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Preparative and Structural Studies of Kostanecki's Compound

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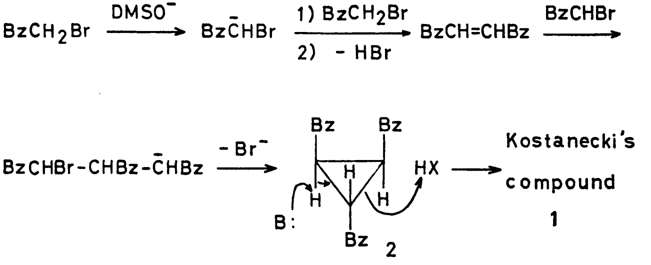
Kostanecki and Tambor[1] have reported that the reaction of α-phenoxyacetophenone with sodium in warm xylene gives an orange compound, $(C_8H_6O)_x$, mp 120°C. In 1956, Yates,[2] Wheeler,[3] and their coworkers studied the structure of Kostanecki's compound (**1**) and concluded that this compound was composed of 1,2,3-tribenzoylpropene in equilibrium with the corresponding enol form.

This paper will be concerned with a reaction leading to Kostanecki's compound (**1**) (Scheme 1) as well as with a structural investigation based on the NMR, mass, IR, and UV spectra.

When phenacyl bromide dissolved in dimethyl sulfoxide (DMSO) was treated with a solution of methylsulfinyl carbanion prepared from DMSO and sodium hydride[4] at room temperature, Kostanecki's compound (**1**) was obtained as orange crystals (10%), mp 120—123°C. Meanwhile, we found that a shorter reaction time (1 hr) at room temperature gave 1,2,3-tribenzoylcyclopropane (**2**) (3%) in addition to **1** (7%). The treatment of **2** with the same carbanion afforded **1** (12%), besides a 60% recovery of **2**. A better yield (50%) of **1** was obtained upon the reaction of **2** with the carbanion prepared from cyclopropyl phenyl sulfone and sodium hydride in hexamethylphosphoric triamide (HMPA).

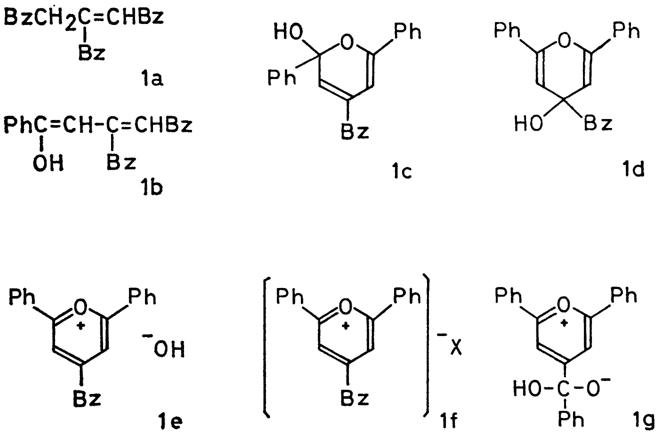


Scheme 1

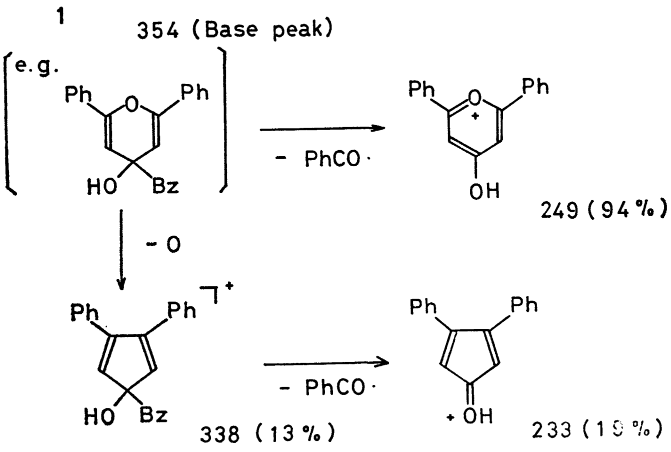
On the basis of these results, we may explain the formation of **1** as is shown in Scheme 1. Initially, **2** is produced by the indicated route[5] and is then transformed to **1** by the basic ring opening.

The spectrometric properties of **1** have now made it impossible for us to believe in the previous conclusion that **1** is an equilibrium mixture of **1a** and **1b** (Scheme 2). It is proposed that the additional tautomeric isomers, **1c**—**1g**, are all in equilibrium and that the contribution of each structure depends on the phase in which the measurement is made. The **1c** isomer is a hemiacetal of **1b** and is isomerized to **1d** by the allyl-rearrangement of OH in **1c**. The **1e** ion pair is derived from **1c** or **1d** and is transformed to the **1f** salt by the substitution of $^-$OH into another anion, X$^-$. The innersalt formula **1g** may be proposed to explain the IR spectrum of Kostanecki's compound in the solid state (*vide infra*).

The mass spectra of **1** exhibited the fragment peaks due to the pyrylium ions shown in Scheme 3. The NMR of **1** in $CDCl_3$ (Fig. 1) consisted of a singlet at 4.73 ppm and a complex multiplet at 7.10—8.20 ppm in a ratio of *ca.* 1 : 11. This singlet disappeared upon the addition of MeOD. These results can not be explained by simply assuming **1a** and **1b**.



Scheme 2



Scheme 3

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[1] St. v. Kostanecki and J. Tambor, *Ber.*, **35**, 1679 (1902).

[2] P. Yates, D. G. Farnum, and G. H. Stout, *Chem. & Ind.* (London), **1956**, 821.

[3] P. E. Devitt, E. M. Philbin, and T. S. Wheeler, *ibid.*, **1956**, 822; Idem., *J. Chem. Soc.*, **1958**, 510.

[4] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

[5] This route reminds us of the formation of **2** from sulfonium phenacylide and phenacyl bromide. See Ref 6.

Fig. 1. NMR spectrum of Kostanecki's compound (**1**) in deuterochloroform.

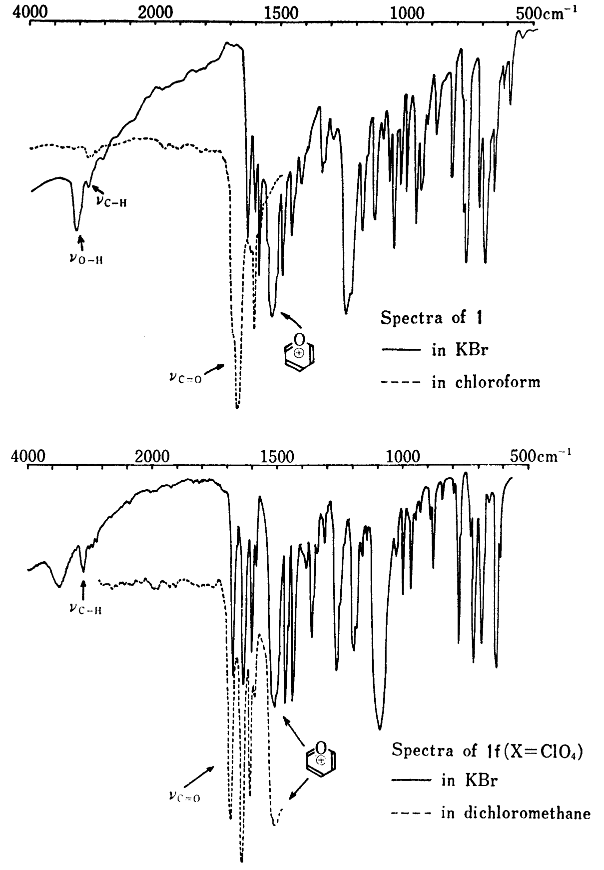

Fig. 2. Comparison of IR spectra of **1** and the pyrylium salt (**1f**) ($X=ClO_4$) in KBr and chloroform or dichloromethane.

Meanwhile, 2,6-diphenyl-4-benzoylpyrylium perchlorate (**1f**, $X=ClO_4$) (18%) was obtained as a crystalline solid, mp 233—235°C, upon the treatment of **1** with perchloric acid in chloroform at room temperature. The IR and UV spectra of **1** were compared with those of the **1f** perchlorate ($X=ClO_4$). The solid state IR of **1** was very analogous to that of the pyrylium perchlorate with the exception of the remarkable difference that the carbonyl band at 1665 cm^{-1} was missing in the IR spectrum of **1** (Fig. 2). As characteristic bands of pyrylium salt and of the hydroxy group were observed in the IR of **1** at 1530 and 3210 cm^{-1} respectively, **1 g** can be said to be the best possibility of explaining the structure of **1** in the solid state.

The UV spectrum of **1** in ethanol was almost superimposable on that of the **1f** pyrylium salt ($X=ClO_4$), as is shown in Fig. 3.

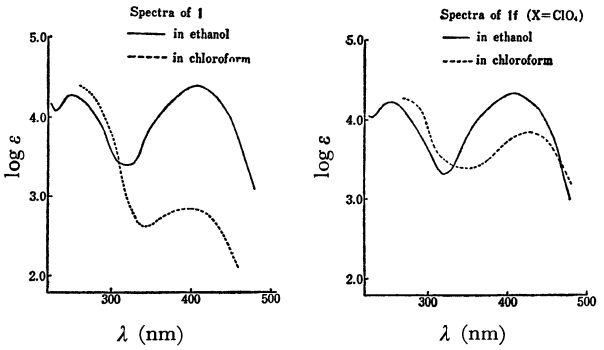

Fig. 3. Comparison of UV spectra of **1** and the pyrylium salt (**1f**) ($X=ClO_4$) in ethanol and chloroform.

This can be explained by assuming that the major contributing structures of **1** in ethanol are **1e** and/or **1f** ($X=OEt$); such an assumption is consistent with the disappearance of one proton singlet at 4.73 ppm upon CH_3OD treatment, as has been mentioned above. As is shown in Fig. 3, the absorptions of **1** in chloroform were completely different from those of **1f** ($X=ClO_4$) and the characteristic strong IR absorption of the pyrylium salt at 1530 cm^{-1} was absent in the spectrum of **1** in chloroform. The **1e**, **1f**, and **1g** structures could, therefore, be excluded in this state; the NMR spectrum (Fig. 1) was consistent with the **1b**, **1c**, and **1d** structures but not with **1a**.

Summarizing these results, we may conclude as follows: (1) The previous assumption of the **1a**$\rightleftarrows$**1b** equilibrium is untenable. (2) The solid IR spectrum of **1** can be explained by means of **1g** in view of the absence of the carbonyl absorption. (3) The UV spectrum in ethanol supports the pyrylium salt formula **1e** and/or **1f** ($X=OEt$). (4) A chloroform solution of **1** gives spectra which are consistent with the **1b**, **1c**, and **1d** structures but not with **1a**, **1e**, **1f**, and **1g**. (5) The **1b**, **1c**, **1d**, **1e**, and **1g** structures are possibly in fast equilibrium, and the contribution of each specific one is controlled by the state in which the measurement is made.

Experimental

All the mps are uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyoto University. The NMR spectra were obtained in $CDCl_3$ on a 100 MHz instrument (Varian HA-100 spectrometer) by the courtesy of Toray Co. The mass spectra were obtained on a Hitachi RMU 6D spectrometer by the courtesy of Takeda Chemical Industries, Ltd.

Reaction of Phenacyl Bromide with Methylsulfinyl carbanion. A solution of sodium methylsulfinyl carbanion was prepared under N_2 from sodium hydride (0.72 g, 30 mmol) and dimethyl sulfoxide (DMSO) (40 m*l*). Into this we stirred a solution of phenacyl bromide (3.9 g, 20 mmol) in DMSO (10 m*l*) under ice-cooling over a period of 2 min. The reaction mixture was then stirred at room temperature for 3 hr, poured into water (300 m*l*), acidified with aqueous hydrochloric acid, and extracted with benzene. The evaporation of the benzene gave a dark-brown oil, to which a small amount of benzene was added again, after which the mixture was allowed to stand overnight. Kostanecki's compound **(1)** was obtained as orange crystals; mp 120—123°C (lit,[1] 120°C) (0.25 g, 10%). Exact mass: 354.127 (base peak), 338.131 (13), 249.092 (94), and 233.099 (19). Calcd for $C_{24}H_{18}O_3$: 354.125, $C_{24}H_{18}O_2$: 338.130, $C_{17}H_{13}O_2$: 249.091, and $C_{17}H_{13}O$: 233.096.

A work-up of the reaction mixture after 1 hr at room temperature gave 1,2,3-tribenzoylcyclopropane **(2)**, mp 216°C (3%), besides **1** (7%). The product, **2**, was identical with an authentic sample.[6]

The Reaction of 1,2,3-Tribenzoylcyclopropane **(2)** *with Carbanion.* A solution of **2** (1.8 g, 5 mmol) in DMSO (20 m*l*) was added to a carbanion solution prepared from sodium hydride (0.14 g, 6 mmol) and DMSO (20 m*l*) under stirring at room temperature. After it had been stirred at room temperature for 3.5 hr, the reaction mixture was treated with water. The precipitating starting material (60%) was removed by filtration. The filtrate was acidified with aqueous hydrochloric acid and extracted with benzene. Concentration gave Kostanecki's compound **(1)** (0.21 g, 12%).[7]

Meanwhile, **2** (1.8 g, 5 mmol) in HMPA (20 m*l*) was treated with a carbanion solution prepared from cyclopropyl phenyl sulfone (4.1 g, 23 mmol) and sodium hydride (0.54 g, 23 mmol) in HMPA (20 m*l*) at 90°C for 24 hr to give **1** (0.89 g, 50%).

Preparation of 2,6-Diphenyl-4-benzoylpyrylium Perchlorate. Kostanecki's compound (0.067 g, 0.19 mmol) was dissolved in chloroform (50 m*l*). To this solution, aqueous perchloric acid (60%) (0.04 m*l*) was added, and the whole mixture was stirred at room temperature for 15 hr. The chloroform solution was dried over anhydrous sodium sulfate and evaporated to yield a yellow oil which solidified upon trituration with ether; mp 233—235°C (17 mg, 18%). The IR spectrum of this solid is shown in Fig 2.

Found: C, 66.1; H, 3.9%. Calcd for $C_{24}H_{17}ClO_6$: C, 66.0; H, 3.9%.

The authors are indebted to Professeor K. Sisido for his help and encouragement. This work was partially supported by the Scientific Research Fund of Ministry of Education, Japanese Government. Financial support from Toray Science Foundation is acknowledged with pleasure.

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[6] H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1965).

[7] The yield is based on the substrates initially added.