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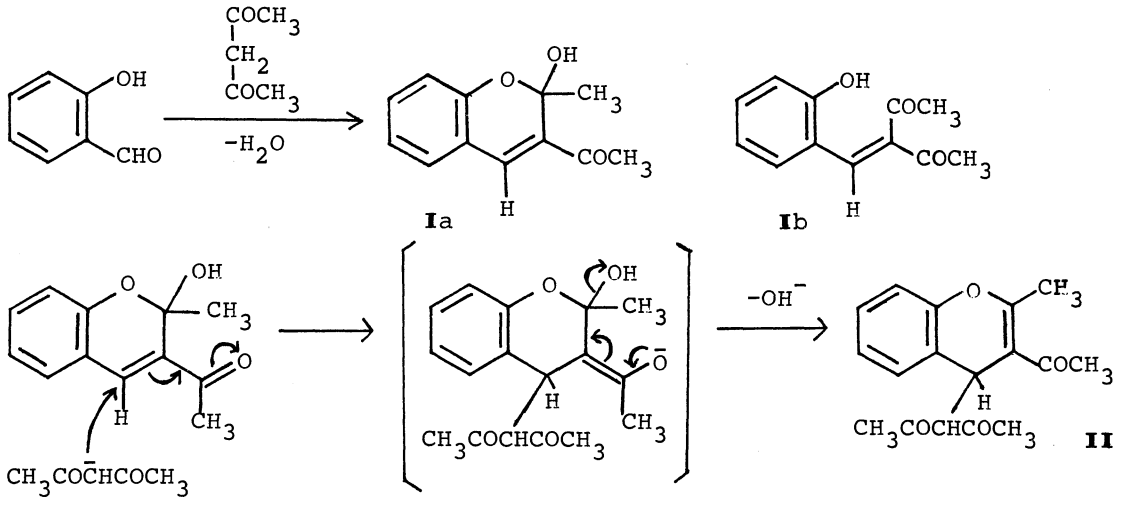
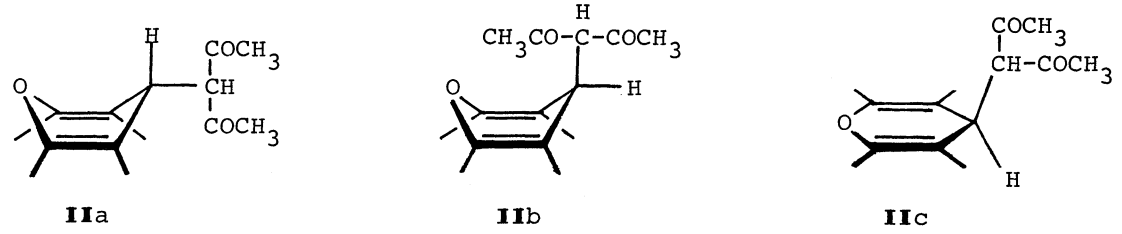
CONFORMATIONAL ISOMERS OF 4H-CHROMENE CONFORMATION OF 4H-PYRAN

Toshio KAWATO and Ichiro MURASE
Laboratory of Chemistry, College of General Education
Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810

By the condensation of salicylaldehyde and acetylacetone, isomeric 3-acetyl-4-diacetylmethyl-2-methyl-4H-chromenes were prepared. From the fact that a pair of conformational isomers of these compounds exists, a boat structure of 4H-pyran was proposed.

Stereochemistry of 1,4-cyclohexadiene has aroused interest widely, and a considerable amount of controversy[1] exists concerning the conformational preferences of it and its derivatives. The conformation of 4H-pyran, which differs from 1,4-cyclohexadiene by substituting an oxygen atom for a carbon atom in the ring, is of interest in the same sense. These compounds should exist either in a boat form or in a flat one because of the planar structure of ethylene. Recently, Paschal and Rabideau using NMR analyses suggested that 1-substituted-1,4-cyclohexadiene was flat shaped.[2] The present paper seems to be the first successful communication dealing with the conformational preference of the 4H-pyran ring.





As a product of the Knoevenagel condensation of salicylaldehyde and acetylacetone, 3-(o-hydroxybenzylidene)-2,4-pentanedione(Ib) had been reported.[3] It was checked in our investigation; however, the condensation product was found to be 3-acetyl-2-hydroxy-2-methyl-2H-chromene(Ia). The structure was determined by means of IR and NMR spectra, whose patterns were in contrast with those of 3-benzylidene-2,4-pentanedione, 3-(m-hydroxybenzylidene)-2,4-pentanedione and 3-(p-hydroxybenzylidene)-2,4-pentanedione.[4] As was expected from its structural formula, this compound behaved as a ketol and enone; it did not produce coloration by ferric chloride test which was used for the determination of phenols. The detailed study on the structure and reactions of Ia will be reported in a later publication.

When a mixture of the equimolar amount of Ia and acetylacetone with a small quantity of piperidine was heated in a water bath, the Michael addition took place, followed by dehydroxylation. After being cooled and treated with dilute ethanol, the reaction mixture gave white crystals of two kinds of 3-acetyl-4-diacetylmethyl-2-methyl-4H-chromenes(II), i.e., a pair of conformers of 4H-pyran derivatives(IIa, IIb). The complete separation of the isomers was accomplished by repetition of fractional recrystallization from ethanol; IIa was much more soluble in ethanol than IIb.

The elemental analyses and melting points of IIa and IIb are shown in Table I. Figure 1 shows their IR spectra, whose marked resemblance indicates that the isomers consist of a common structural unit.

The NMR spectra are recorded in Fig. 2, in which the neighbouring methine protons exhibit AB patterns; the coupling constants are about 3 Hz. The doublets at τ 7.15 for IIa and at τ 6.93 for IIb are assigned to the proton of 4-position respectively. The anisotropy of the benzene ring gives a good account of the difference between their chemical shifts. According to the molecular model of II, in which the pyran ring is boat shaped, the methine proton of IIb is in the same plane as the benzene ring, while the one of IIa is out of the plane. The methine proton of the diacetylmethyl group appears at τ 5.45 for IIa and τ 5.37 for IIb respectively. The chemical-shift data are understood as a result of the anisotropy of the carbonyl groups rather than the long-range shielding of the aromatic ring. Since the diacetylmethyl group attaches to a very large group, it seems that a free rotation of the group is impaired; moreover, it is hard that all the carbon atoms of it are in one plane because of strong steric hindrance. From these reasons, the enolization of the acetylacetone moiety is inhibited, and the methine proton exhibits a broad peak.

The conditions of their preparations and the spectral patterns exclude any other isomeric structure for these compounds. The existence of the conformers, thus, concludes that the 4H-pyran ring must not exist in a planar structure(IIc), contrary to 1,4-cyclohexadiene.

Table I. The materials studied

Compd	Formula	mp(°C)	Anal(Calcd %) C	H
IIa	$C_{17}H_{18}O_4$	142-145	71.45(71.31)	6.34(6.34)
IIb	〃	181-183	71.43(〃)	6.46(〃)

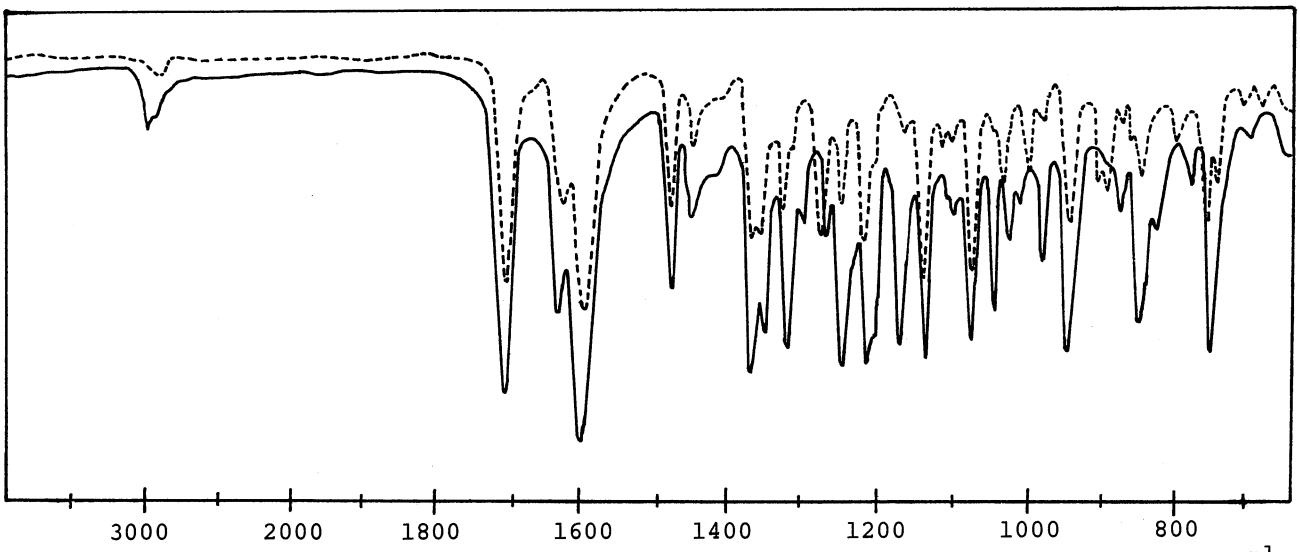


Fig. 1 IR spectra of IIa(——) and IIb(---).[5]

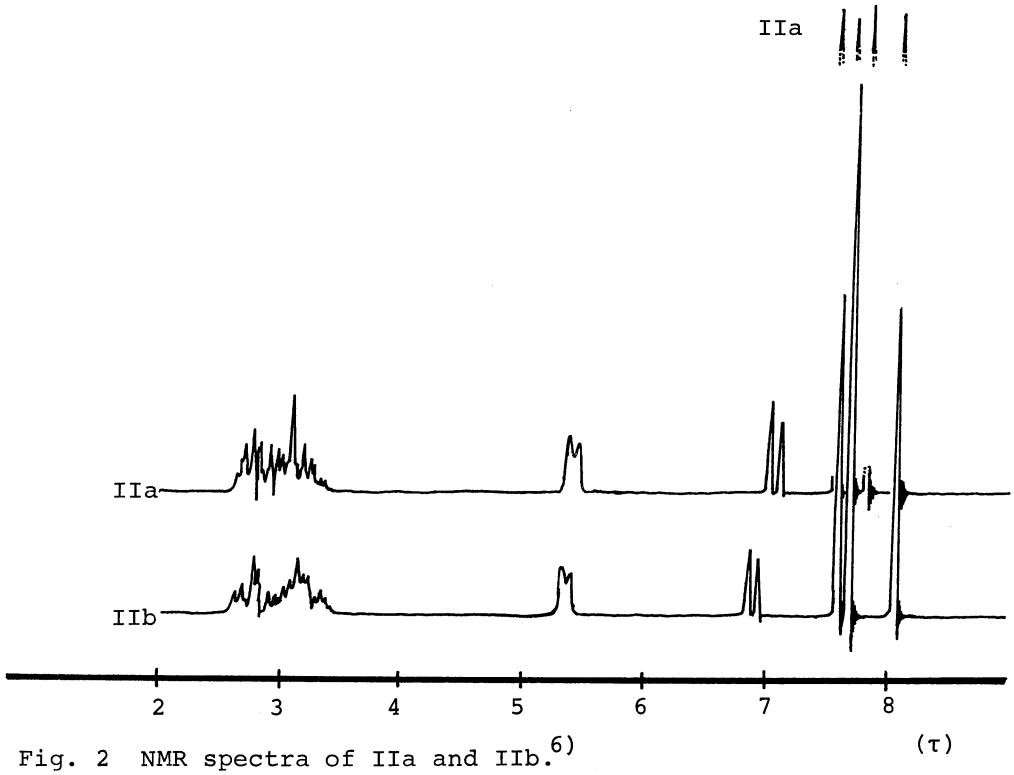


Fig. 2 NMR spectra of IIa and IIb.[6]

The interconversion of IIa and IIb was then investigated. By being heated in ethanol with a few drops of piperidine, IIa could be isomerized to IIb. Because of the steric hindrance between the diacetylmethyl group and the proton of 5-position and/or the acetyl group of 3-position, IIa is condidered to be labilized compared with IIb. It should be noted that boat to boat inversion of the pyran ring, however, could not take place by being heated to 183 °C(mp of IIb) in both isomers.

References and Footnotes

1) See Ref. 2) and references(1-11, 13-15) therein.
2) J. W. Paschal and P. W. Rabideau, J. Amer. Chem. Soc., 96, 272(1974).
3) E. Knoevenagel and R. Arnot, Ber., 37, 4499(1904).
4) T. Kawato, H. Kanatomi, Y. Demura and I. Murase, Bull. Chem. Soc. Japan, 48, No. 3(1975) in press.
5) The IR spectra were determined in KBr disks with a Hitachi EPI-S2 spectrophotometer.
6) The NMR spectra were measured at 60 MHz in $CDCl_3$ with a Hitachi Model R-24 NMR spectrometer. The chemical shifts are quoted as τ values relative to TMS. The two-spin systems(AB) in the spectra were confirmed by decoupling techniques.

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