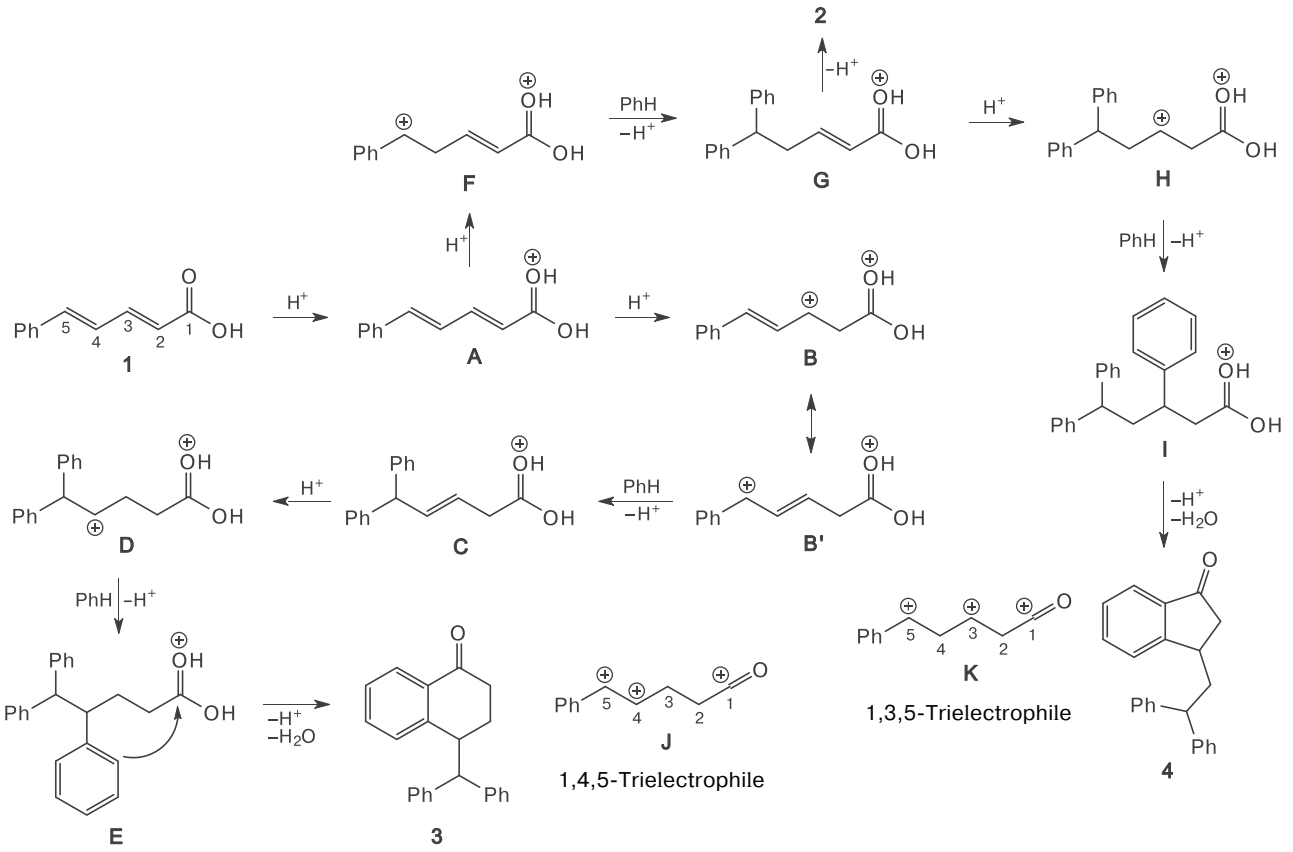


Fig. 1. The structures of compounds **3** (*a*) and **4** (*b*) according to X-ray diffraction data.

Scheme 2



is due to the impossibility of protonation in this system of the C=C double bond conjugated with a strongly accepting protonated carboxy group, which sharply reduces the basicity of this double bond. In contrast to this, protonation of the C=C double bond in cation **C** having no strong accepting substituents occurs readily in the TfOH—pyridine system, which finally gives tetralone **3** (see entries *5* and *6*).

In the studied transformations leading to compounds **3** and **4**, dienoic acid **1**, if take into account the formation of cationic centers upon protonation of the conjugated pentadiene system of acid **1** in TfOH, can be considered as a precursor of two three-centered electrophilic species, namely, **J** (1,4,5-trielectrophile) and **K** (1,3,5-trielectrophile), respectively (see Scheme 2).

Note that the preparation and study of chemical transformations of such structurally related pentadienoic acids is of great importance for organic synthesis.[15]

In conclusion, the reaction of 5-phenylpenta-2,4-dienoic acid (**1**) with benzene in TfOH initially leads to the products of hydrophenylation of different positions of the pentadienone system, which are then converted into benzocarbocyclic derivatives of tetralone **3** and indanone **4** series.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 instrument (500 and 125 MHz, respectively) in $CDCl_3$. High-resolution mass spectra were recorded on a Bruker maXis HRMS-ESI-QTOF instrument. Chromato-mass spectral analysis was carried out on a G 2570A GC/MSD instrument (Agilent Technologies 6850c), an HP-5MS capillary column (3 m×0.25 mm), stationary phase thickness 0.25 μm, carrier gas helium.

5-Phenylpenta-2,4-dienoic acid (1) was synthesized by the reaction of cinnamaldehyde (5.25 mL, 38 mmol) with malonic acid (4.7 g, 45 mmol) in pyridine (10 mL) and piperidine (0.2 mL). The reaction mixture was stirred at 100 °C for 4 h and poured into concentrated hydrochloric acid (30 mL), the formed precipitate was collected by filtration and recrystallized from ethanol. The yield was 60%. M.p. 164—167 °C (Ref. 16: m.p. 165—166 °C). ^{1}H NMR ($CDCl_3$), δ: 6.01 (d, 1 H, J = 15 Hz); 6.88—6.98 (m, 2 H); 7.31—7.58 (m, 4 H); 7.49 (d, 1 H, J = 7 Hz). ^{13}C NMR ($CDCl_3$), δ: 120.2, 126.0, 127.3, 128.9, 129.3, 135.8, 141.6, 146.9, 171.9. MS (gas chromatography-mass spectrometry data), m/z (I_{rel} (%)): 174 $[M]^+$ (25), 129 (100), 115 (8), 102 (8), 77 (9), 51 (8).

Reaction of dienoic acid 1 with benzene under the action of TfOH (general procedure): synthesis of compounds 2, 3, and 4. Acid **1** (100 mg, 5.7 mmol) was added to a mixture of benzene (1 mL) and TfOH (1 mL). The mixture was stirred at room

Table 2. Crystallographic data and parameters of X-ray diffraction experiment for compounds **3** and **4**

Parameter	**3**	**4**
Molecular formula	$C_{23}H_{20}O$	$C_{23}H_{20}O$
Molecular weight	312.39	312.39
T/K	293	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	9.0544(4)	14.1591(6)
b/Å	19.1430(8)	15.6726(8)
c/Å	10.3358(4)	7.7444(3)
α/deg	90	90
β/deg	111.570(5)	102.226(5)
γ/deg	90	90
V/Å^3	1666.02(13)	1679.59(14)
Z	4	4
d_{calc}/g cm^{-3}	1.245	1.235
2θ-Range for data collection/deg	5.552—54.992	5.198—54.996
Number of reflections		
collected (R_{int})	12724	27562
($I \geq 2\sigma(I)$)	3833	3855
(R_{int})	(0.0274)	(0.0316)
(R_{sigma})	(0.0277)	(0.0198)
Number of refined parameters	217	217
R-factors ($I \geq 2\sigma(I)$)		
R_1	0.0406	0.0528
wR_2	0.0999	0.1118
R-factors (for all reflections)		
R_1	0.0500	0.0611
wR_2	0.1074	0.1168

temperature for 1 h, poured into water (60 mL), and extracted with chloroform (3×30 mL). The combined extracts were washed with water (2×30 mL), dried with Na_2SO_4, the solvent was evaporated *in vacuo*. The reaction products **2**, **3**, and **4** were isolated by column chromatography on silica gel, their yields are given in Table 1. The reactions were carried out similarly in the systems TfOH—CH_2Cl_2 and TfOH—pyridine or under the action of FSO_3H or AlX_3 (X = Cl, Br) at the corresponding temperature and the reaction time (see Table 1).

5,5-Diphenylpent-2-enoic acid (2). A crystalline compound, m.p. 69—70 °C. ^{1}H NMR ($CDCl_3$), δ: 2.96 (t, 2 H, J = 7.5 Hz); 4.08 (t, 1 H, J = 7.5 Hz); 5.78 (d, 1 H, J = 15.7 Hz); 6.95 (dt, 1 H, J = 15.7 Hz, J = 7.5 Hz); 7.16—7.21 (m, 5 H); 7.25—7.30 (m, 5 H). ^{13}C NMR ($CDCl_3$), δ: 38.3, 50.1, 122.0, 126.5, 127.8, 128.6, 143.4, 149.8, 152.4. HRMS (ESI), found m/z: 253.1226 $[M + H]^+$; calculated for $C_{17}H_{17}O_2$ 253.1223.

4-Diphenylmethyl-3,4-dihydronaphthalen-1(2*H*)-one (3). A crystalline compound, m.p. 149—151 °C. ^{1}H NMR ($CDCl_3$), δ: 2.15—2.22 (m, 2 H); 2.45—2.50 (m, 1 H); 2.72—2.28 (m, 1 H); 3.69—3.72 (m, 1 H); 4.03 (d, 1 H, J = 12 Hz); 6.40 (d, 1 H, J = 8 Hz); 6.9 (d, 2 H, J = 8 Hz); 7.05—7.11 (m, 4 H); 7.21—7.24 (m, 2 H); 7.36 (t, 2 H, J = 8 Hz); 7.44 (d, 2 H, J = 8 Hz); 8.01 (d, 1 H, J = 8 Hz). ^{13}C NMR ($CDCl_3$), δ:25.7, 33.5, 43.0, 56.5, 126.4, 126.8, 126.9, 127.3, 128.0, 128.2, 128.4, 128.9, 129.9, 132.2, 142.6, 142.9, 146.2, 160.1, 198.4. MS (gas chromatography-mass spectrometry data), m/z (I_{rel} (%)): 312 $[M]^+$ (8), 167 (100), 152 (20), 115 (9), 103 (10), 77 (10). HRMS (ESI), found m/z: 313.1592 $[M + H]^+$; calculated for $C_{23}H_{21}O$ 313.1587.

3-(2,2-Diphenylethyl)indan-1-one (4). A crystalline compound, m.p. 120—121 °C. ^{1}H NMR ($CDCl_3$), δ: 2.09—2.15 (m, 1 H); 2.38—2.42 (m, 1 H); 2.72—2.81 (m, 2 H); 3.18—3.23 (m, 1 H); 4.07—4.10 (m, 1 H); 7.16—7.19 (m, 1 H); 7.21—7.23 (m, 1 H); 7.24—7.27 (m, 4 H); 7.32—7.37 (m, 5 H); 7.50 (d, 1 H, J = 8 Hz); 7.57—7.60 (m, 1 H); 7.71 (d, 1 H, J = 8 Hz). ^{13}C NMR ($CDCl_3$), δ: 36.5, 42.6, 43.2, 50.0, 123.6, 125.5, 126.4, 126.7, 127.5, 127.6, 128.0, 128.6, 128.8, 134.7, 136.6, 143.52, 144.5, 158.7, 205.9. MS (gas chromatography-mass spectrometry data), m/z (I_{rel} (%)): 312 $[M]^+$ (8), 167 (100), 152 (19), 115 (7), 103 (8), 77 (7). HRMS (ESI), found m/z: 313.1584 $[M + H]^+$; calculated for $C_{23}H_{21}O$ 313.1587.

X-ray diffraction analysis of single crystals of compounds 3 and 4 obtained by crystallization from a chloroform—hexane solvent mixture was carried out on an Xcalibur diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, temperature 293 K (for compound **3**) and 100 K (for compound **4**), θ/2θ-scan technique). The crystallographic data and the main refinement parameters for compounds **3** and **4** are given in Table 2. The structures were solved using the Superflip[17—19] and Olex2[20] programs and refined using the ShelXL[21] program (least squares method). The structures were deposited with the Cambridge Crystallographic Data Center, CCDC 1966168 (**3**) and 1966169

(**4**) at www.ccdc.cam.ac.uk/conts/retrieving.htmL, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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