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THERMAL REARRANGEMENT OF 1-ACYL-2-ALKYL-6-HYDROXYFULVENES TO 1-ACYL-3-ALKYL-6-HYDROXYFULVENES

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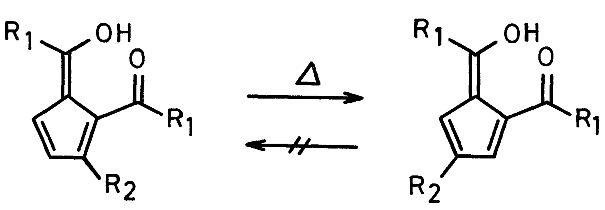
1-Acyl-2-alkyl-6-hydroxyfulvenes have been found to rearrange to 1-acyl-3-alkyl-6-hydroxyfulvenes on heating. Kinetics and other mechanistic studies including ^{13}C-labeling experiment indicate that the acyl group migrates intramolecularly. The acyl migration may proceed by two consecutive [1,5] acyl shifts via a 5,5-diacylcyclopentadiene toward the less crowded 3-alkyl isomer.

A good number of physical and chemical studies of 1-acyl-6-hydroxyfulvenes have been reported.[1] In the course of our investigation on 1-acyl-2-alkyl-6-hydroxyfulvenes, we have found that these compounds thermally rearrange to 1-acyl-3-alkyl-6-hydroxyfulvenes. We wish here to report the results of some mechanistic studies of the rearrangement including ^{13}C-labeling experiment.

Heating of 1-formyl-2-methyl-6-hydroxyfulvene (Ia)[2] in refluxing xylene under nitrogen gave 1-formyl-3-methyl-6-hydroxyfulvene (IIa) in quantitative yield. Other five derivatives (Ib-If)[2] gave similar results to indicate that the rearrangement is general in this system. No reverse reaction was observed.



(I) (II)

(a) R_1 = H , R_2 = Me
(b) R_1 = Me , R_2 = Me
(c) R_1 = Ph , R_2 = Me
(d) R_1 = Ph , R_2 = Allyl
(e) R_1 = Ph , R_2 = n-Pr
(f) R_1 = Ph , R_2 = Ph

These reactions cleanly obeyed the first order kinetics.[5] The rate constants and relative rates at 131.7°C are listed in Table 1.

Table 1. The first order rate constants (k_1) and relative rates for the rearrangement of 1-acyl-2-alkyl-6-hydroxyfulvenes in carbon tetrachloride at 131.7°C.

2-alkyl compounds	Mp (°C) Bp (°C/mmHg)	R_1	R_2	3-alkyl compounds	Mp (°C)	k_1 (sec^{-1})	relative k_1
Ia	27∿28	H	Me	IIa	60∿61	1.48×10^{-6}	1
Ib	53∿54	Me	Me	IIb	82∿83	9.67×10^{-5}	65
Ic	101∿102	Ph	Me	IIc	134∿135	7.86×10^{-5} 2.29×10^{-4} a)	53 155
Id	95∿96/0.023	Ph	Allyl	IId	94∿95	2.25×10^{-4} b)	152
Ie	61∿62	Ph	n-Pr	IIe	108∿109	1.33×10^{-4}	90
If	146∿147	Ph	Ph	IIf	167∿168	8.67×10^{-5}	59

a) in acetonitrile b) Side reactions were observed.

The rate of rearrangement of Ia is about 10^2 times slower than those of Ib-If. Since compound (Ia) is the least crowded, the difference in the rate constants may reflect the steric repulsion between the acyl group at C-1 and the alkyl substituent at C-2. Activation energies and activation entropies for Ic to IIc are 30.1± 0.3 kcal/mol and -4.2 eu in carbon tetrachloride and 22.7±1.0 kcal/mol and -18.2 eu in acetonitrile, respectively. The solvent effect suggests that the transition state in rate determining step has a polar character.

When a 1:1 mixture of Ib and Ie, which show the nearly comparable rate constants, was heated in refluxing xylene, only IIb and IIe were obtained and no cross-products were detected. This and kinetic results indicate that the rearrangement is intramolecular reaction. There may be three possible intramolecular rearrangements leading to II: (i) migration of acyl group, (ii) migration of alkyl group, and (iii) skeletal rearrangement of the five membered ring. However, the foregoing results do not allow us to distinguish any process. In order to obtain definite information concerning the migrating group by carbon labeling in combination with ^{13}C-NMR spectroscopy, we prepared ^{13}C enriched Ic at C-2 (Ic*) and ^{13}C enriched IIc at C-3 (IIc*), starting from ^{13}C enriched potassium cyanide.[6] In ^{13}C-NMR spectra of these compounds,[7] the intensities of signals of C-2 of Ic* (153.6 ppm from ^{13}C of TMS) and C-3 of IIc* (135.2 ppm) are enhanced by about three fold compared with those of Ic and IIc with natural abundance. ^{13}C-NMR spectrum (Fig. 1c) of the product obtained by the rearrangement of Ic* was almost identical with that of IIc* (Fig. 1b). This result indicates that the benzoyl group migrates during the rearrangement.

A possible mechanism of the acyl migration is double [1,5] acyl shift via a 5,5-diacylcyclopentadiene (III). Since 6-hydroxyfulvenes can equilibrate with the keto form,[8] the first [1,5] acyl shift may occur on the 1,5-diacylcyclopentadiene (IV) to give (III). 5,5-Disubstituted cyclopentadienes have been reported to undergo [1,5] alkyl[9] or methoxycarbonyl shift.[10] The rate determining step of this rearrangement may be (IV) to (III) since no signals to be assigned to (III) have been found during the kinetic studies by NMR spectroscopy. The irreversibility in the rearrangement of (I) to (II) may be due to the higher thermodynamic stability of (II) because of the absence of crowdedness between the acyl and alkyl groups.

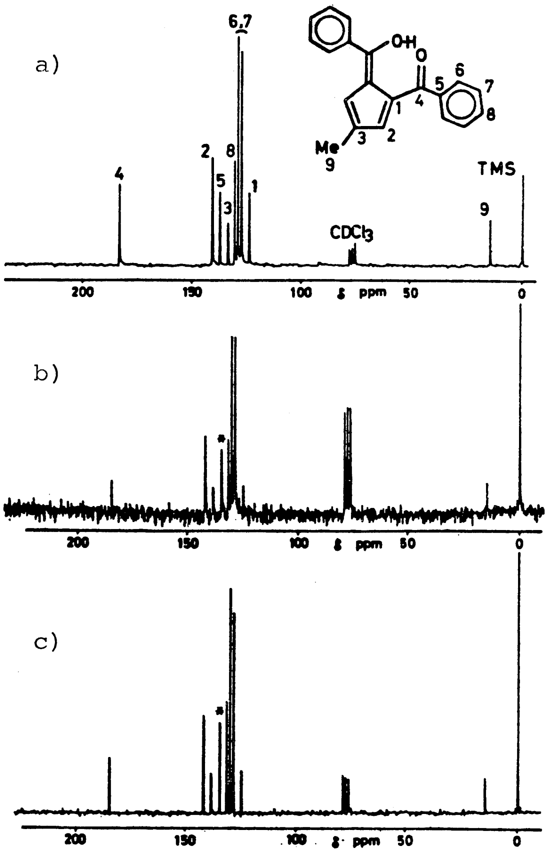
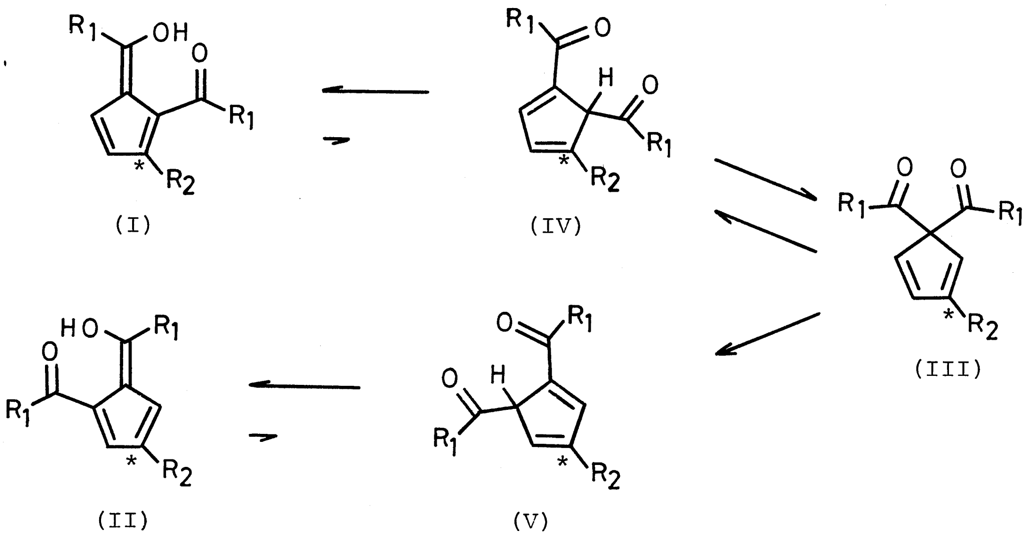


Fig. 1. PFT-^{13}C-NMR spectra of IIc (a), ^{13}C enriched IIc at C-3 position (b) and product (c).



References and Notes

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2) The materials were prepared from alkylcyclopentadienes according to Hafner's[3] or Linn's method[4], and purified by column chromatography on alumina. The compounds Ie and IIe were prepared from Id and IId, respectively, by hydrogenation on palladium-carbon. All the compounds gave satisfactory elementary analytical results and showed reasonable spectra.

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5) Kinetics were traced by the NMR method. The reactions were carried out using a solution of 0.1 mmol of sample in 0.3 ml of carbon tetrachloride or acetonitrile.

6) The ^{13}C-enriched compounds were prepared as follows; K^{13}CN which was adjusted to ca. 3% enrichment by dilution of 90% K^{13}CN was converted into cyclopentanone -1-^{13}C by known method. The cyclopentanone was then converted into 1-methylcyclopentene -1-^{13}C by Grignard reaction followed by dehydration. Allylic bromination by NBS, dehydrobromination and anionization with excess lithium dicyclohexylamide, and benzoylation gave the mixture of Ic* and IIc* (overall yield 0.5%, Ic* : IIc* = 4 : 1).

7) PFT-^{13}C-NMR spectra were measured by JNM-PS-100 spectrometer at 25.15 MHz, and the signals were assigned as shown in Fig. 1a by comparison with other hydroxyfulvenes.

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