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β-Diketone Involving Fluorine. V.[1] NMR Studies of Pivaloyltrifluoroacetone in Various Alcohols

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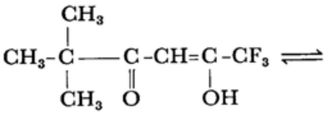
It was noted, in our previous papers,[1,3-5]— that an equilibrium existed between β-diketones involving fluorine and alcohols by the activation of the carbonyl carbon adjacent to a trifluoromethyl (CF_3-) group due to the *I* effect exerted by the fluorine atom. Such a phenomenon has already been described with β-diketones like trifluoroacetylacetone (TFA),[1,3] benzoyltrifluoroacetone (BTA), 2-furoyltrifluoroacetone (FTA), 2-thenoyltrifluoroacetone (TTA)[4] or hexafluoroacetylacetone (HFA),[1] and with alcohols like methanol, ethanol, 1-propanol, 2-propanol, allyl alcohol, propargyl alcohol, benzyl alcohol, ethylene glycol or some halohydrins. The equilibrium is affected by the steric effect and the nucleophilicity of alcoholic oxygen, therefore some changes in property are expected to be found by changing not only the variety of alcohols but also that of β-diketones. For these reasons, pivaloyltrifluoroacetone (PTA) with a bulky functional group was newly synthesized, and the behavior of that β-diketone (PTA) in alcohols and water has been studied by means of high resolution NMR spectroscopy.

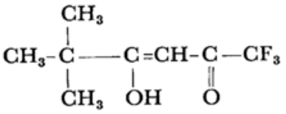
Results and Discussion

The proton magnetic resonance signals of PTA appeared at 8.77 ppm due to the pivaloyl proton and at 4.01 ppm due to methine proton, but any signals which should be attributed to methylene proton did not appear. Thus PTA exists as 100% enolized structure of either Ia or Ib.



$$CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{——}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH{=}\underset{\displaystyle OH}{C}\text{-}CF_3 \rightleftharpoons$$

(Ia)



$$CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{——}\underset{\displaystyle OH}{C}{=}CH\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}CF_3$$

(Ib)

As (Ia) was probably regarded as the preferred enol form in the equilibrium (Ia) and (Ib),[6] the following discussions were carried out assuming that the structure of PTA was (Ia).

Table 1 lists the values of chemical shifts in the fluorine magnetic resonance spectra of various kinds of β-diketone-alcohol solutions mixed at the volume ratio, 1 : 1. Two signals appeared at about 76 ppm

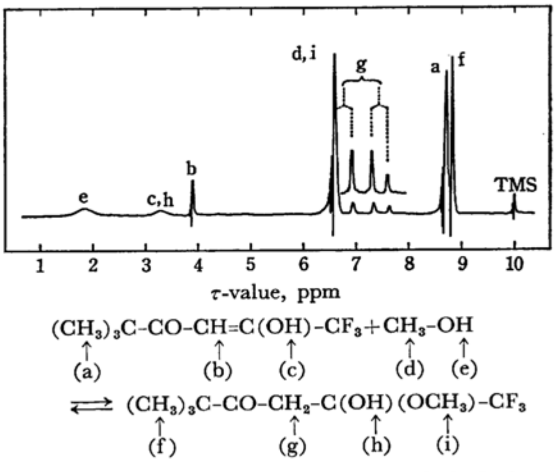


Fig. 1. PMR spectrum of a mixture of pivaloyltrifluoroacetone (PTA) and methanol in CCl_4 at 60 Mc.

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[1] Part IV of this series: K. Sato, Y. Kodama and K. Arakawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 968 (1967).

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[3] K. Sato, Y. Kodama and K. Arakawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 821 (1966).

[4] Y. Kodama, K. Sato and K. Arakawa, *ibid.*, **87**, 1092 (1966).

[5] K. Sato and K. Arakawa, *ibid.*, **88**, 470 (1967).

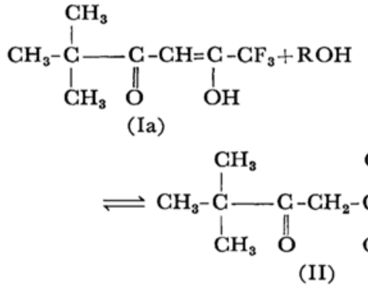
[6] K. Sato and K. Arakawa, *ibid.*, **89**, 1110 (1968).

TABLE 1. THE VALUES OF CHEMICAL SHIFT IN FLUORINE MAGNETIC RESONANCE SPECTRA OF SOLUTIONS

Alcohol	R	$(CH_3)_3CCOCH{=}C(OH)C\underline{F}_3$ (ppm)	$(CH_3)_3CCOCH_2C(OH)(OR)C\underline{F}_3$ (ppm)	$\frac{II}{Ia+II}$
(PTA)		76.0	—	—
CH_3OH	CH_3-	75.1	80.7	0.50
CH_3CH_2OH	CH_3CH_2-	75.4	81.1	0.21
$CH_3(CH_2)_2OH$	$CH_3(CH_2)_2$-	75.5	80.8	0.15
$(CH_3)_2CHOH$	—	75.5	—	—
$BrCH_2CH_2OH$	$BrCH_2CH_2$-	75.2	81.2	0.19
$CNCH_2CH_2OH$	$CNCH_2CH_2$-	74.3	80.9	0.50
$ClCH_2CH_2OH$	$ClCH_2CH_2$-	75.4	81.5	0.18
$CH_2{=}CHCH_2OH$	—	75.4	—	—
$PhCH_2OH$	$PhCH_2$-	75.3	80.7	0.18
H_2O	H-	74.9	84.8	0.18

and 81 ppm in the spectra of these solutions: the signal at 76 ppm was equal to PTA, $(CH_3)_3CCOCH C(OH)CF_3$, and that at 81 ppm may be due to the new reaction product(II). Figure 1 shows the case of PTA-methanol solution as an example in the PMR spectra of those solutions. Of the two signals at 8.74 and 8.84 ppm, the down-field one was apparently due to the pivaloyl proton of PTA because of having a definite intensity in spite of the values of II/(Ia+II), and the up-field one might be due to the pivaloyl proton of the new product (II). It was easily estimated that the AB-type signal at 7.11 ppm was based on methylene proton in comparison with the case of TFA[4] and the integrated ratios between the signal at 7.11 ppm and at 8.84 ppm were about 2 : 9. The signal at 6.61 ppm might be due to not only methyl proton of methanol but also methoxy proton, since that intensity was much stronger than that due to only methanol. It was thought that the broad signals at about 2 and 3 ppm must be based on some hydroxyl protons. Therefore, it was expected that the new reaction product consisted of such functional groups as pivaloyl,methoxyl, hydroxyl, methylene and trifluoromethyl in this equilibrium.

From these results, it has been deduced that the following equilibrium exists also in PTA similar to TFA, TTA, *etc.*:



$$CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}\text{-}CH{=}\underset{\displaystyle OH}{\underset{|}{C}}\text{-}CF_3+ROH$$

(Ia)

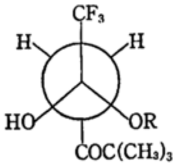
$$\rightleftharpoons CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH_2\text{-}\overset{\displaystyle OR}{\underset{\displaystyle OH}{C}}\text{-}CF_3$$

(II)

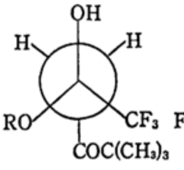
R = H-, CH_3-, CH_3CH_2-, $CH_3(CH_2)_2$-, $BrCH_2CH_2$-
$CNCH_2CH_2$-, $ClCH_2CH_2$-, $PhCH_2$-.

It was found, however, that PTA hardly reacted with isopropyl alcohol, allyl alcohol and propargyl alcohol in such equilibrium. This is probably due to the steric hindrance or the less nucleophile nature of alcoholic oxygen effective in such alcohols.

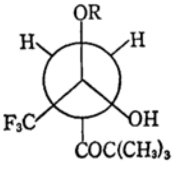
Such exceptions found in isopropyl, allyl and propargyl alcohol solutions have never been found with β-diketones like TFA, HFA, TTA, BTA and FTA reported in the previous papers.[1,3,5] This may be due to the fact that the steric hindrance of pivaloyl group mainly contributes to these phenomena. The carbon atom adjacent to the trifluoromethyl group is optically active in the new reaction product (II), which is consequently possible to take conformations IIIa, IIIb and IIIc.



(IIIa)



(IIIb)



(IIIc)

It seems reasonable to conclude that IIIa is the most preferred of three conformations and is major conformation in the sample solution. It was estimated that PTA hardly reacted with isopropyl, allyl and propargyl alcohols because of the considerable contribution of steric hindrance even in IIIc conformation together with nucleophilicity of alcoholic oxygen. Above-mentioned characteristics of PTA are apparently different from that of TFA, TTA and HFA.

Experimental

Measurements. A JNM C-60 high-resolution nuclear magnetic resonance spectrometer was used. Proton resonance spectra and fluorine resonance spectra were run at 60 Mc and 56.45 Mc, respectively. Each sample was dissolved in carbon tetrachloride at a concentration of 25 vol%. The temperature was maintained at 23±1°C. Tetramethylsilane (TMS: proton) and monofluorotrichloromethane ($CFCl_3$:

fluorine) were employed as the internal standards.

Materials. *Commercial alcohols and halohydrins* were used without further purification. Water was purified by passing it through an ion exchange resin.

Pivaloyltrifluoroacetone (PTA) used in this investigation was prepared in the following method, a modification of Henne's[7]: Sodium ethylate freshly prepared by treating 14 g of absolute ethanol with 7.6 g of finely dispersed sodium was dissolved in ether. To the resulting suspension was added slowly 42.6 g of ethyl trifluoroacetate in 40 m*l* of ether. Privaloylmethane, 30 g, in 30 m*l* of ether was then added, and the mixture refluxed for about six hours. On account of the avidity of the condensates for moisture, the following procedure of isolation was adopted. The reaction mixture was treated with a 50% solution of sodium bisulfide in a very slight excess over neutralization requirements, then with a saturated aqueous solution of cupric aectate (180 m*l*). The organic layer was distilled off, then 43.6 g of crystalline copper derivative, mp 85—87°C, was extracted with ether. The dry copper derivative was suspended in 500 m*l* of dry ether, in which it was partly dissolved, and was subjected to a stream of hydrogen sulfide. After removal of the cupric sulfide, the condensed compound was separated from the ether by fractional distillation, with rigorous precautions to avoid loss by volatility, to give 23.5 g of a light yellow oil, bp 129.5—130.5°C.

UV: $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (ε); 288 (8700).

Found: C, 49.51; H, 5.99%. Calcd for $C_8H_{11}O_2F_3$: C, 48.98; H, 5.64%.

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[7] A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *J. Am. Chem. Soc.*, **69**, 1819 (1957).