

First Authentication of *Kostanecki's* Triketone and Multimolecular Reaction of Aromatic Aldehydes with Acetophenone

by **Zixing Shan***, Xiaoyun Hu, Lin Hu, and Xitian Peng

Department of Chemistry, Wuhan University, Wuhan, 430072, Hubei, P. R. China
(fax: +86-27-68754067; e-mail: zxshan@whu.edu.cn)

A double-component, multimolecular reaction between acetophenone and aromatic aldehydes was achieved under catalysis by the solid-base mixture NaOH/K₂CO₃, and *Kostanecki's* triketone, supposed to exist for more than 110 years, was successfully separated for the first time as an accompaniment of a pentane-1,5-dione or a 1,2,3,4,5-pentasubstituted cyclohexanol (*Scheme 1*) and authenticated by spectroscopic and single-crystal X-ray diffraction analysis. Thus, the multimolecular-reaction mechanism of the formation of 1,2,3,4,5-pentasubstituted cyclohexanols from 1-phenylalkan-1-ones and aromatic aldehydes was fully validated based on the results (*Scheme 3*).

1. Introduction. – Reaction of an aldehyde with an alkanone is one of the most extensively applied reactions in organic syntheses. A great number of investigations have revealed that in most cases, the alkanone undergoes a two-component, bimolecular reaction with the aldehyde to form an α,β -unsaturated ketone [1] or a β -hydroxy ketone [2], while reports on multimolecular reactions between them are rather scarce. As far as the reactions of acetophenone (=1-phenylethanone) with aromatic aldehydes are concerned, four classes of products, shown in *Fig. 1*, have been separated and characterized, *i.e.*, chalcones, β -hydroxy ketones, pentane-1,5-diones, and penta-substituted cyclohexanols [1–4]. *Kostanecki's* triketone, belonging to a class of five-molecular reaction products from acetophenone and aromatic aldehydes, has never been successfully separated and substantiated¹⁾ although its structure was supposed to be 4-benzoyl-1,3,5,7-tetraphenylheptane-1,7-dione (CAS Registry number 7149-37-3) as early as in 1896 [5]. This might be due to the fact that linear triketones are unstable compounds, and their synthesis is difficult to control.

Kostanecki's triketone is a key intermediate in the formation of multifunctional 1,2,3,4,5-pentasubstituted cyclohexanols. Surely, this does not mean that the linear triketone is impossible to be isolated as a self-existent chemical entity. The known reactions of acetophenone and aromatic aldehydes were carried out almost always in aqueous or alcoholic caustic-base solutions [8] or in the presence of a solid-supported catalyst [9]; probably, these reaction conditions were unsuitable for the formation of

¹⁾ In the literature, some authors purported that they had prepared the *Kostanecki's* triketone, the m.p. being 256° [5][6] and 189° [7], respectively; however, later, the structure of the compound with m.p. 189° was established as 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol [8], while the structure of the compound with m.p. 256° has not been elucidated to date.

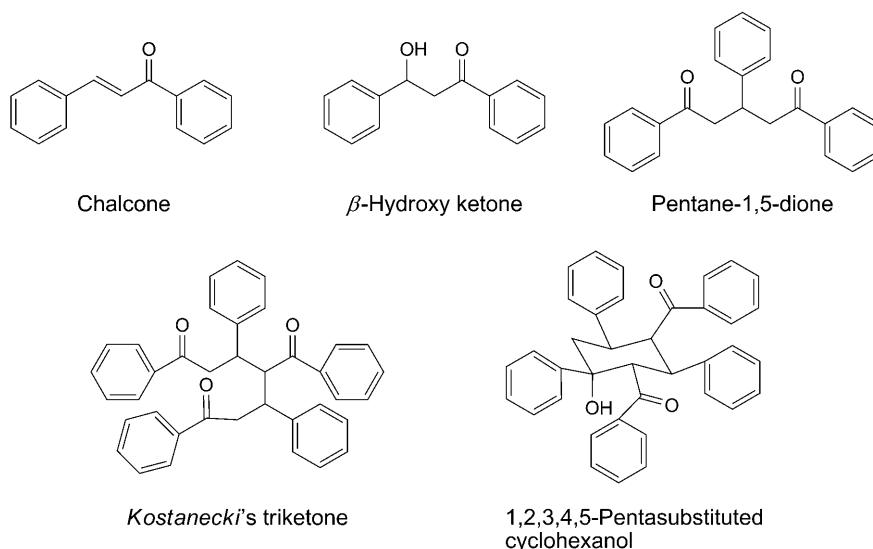


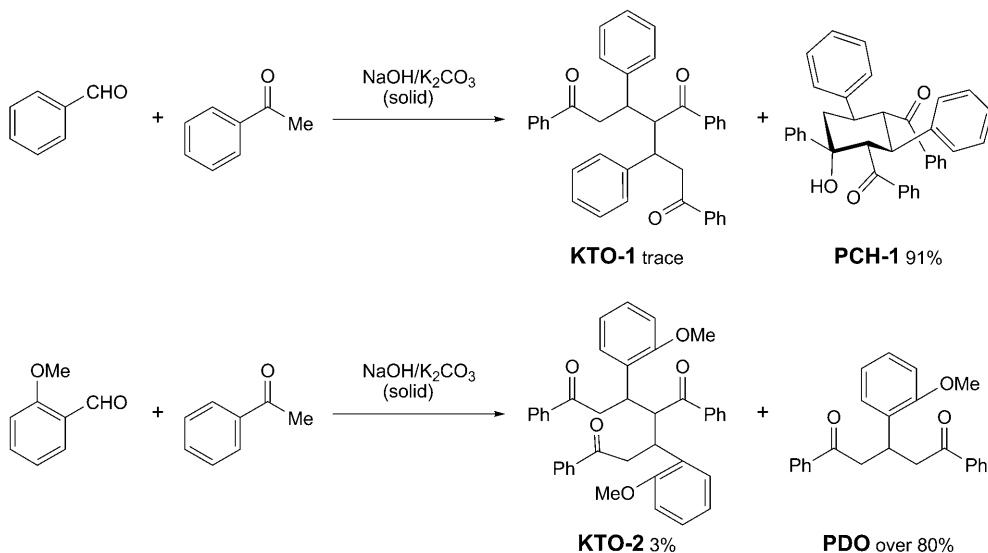
Fig. 1. Five classes of possible products from the reaction of aromatic aldehydes and acetophenone

this class of triketones. Considering that the two-component solid-base system NaOH/ K_2CO_3 has been successfully applied to a highly chemoselective preparation of 1,2,3,4,5-pentasubstituted cyclohexanols [10], we attempted to prepare *Kostanecki's* triketone by such a solvent-free reaction of acetophenone with aromatic aldehydes or chalcone (= 1,3-diphenylprop-2-en-1-one). Thus we now could isolate successfully two *Kostanecki's* triketones, 4-benzoyl-1,3,5,7-tetraphenylheptane-1,7-dione (**KTO-1**) and 4-benzoyl-3,5-bis(2-methoxyphenyl)-1,7-diphenylheptane-1,7-dione (**KTO-2**), as by-products of 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol (**PCH-1**) and 3-(2-methoxyphenyl)-1,5-diphenylpentane-1,5-dione (**PDO**), respectively. In the present work, we describe the preparation and characterization of these two *Kostanecki's* triketones as well as a plausible mechanism for the formation of 1,2,3,4,5-pentasubstituted cyclohexanols.

2. Results and Discussion. – 2.1. *Preparation of Kostanecki's Triketones.* A mixture NaOH/ K_2CO_3 2 : 1 was finely ground and then added to a mixture of benzaldehyde and acetophenone while grinding discontinuously for about 4 h at room temperature (*Scheme 1*). The obtained nonsticking yellow solid powder was extracted with AcOEt, and the residue obtained after concentration of the extract was heated to reflux in EtOH, then cooled to *ca.* 50° and filtrated. The resulting insoluble solid was recrystallized in AcOEt to afford 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol [11] (**PCH-1**) in 91% yield; the EtOH solution was concentrated and the residue separated by column chromatography (silica gel) to afford a trace of *Kostanecki's* triketone 4-benzoyl-1,3,5,7-tetraphenylheptane-1,7-dione (**KTO-1**). A similar reaction of 2-methoxybenzaldehyde with acetophenone gave *Kostanecki's* triketone 4-benzoyl-3,5-bis(2-methoxyphenyl)-1,7-diphenylheptane-1,7-dione (**KTO-2**) in 3% yield and 3-(2-

methoxyphenyl)-1,5-diphenylpentane-1,5-dione [12] (**PDO**) in more than 80% yield after recrystallization in EtOH (*Scheme 1*). On the other hand, acetophenone reacted with 4-methoxybenzaldehyde under similar conditions to furnish 2,4-dibenzoyl-3,5-bis(4-methoxyphenyl)-1-phenylcyclohexanol (**PCH-2**) in 93% yield [10]. These facts reveal that the products of the solvent-free reaction are not only in close relationship with the substituent at the aromatic aldehyde but also with the position of the substituent at the aromatic ring.

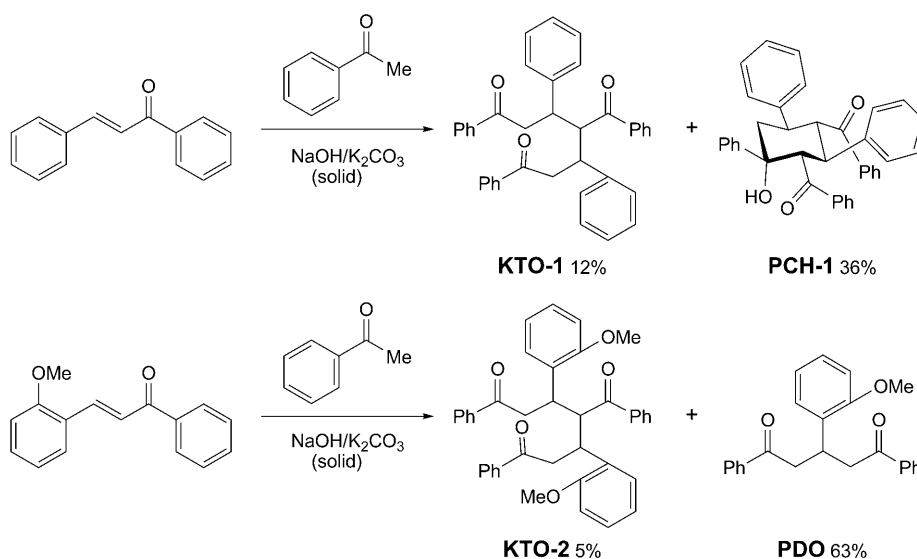
Scheme 1. Preparation of Kostanecki's Triketones **KTO-1** and **KTO-2** from Acetophenone and Aromatic Benzaldehydes via a Solvent-Free Reaction



Attempts to upgrade the **KTO-1** and **KTO-2** yield by increasing the NaOH loading in the mixed-solid catalyst and by changing the molar ratio of both the reactants did not meet with success. Nevertheless, the yields of Kostanecki's triketones **KTO-1** and **KTO-2** were upgraded to 12% and 5%, respectively, when acetophenone was allowed to react with the chalcones 1,3-diphenylprop-2-en-1-one or 3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one under the same condition as described above (*Scheme 2*); the chalcones were synthesized from acetophenone and benzaldehyde or 2-methoxybenzaldehyde.

The reaction of acetophenone and chalcone (=1,3-diphenylprop-2-en-1-one) affords 1,3,5-triphenylpentane-1,5-dione in 86% yield in the presence of solid NaOH as catalyst [12]. This is in striking contrast to the above result and reveals that the two-component solid-base catalyst NaOH/K₂CO₃ has a different catalytic activity from that of solid NaOH.

The above results indicate that under catalysis with the two-component solid-base system, Kostanecki's triketones **KTO-1** and **KTO-2** can be synthesized in low yield from acetophenone and 2-methoxybenzaldehyde, 1,3-diphenylprop-2-en-1-one, or 3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one. The low yields of **KTO-1** and **KTO-2** and

Scheme 2. Preparation of Kostanecki's Triketones **KTO-1** and **KTO-2** from Acetophenone and Chalcones via a Solvent-Free Reaction

the concomitant formation of 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol or 3-(2-methoxyphenyl)-1,5-diphenylpentane-1,5-dione display the diverse idiosyncrasy of the two *Kostanecki's* triketones.

2.2. Properties and Crystal Structure of Kostanecki's Triketones. **KTO-1** and **KTO-2** are colorless crystalline compounds with a defined melting point and have similar spectroscopic properties. The stretching vibrations of the CO groups are at 1677 cm^{-1} (strong sharp band) for **KTO-1** and $1640\text{--}1700\text{ cm}^{-1}$ (strong broad band) for **KTO-2**. Their $^1\text{H-NMR}$ spectra (Fig. 2) show four sets of resonances in a 1 : 1 : 1 : 4 intensity ratio in the upper-field region, which correspond to the seven aliphatic H-atoms, and the geminal H-atoms at C(2) and C(6) (4 H) are not equivalent, as revealed by a complicated coupling pattern. In addition, the chemical shifts of the aliphatic H-atoms of **KTO-2** always appear at lower field than the corresponding ones of **KTO-1**, implying that the presence of the 2-MeO group increases the deshielding effect of the benzene ring. The $^{13}\text{C-NMR}$ spectra of **KTO-1** and **KTO-2** reveal the chemical shifts for three CO groups at $\delta\ 195\text{--}205$; among them, the two at $\delta\ 195\text{--}200$ are attributed to C(1)O and C(7)O, and the one near $\delta\ 204.5$ to the CO group bound at C(4). The other five aliphatic C-atoms are at $\delta\ 55\text{--}35$. These are basic characteristics of *Kostanecki's* triketones.

The composition and structure of the two *Kostanecki's* triketones were also confirmed by the single-crystal X-ray diffraction analysis of **KTO-1**²⁾. A single crystal suitable for X-ray crystallographic analysis was obtained by slow recrystallization in

²⁾ CCDC-695978 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

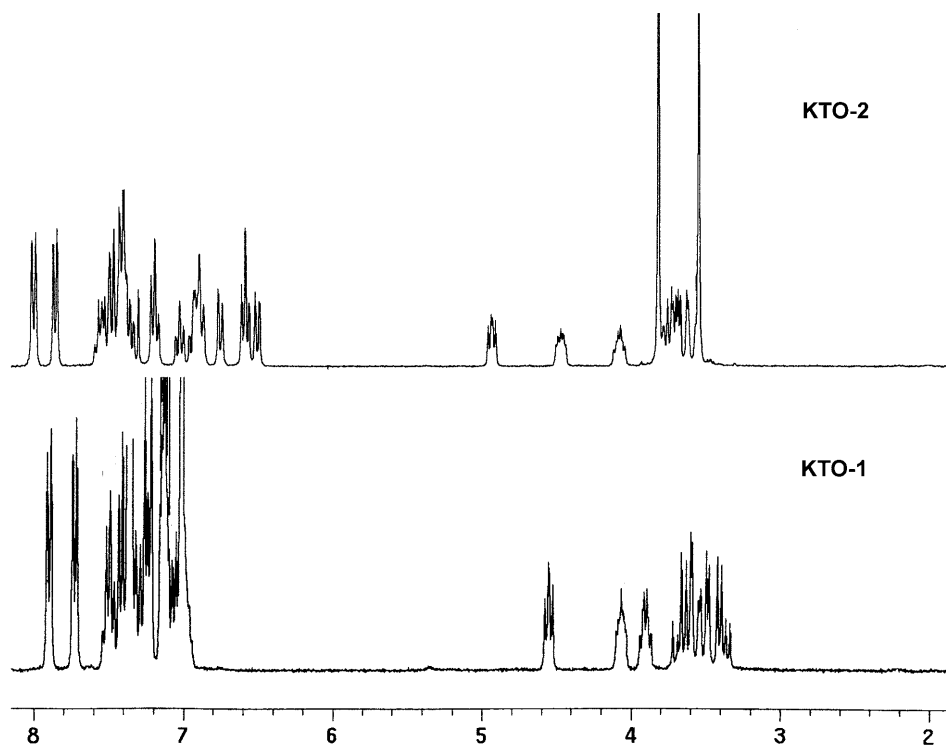


Fig. 2. $^1\text{H-NMR}$ Spectra (CDCl_3 , 300 MHz) of **KTO-1** (bottom) and **KTO-2** (top)

AcOEt. The structure of **KTO-1** (Fig. 3) showed that the Ph groups at C(9) and C(17) are in a relative ‘*trans*-arrangement’ to each other; energetically, this conformation may be unfavorable for the isomerization into a cyclohexanol. However, experiment established that pure **KTO-1** can undergo cyclization into 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol (**PCH-1**) in the presence of the two-component solid-base catalyst. Perhaps a base-catalyzed epimerization at the benzylic positions C(9) or C(17) takes place prior to cyclization.

The bond distances and bond angles of the aliphatic molecular skeleton of **KTO-1** are summarized in the Table 1. The three carbonyl groups have almost identical bond distances (*ca.* 1.215 Å) and form nearly identical bond angles with the adjacent atoms (*ca.* 119.5°), meaning that they are in almost the same environment. The data indicate that **KTO-1** belongs to the orthorhombic crystal system, and its space group is *Pbcn*.

2.3. *Formation Mechanism of the Pentasubstituted Cyclohexanol.* As described above (Scheme 1), acetophenone reacted with 2-methoxybenzaldehyde or benzaldehyde in the presence of the two-component solid-base catalyst to afford 3-(2-methoxyphenyl)-1,5-diphenylpentane-1,5-dione (**PDO**) or 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol (**PCH-1**) in high yield as well as small amounts of the *Kostanecki*’s triketones **KTO-1** and **KTO-2**, meaning that the solid catalyst $\text{NaOH}/\text{K}_2\text{CO}_3$ is especially favorable for a multimolecular reaction between an alkyl arylketone and an

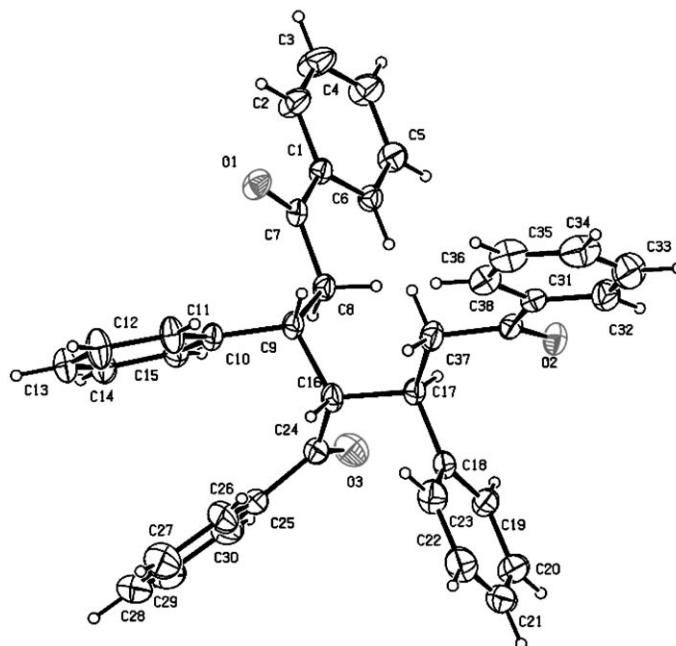


Fig. 3. X-Ray crystal structure of 4-benzoyl-1,3,5,7-tetraphenylheptane-1,7-dione (**KTO-1**). Arbitrary atom numbering.

Table. Selected Bond Distances and Bond Angles of **KTO-1**. For atom numbering, see Fig. 3.

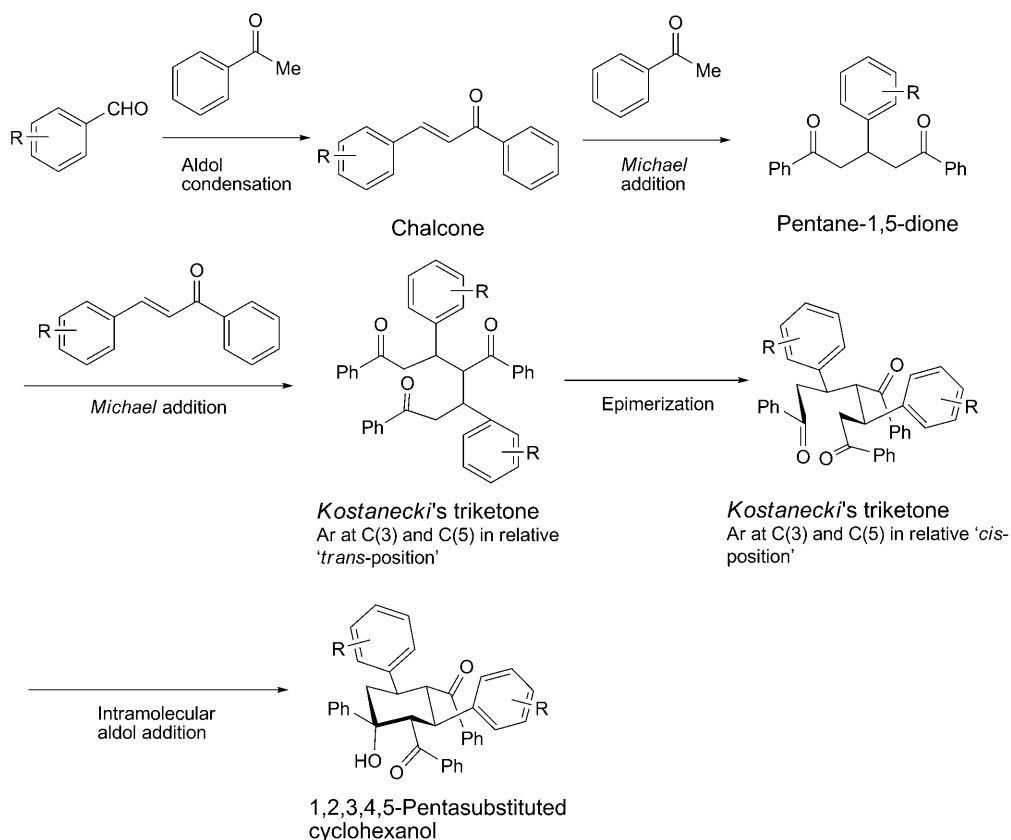
Bond distance [Å]			
C(7)–O(1)	C(24)–O(3)	C(38)–O(2)	
1.217(4)	1.215(5)	1.216(4)	
C(7)–C(8)	C(8)–C(9)	C(9)–C(10)	C(9)–C(16)
1.496(4)	1.528(4)	1.526(4)	1.565(4)
C(16)–C(24)	C(16)–C(17)	C(17)–C(18)	C(17)–C(37)
1.508(5)	1.555(4)	1.518(5)	1.523(5)
C(24)–C(25)	C(31)–C(38)	C(37)–C(38)	
1.480(4)	1.490(5)	1.505(4)	
Bond angle [°]			
C(1)–C(7)–C(8)	C(7)–C(8)–C(9)	C(8)–C(9)–C(16)	C(10)–C(9)–C(8)
119.0(3)	113.8(3)	112.5(2)	113.7(3)
C(10)–C(9)–C(16)	C(17)–C(16)–C(9)	C(18)–C(17)–C(37)	C(25)–C(24)–C(16)
110.2(3)	115.3(3)	111.2(3)	120.8(4)
C(24)–C(16)–C(17)	C(24)–C(16)–C(9)	C(37)–C(17)–C(16)	C(31)–C(38)–C(37)
110.7(3)	109.4(3)	111.5(3)	119.2(3)
O(1)–C(7)–C(1)	O(1)–C(7)–C(8)	O(2)–C(38)–C(31)	O(2)–C(38)–C(37)
119.5(3)	121.5(3)	120.4(3)	120.4(3)
O(3)–C(24)–C(25)	O(3)–C(24)–C(16)		
119.2(4)	119.9(3)		

aromatic aldehyde. The pentane-1,5-dione **PDO** is formed *via* a three-molecule reaction between acetophenone (2 equiv.) and 2-methoxybenzaldehyde (1 equiv.), while *Kostanecki's* triketones **KTO-1** and **KTO-2** and the pentasubstituted cyclohexanols **PCH-1** and **PCH-2** are formed *via* a five-molecule reaction between acetophenone (3 equiv.) and an aromatic aldehyde (2 equiv. of benzaldehyde or 2-methoxybenzaldehyde). The reactions of *Scheme 2* further reveal that the chalcone is a key building block of these multimolecular-reaction products. The *Kostanecki's* triketone is always generated as by-product of a pentane-1,5-dione or of a pentasubstituted cyclohexanol, meaning that in this kind of reaction, *Kostanecki's* triketone plays a dual role. On the one hand, *Kostanecki's* triketone is a product of the reaction of a pentane-1,5-dione and a chalcone, which can be generated *in situ* from acetophenone and an aromatic aldehyde. On the other hand, *Kostanecki's* triketone is a precursor of the pentasubstituted cyclohexanols. The structure of the chalcone influences considerably the efficiency of the formation of pentane-1,5-diones and *Kostanecki's* triketone as well as the course of the reactions. Most of the chalcones bearing a halo and electron-donating group readily give pentane-1,5-diones and *Kostanecki's* triketone, but these dione and trione products are unstable under the experimental conditions, and are immediately transformed into the pentasubstituted cyclohexanols. However, in the case of 2-methoxychalcone, the presence of the 2-MeO group not only stops the reaction with acetophenone at the stage of the pentane-1,5-dione but also hinders the further reaction of the latter with acetophenone to form *Kostanecki's* triketone and its transformation into a pentasubstituted cyclohexanol.

The above results clearly indicate that *Kostanecki's* triketone is an intermediate between pentane-1,5-dione and the pentasubstituted cyclohexanol, and this intermediate is often elusive due to its sensitivity to experimental conditions. The successful isolation and characterization of all three possible intermediates of the formation of 1,2,3,4,5-pentasubstituted cyclohexanols by us, in particular of *Kostanecki's* triketone, provides a direct gist for the elucidation of the formation mechanism of the pentasubstituted cyclohexanols from acetophenone and aromatic aldehydes (*Scheme 3*). The possibility of an epimerization at C(3) and C(5) of the molecular skeleton of *Kostanecki's* triketone, *i.e.*, the epimerization from the 'trans-arrangement' as established for **KTO-1** by its crystal structure (*Fig. 3*) to the 'cis-arrangement' of the Ph groups at C(3) and C(5), would produce an intermediate suitable for cyclization to the pentasubstituted cyclohexanol.

3. Conclusions. – In summary, we validate for the first time the existence of *Kostanecki's* triketone in the reaction of aromatic aldehydes with 1-phenylalkan-1-ones through spectroscopic and single-crystal X-ray diffraction analysis, after the triketone was supposed to exist for more than 110 years. *Kostanecki's* triketones are either difficult to form owing to the composition of the aldehyde or chalcone, or instable under the experimental conditions and transformed rapidly into multisubstituted cyclohexanols *via* an intramolecular addition. The successful separation and characterization of *Kostanecki's* triketone not only afford a practical gist for the establishment of the formation mechanism of 1,2,3,4,5-pentasubstituted cyclohexanols from 1-phenylalkan-1-ones and aromatic aldehydes but also provide a reliable model for understanding the reactions of alkyl heteroaryl ketones [4c][4d][13] with aromatic aldehydes

Scheme 3. Mechanism of the Formation of 1,2,3,4,5-Pentasubstituted Cyclohexanols



or heteroaromatic aldehydes and the reactions of chalcones with active-methylene compounds, such as alkyl heteroaryl ketones, nitroalkanes [14], alkanenitriles [15], alkyl cyanoacetates [16], malononitrile [17], *etc.*, to form multisubstituted cyclohexanol derivatives.

We thank the *National Natural Science Foundation of China* (20372053 and 20672083) for financial support.

Experimental Part

General. Commercially available starting materials and solvents were used without further purification if not specified. All known products were confirmed by comparison with those of the authentic samples. M.p.: *VEB-Wagetechnik-Rapio-PHMK05* instrument; uncorrected. IR Spectra: *Testscan Shimadzu FTIR 8000*; KBr disc; selected characteristic peaks in cm^{-1} . ^1H - and ^{13}C -NMR Spectra: *Varian-Mercury-VX-300* spectrometer; chemical shifts δ in ppm rel. to internal Me_4Si ($=0$ ppm); field lock by external referencing to the relevant deuterium resonance. MS: *VG-ZAB-HF-3F* spectrometer; in m/z (rel. %).

Preparation and Characterization of Kostanecki's Triketones. The finely ground mixture of NaOH (0.34 g, 8.5 mmol) and K_2CO_3 (0.6 g, 4.2 mmol) was added to a mixture of acetophenone (1 g, 8.3 mmol)

and chalcone (3.48 g, 16.7 mmol) and ground continuously at r.t. until the liquid disappeared (ca. 20–30 min), and then ground from time to time for ca. 4 h to furnish a nonsticking yellow solid powder. This solid was washed with H₂O, and the insoluble residue was refluxed in EtOH (80 ml) for 2 h. The temp. was reduced to ca. 50°, the mixture filtered, and the filtrate cooled to r.t. to yield precipitated 4-benzoyl-1,3,5,7-tetraphenylheptane-1,7-dione (**KTO-1**; 0.53 g, 12%). Colorless crystals. M.p. 144–146°. ¹H-NMR (CDCl₃, 300 MHz): 7.90 (d, *J* = 7.5, 2 H); 7.72 (d, *J* = 7.5, 2 H); 7.54–7.22 (m, 11 H); 7.16–7.01 (m, 10 H); 4.56 (t, *J* = 6.3, 1 H); 4.12–4.02 (m, 1 H); 3.94–3.87 (m, 1 H); 3.72–3.33 (m, 4 H). ¹³C-NMR (CDCl₃, 75 MHz): 204.3; 198.9; 198.6; 142.1; 141.3; 139.8; 137.4; 137.3; 133.2; 132.6; 128.9; 128.8; 128.7; 128.7; 128.5; 128.4; 128.3; 128.2; 128.1; 128.0; 55.4; 42.6; 42.5; 41.9; 40.1. Anal. calc. for C₃₈H₃₂O₃: C 85.04, H 6.01; found: C 84.82, H 5.95.

The EtOH filtrate removed from **KTO-1** was concentrated to give a small amount of **PCH-1**. The solid, insoluble in hot EtOH, was recrystallized from AcOEt to yield pure 2,4-dibenzoyl-1,3,5-triphenylcyclohexanol (**PCH-1**; 1.6 g, 36%). M.p. 188–190° ([18]: 189°). IR: 3442s (OH), 1696s, 1677s, 1660s (C=O). ¹H-NMR (CDCl₃, 300 MHz): 7.78 (d, *J* = 7.8, 2 H); 7.45 (d, *J* = 7.5, 2 H); 6.94–7.30 (m, 18 H); 6.81 (t, *J* = 6.6, 3 H); 5.71 (d, *J* = 12, 1 H); 5.21 (s, OH); 4.37 (t, *J* = 4.5, 1 H); 4.12–4.20 (m, 2 H); 3.41 (t, *J* = 12, 1 H); 2.05 (d, *J* = 8.4, 1 H). ¹³C-NMR (CDCl₃, 75 MHz): 208.5; 207.0; 147.1; 141.9; 140.4; 139.5; 138.5; 133.1; 132.1; 129.0; 128.4; 128.4; 128.3; 128.0; 128.0; 127.9; 127.6; 127.1; 126.8; 125.4; 53.0; 50.4; 48.3; 42.4; 38.6.

A similar reaction of acetophenone (1.200 g, 10 mmol) with 2-methoxybenzaldehyde (0.680 g, 5 mmol) yielded 3-(2-methoxyphenyl)-1,5-diphenylpentane-1,5-dione (**PDO**) and 4-benzoyl-3,5-bis(2-methoxyphenyl)-1,7-diphenylheptane-1,7-dione (**KTO-2**).

Data of PDO: Yield 63%. M.p. 113–114° ([12]: 115°). IR: 1678s, 1634m. ¹H-NMR (300 MHz, CDCl₃ + D₂O): 3.38–3.53 (m, 2 CH₂); 3.77 (s, MeO); 4.30 (quint., *J* = 7.50, H–C(3)); 6.81–6.89 (m, 2 H); 7.14–7.22 (m, 2 H); 7.41–7.56 (m, 6 H); 7.98 (d, *J* = 9, 4 H). ¹³C-NMR (75 MHz, CDCl₃): 199.5; 157.3; 137.3; 133.1; 131.6; 128.7; 128.4; 127.9; 120.9; 111.0; 55.5; 55.4; 43.3; 33.0. ES-MS (MeOH), 381 (100, [M + Na]⁺).

Data of KTO-2: Yield 5%. M.p. 164–166°. ¹H-NMR (300 MHz, CDCl₃): 3.54 (s, MeO–C(2)); 3.61–3.77 (m, 2 CH₂); 3.80 (s, MeO); 4.10–4.00 (m, CH); 4.50–4.40 (m, CH); 4.94–4.87 (m, CH); 6.47 (d, *J* = 8.10, 1 H); 6.55 (t, *J* = 7.20, 2 H); 6.71 (d, *J* = 8.10, 1 H); 6.95–6.82 (m, 4 H); 6.98 (t, *J* = 9.00, 1 H); 7.15 (t, *J* = 7.50, 2 H); 7.52–7.29 (m, 8 H); 7.80 (d, *J* = 7.50, 2 H); 7.95 (d, *J* = 7.50, 2 H). ¹³C-NMR (CDCl₃, 75 Hz): 204.7; 199.4; 199.3; 157.3; 157.2; 139.5; 137.7; 137.6; 132.9; 132.8; 132.2; 131.0; 130.5; 129.5; 128.6; 128.5; 128.4; 128.2; 127.9; 127.8; 127.6; 120.7; 120.4; 111.0; 110.4; 55.5; 54.8; 50.8; 40.2; 38.5; 35.9. ES-MS (MeOH): 619 (100, [M + Na]⁺). Anal. calc. for C₄₀H₃₆O₅: C 80.51, H 6.08; found: C 80.42, H 6.02.

Crystal Structure of KTO-1. X-Ray diffraction intensity data collection and cell refinement for 4-benzoyl-1,3,5,7-tetraphenylheptane-1,7-dione (**KTO-1**) was performed on an automated Bruker-SMART-IK-CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ 0.71073 Å). The crystal structure was solved by the direct method and refined by full-matrix least squares for all unique data with SHELX-97.

Crystal Data of KTO-1: Empirical formula, C₃₈H₃₂O₃; *M_r*, 536.64; crystal size, 0.50 × 0.34 × 0.32 mm; calculated density, 1.196 g/cm³; volume (*V*), 5959.4(8) Å³; crystal system, orthorhombic; space group, *Pbcn*; *Z* = 8; unit cell dimensions, *a* = 13.0844 (11) Å, *b* = 22.6482 (18) Å, *c* = 20.1066 (16) Å, α = 90°, β = 90°, γ = 90°; absorption coefficient (μ), 0.074 mm⁻¹; index ranges: –15 ≤ *h* ≤ 15, –26 ≤ *k* ≤ 21, –23 ≤ *l* ≤ 23; *F*(000), 2272; g.o.f., 1.033; *T* 273(2) K; μ(MoK_α) = 0.71073 mm⁻¹.

REFERENCES

- [1] L. Chaisen, A. Claparède, *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 2460; J. G. Schmidt, *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 1459; M. Kalesse, *Topics Curr. Chem.* **2005**, *244* (Natural Products Synthesis II), 43; R. Mestres, *Green Chem.* **2004**, *6*, 583; J. H. Furhopp, G. Li, in 'Organic Synthesis', 3rd edn., Wiley–VCH, Weinheim, 2003, p. 44; M. M. Green, H. A. Wittcoff, 'Organic Chemistry Principles and Industrial Practice', Wiley–VCH, Weinheim, 2003; M. B. Smith, J. March, 'Advanced Organic Chemistry', 5th edn., Wiley–Interscience, New York, 2001, p. 1218; F. A. Carey, R. J. Sundberg,

- 'Advanced Organic Chemistry Part B', 4th edn., Kluwer Academic/Plenum Press, New York, 2000, p. 57.
- [2] D. B. Kimball, L. A. Silks, III, *Curr. Org. Chem.* **2006**, *10*, 1975; 'Modern Aldol Reactions', Ed. R. Mahrwald, Wiley-VCH, Weinheim, 2004, Vols. 1 and 2; C. Palomo, M. Oiarbide, J. M. Garcia, *Chem. Soc. Rev.* **2004**, *33*, 65.
- [3] C. B. Smith, C. L. Raston, A. N. Sobolev, *Green Chem.* **2005**, *7*, 650; N. M. Smith, C. L. Raston, C. B. Smith, A. N. Sobolev, *Green Chem.* **2007**, *9*, 1185; G. W. V. Cave, C. L. Raston, J. L. Scott, *Chem. Commun.* **2001**, 2159; H. Wu, L. Lu, Y. Shen, Y. Wan, K. Yu, *Synth. Commun.* **2006**, *36*, 1193; T. Kobayashi, H. Kawate, H. Kakiuchi, H. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1937.
- [4] a) H. Kessler, S. Mrona, B. Kutscher, A. Müller, W. S. Sheldrick, *Liebigs Ann. Chem.* **1991**, 1337; b) H. Noguchi, *Chem. Eng. News* **1995**, 51; c) G. W. V. Cave, C. L. Raston, *Chem. Commun.* **2000**, 2199; d) G. W. V. Cave, C. L. Raston, *J. Chem. Soc., Perkin Trans. 1* **2001**, 3258.
- [5] S. v. Kostanecki, G. Rossbach, *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 1488.
- [6] E. M. Hodnett, W. W. Ross, *Proc. Oklahoma Acad. Sci.* **1951**, *32*, 69.
- [7] R. Georgi, A. Schwyzer, *J. Prakt. Chem.* **1913**, *86*, 273.
- [8] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tachell, 'Vogel's Textbook of Practical Organic Chemistry', 5th edn., Longmann Scientific & Technical, UK, 1989, p. 1034; F. L. Ansari, S. Nazir, H. Noureen, B. Mirza, *Chem. Biodiversity* **2005**, *2*, 1656.
- [9] M. Lakshmi Kantam, B. Veda Prakash, C. Venkat Reddy, *Synth. Commun.* **2005**, *35*, 1971; B. M. Choudary, M. L. Kantam, C. R. V. Reddy, B. Bharathi, F. Figueras, *J. Catal.* **2003**, *218*, 191; M. J. Climent, A. Corma, S. Iborra, A. Velty, *J. Catal.* **2004**, *221*, 474; B. Siebenhaar, B. Casagrande, in 'Synthetic Methods of Organometallic and Inorganic Chemistry', Ed. W. A. Hermann, Georg Thieme Verlag, New York, 2002, Vol. 10, p. 114; M. Lakshmi Kantam, P. Sreekanth, P. Lakshmi Santhi, *Green Chem.* **2000**, *2*, 47; S. S. Chaphekar, S. D. Samant, *J. Chem. Technol. Biotechnol.* **2004**, *79*, 769; R. S. Natekar, S. D. Samant, *Indian J. Chem., Sect. B* **1996**, *35*, 1347.
- [10] X. Luo, Z. Shan, *Tetrahedron Lett.* **2006**, *47*, 5623.
- [11] K. Inoue, H. Noguchi, M. Hidai, Y. Uchida, *Yukagaku* **1983**, *32*, 219 (*Chem. Abstr.* **1983**, *99*, 53275); B. K. Vasilyev, N. P. Bagrina, V. I. Vysotskii, S. V. Lindeman, Yu. T. Struchkov, *Acta Crystallogr., Sect. C* **1990**, *46*, 2265.
- [12] W.-Y. Liu, J.-F. Li, Y.-X. Ma, Y.-M. Liang, *Gaodeng Xuexiao Huaxue Xuebao* **2001**, *22*, 141.
- [13] G. W. V. Cave, M. J. Hardie, B. A. Roberts, C. L. Raston, *Eur. J. Org. Chem.* **2001**, 3227; H. L. Anderson, S. Anderson, J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1* **1995**, 2231; Y. G. Yin, K. K. Cheung, W. T. Wong, *Chin. Chem. Lett.* **1998**, *9*, 329.
- [14] O. Correc, K. Guillou, J. Hamelin, L. Paquin, F. Texier-Boulleta, L. Toupet, *Tetrahedron Lett.* **2004**, *45*, 391; J. P. Jiang, J. Gao, W. B. Shen, W. X. Chen, *Acta Chim. Sin.* **1992**, *50*, 1134; J. Y. Gao, W. X. Chen, K. Jiang, *Acta Chim. Sin.* **1982**, *40*, 91.
- [15] M. M. Al-Arab, B. S. Ghanem, M. M. Olmstead, *Synthesis* **1992**, *10*, 1003; M. M. Al-Arab, D. T. Hani, S. G. Bader, M. O. Marilyn, *Synthesis* **1990**, *12*, 1157.
- [16] A. I. Darwish, *Egypt. J. Chem.* **2002**, *45*, 695; M. M. Al-Arab, B. S. Ghanem, A. O. Fitton, *Tetrahedron* **1989**, *45*, 6545; A. M. Mansilla, M. C. Pardo, *Tetrahedron Lett.* **1981**, *22*, 4845.
- [17] L.-C. Rong, X.-Y. Li, F. Yang, H.-Y. Wang, D.-Q. Shi, *Acta Crystallogr., Sect. E* **2006**, *62*, o1766; A. I. Darwish, *Egypt. J. Chem.* **2001**, *44*, 373; J. Mirek, *Chem. Scr.* **1988**, *28*, 295; P. Victory, J. I. Borrell, A. Vidal-Ferran, C. Seoane, J. L. Soto, *Tetrahedron Lett.* **1991**, *32*, 5375; S. K. El-Sadany, S. M. Sharaf, A. I. Darwish, A. A. Youssef, *Indian J. Chem., Sect. B* **1991**, *30*, 567.
- [18] W. Dilthey, E. Floret, *Justus Liebigs Ann. Chem.* **1924**, *440*, 89.

Received November 16, 2008