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# ELECTRONIC FACTORS AND THE STRUCTURE OF ORGANOANTIMONY CARBONYL COMPOUNDS

## ORGANOANTIMONY DERIVATIVES OF ALIPHATIC-AROMATIC KETONES*

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**Summary**

A number of organoantimony aliphatic-aromatic ketones have been synthesized. Spatial effects are more important than electronic effects in stabilising the *O*-species in the tautomeric mixtures.

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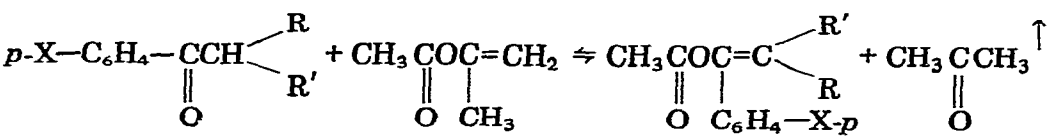
The preceding paper [1] was concerned with the role played by spatial factors in relative stabilities of *O*- and *C*-isomers of organoantimony carbonyl compounds. Now we have synthesized a number of organoantimony aliphatic-aromatic ketones to clarify the role of electronic factors and collate this with the data known [2] for organogermanium compounds.

Enol acetates of the starting ketones were obtained by acylating the ketones with a three- or four-fold excess of isopropenyl acetate in the presence of sulphuric acid. Yields are as high as 80-90% when acetone is slowly (for 8-9 h) distilled off on a 12-plate column; they are highly dependent on substituents in the aromatic ring in the case of propiophenones or isobutyrophenones; donor substituents raise the yield ( see Table 1).



R = R′ = H; X = Cl, Br

R = H, R′ = $CH_3$; X = H, Cl, $CH_3$, $CH_3O$

R = R′ = $CH_3$; X = H, $CH_3O$

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* In honour of Academician A.N. Nesmeyanov on the occasion of his 75th birthday.

TABLE 1

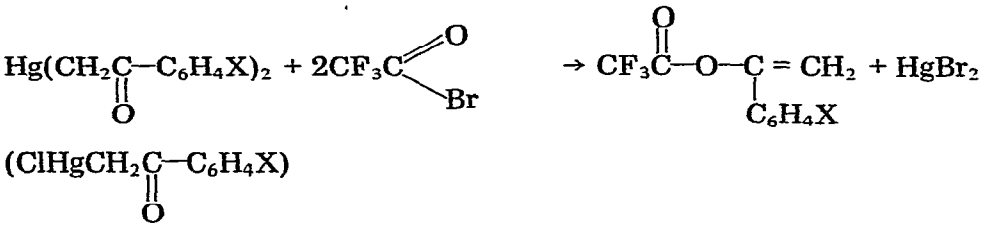
ENOL ACETATES AND ENOL TRIFLUOROACETATES OF ALIPHATIC-AROMATIC KETONES

| No. | Enol acetates and trifluoroacetates | Yield (%) | B.p. (°C/mm) | $n_D^{20}$ | $d_4^{20}$ | Empirical formula | Analysis found (calcd.) (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H |
| 1 | $CF_3COCC_6H_5$ [a] (O, $CH_2$) | 69 | 68-70/12 | 1.4640 | | | | |
| 2 | $CF_3COCC_6H_4Cl$-*p* (O, $CH_2$) | 70 | 88-89/6 | 1.4980 | 1.1357 | $C_{10}H_7ClF_3O_2$ | 47.61, 47.70 (47.94) | 2.15, 2.21 (2.40) |
| 3 | $CF_3COCC_6H_4CF_3$-*m* (O, $CH_2$) | 60 | 66-66/15 | 1.4515 | 1.0918 | $C_{11}H_6F_6O_2$ | 46.31, 46.25 (46.48) | 2.01, 2.10 (2.12) |
| 4 | $CH_3COCC_6H_5$ [c] (O, $CHCH_3$) | 18 | 82-86/1 | 1.5317 | 1.0620 | $C_{11}H_{12}O_2$ | 74.20, 74.06 (74.97) | 7.07, 7.32 (6.87) |
| 5 | $CH_3COCC_6H_4CH_3$-*p* [b] (O, $CHCH_3$) | 60 | 118-122/6 | 1.5317 | 1.0400 | $C_{12}H_{14}O_2$ | 76.35, 76.31 (75.76) | 6.95, 6.86 (7.42) |
| 6 | $CH_3COCC_6H_4Cl$-*p* [b] (O, $CHCH_3$) | 13 | 103-106/1 m.p. 35° | | | $C_{11}H_{11}ClO_2$ | 62.24, 62.20 (62.72) | 5.17, 5.34 (5.26) |
| 7 | $CH_3COCC_6H_4OCH_3$-*p* [b] (O, $CHCH_3$) | 85 | 129-131/1 m.p. 42° | | | $C_{12}H_{14}O_3$ | 69.13, 69.19 (69.88) | 7.04, 7.27 (6.84) |
| 8 | $CH_3COCC_6H_5$ (O, $C(CH_3)_2$) | 10 | 70-76/0.5 | 1.5204 | 1.0370 | $C_{12}H_{14}O_2$ | 75.48, 75.50 (75.77) | 7.48, 7.52 (7.42) |
| 9 | $CH_3COCC_6H_4OCH_3$-*p* (O, $C(CH_3)_2$) | 15 | 112-114/0.5 | 1.5301 | 1.0870 | $C_{13}H_{17}O_3$ | 70.92, 71.03 (70.86) | 7.17, 7.24 (7.32) |
| 10 | $CF_3COCC_6H_4CH_3$-*p* [d] (O, $CHCH_3$) | 21 | 50-51/0.5 | 1.4730 | 1.1670 | $C_{12}H_{11}F_3O_2$ | 59.40, 59.32 (59.01) | 4.56, 4.49 (4.54) |

[a] Lit.[3] b.p. 64°/10 mm, $n_D^{20}$ 1.4630. [b] For pure *E* isomers. [c] For the enol acetate containing 87% *E* isomer, 13% *Z* isomer. [d] Synthesised [3] by acylating the crude organotin derivative with trifluoroacetic anhydride.

For enol acetates of propiophenones (X = $CH_3O$, $CH_3$, H or Cl), that are mixtures of the *Z* and *E* isomers, the rectification has given fractions containing (PMR data in Table 3, and GLC data) above 90% of the high-boiling *E* isomer.

Enol trifluoroacetates of acetophenone, *p*-chloroacetophenone, and *m*-trifluoromethylacetophenone (Table 1) were obtained by acylating the respective mercurated carbonyl compounds with trifluoracetyl bromide [3].



To synthesise the organoantimony ketones (Table 2), enol trifluoroacetates were treated with di-tert-butylmethoxystibine (method A, [1,4]), enol acetates with di-tert-butyl(dimethylamino)stibine (method B, [1,4]).

Note that the side formation of enamines, only slightly apparent in the synthesis of organoantimony derivatives of aliphatic ketones [1], complicates the present syntheses (method B, propiophenones containing donor substituents) considerably. The propiophenone proper gives 12% enamine at 90° in 3 h whereas with the *p*-$CH_3$ or *p*-$CH_3O$ derivatives the conversion in the side reaction is 20 or 37%, respectively. The antimony derivative of *p*-methylpropiophenone could not be isolated by method B although if the reaction between di-tert-butyl(dimethylamino)stibine and *p*-methylpropiophenone enol acetate is carried out at lower temperatures for three days, PMR spectra of the reaction mixture demonstrate that there are no enamine signals when the main reaction conversion is below 30%. On keeping the mixture in the cold for a longer time enamines become observable, and in six days the organoantimony *p*-methylpropiophenone signals disappear from the spectra completely. Distillation gives the enamine, the unreacted enol acetate, and the organostibine oxide.

It is essential that the distillation temperature be as low as possible and the operation take the shortest possible time (5-10 minutes). Organoantimony derivatives of *p*-methoxypropiophenone and *p*-methoxyisobutyrophenone are formed in almost quantitative yields (PMR data), but they are decomposed to a considerable degree during distillation in vacuo.

The compounds synthesized are listed in Table 2. The structures were established by IR and PMR spectroscopy [1]; see Table 4 for data. The data suggest that the di-tert-butylantimony derivatives of the unsubstituted or substituted (Cl, Br, $CF_3$) acetophenones are *C*-isomers. No *O*-isomers could be found in the organoantimony acetophenone or *p*-chloroacetophenone even after five months.

Germylated acetophenones containing —*I* substituents are known to have higher *O*-isomer contents in the equilibrated mixtures [2]. For the organoantimony derivatives of acetophenone, the effect of the acceptor substituents studied is insufficient to raise the *O*-isomer concentration up to a value detectable in the spectra. In the propiophenone derivative, however, in which (unlike acetophenone) there is an α-methyl that destabilises the *C*-isomer [1], the

TABLE 2

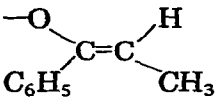
ORGANOANTIMONY ALIPHATIC-AROMATIC KETONES

| No. | Starting carbonyl compound | Yield (%) via | | Products composition, percentage of | | B.p. (°C/mm) | Empirical formula | Analysis found (calcd) (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | method A | method B | $t\text{-Bu}_2\text{SbOC=C}<$ *O*-isomer | $t\text{-Bu}_2\text{SbC(}-\text{)C=O}$ *C*-isomer | | | C | H |
| 1 | $CH_3CC_6H_5$ (=O) | 73 | | | 100 | 118-119/4·10$^{-2}$ | $C_{16}H_{25}OSb$ | 53.70, 53.81 (54.13) | 7.33, 6.94 (7.10) |
| 2 | $CH_3CC_6H_4$—Cl-*p* (=O) | 60 | | | 100 | 133-135/4·10$^{-2}$ | $C_{16}H_{24}ClOSb$ | 48.51, 48.68 (49.33) | 6.41, 6.51 (6.21) |
| 3 | $CH_3CC_6H_4$—Br-*p* (=O) | | *a* | | 100 | | | | |
| 4 | $CH_3CC_6H_4$—$CF_3$-*m* (=O) | 75 | | | 100 | *b* | $C_{17}H_{24}F_3OSb$ | 47.95, 47.87 (48.26) | 5.61, 5.77 (5.71) |
| 5 | $CH_3CH_2CC_6H_5$ (=O) | | 57 | 27 | 73 | 94-96/3·10$^{-2}$ | $C_{17}H_{27}OSb$ | 54.91, 55.33 (55.33) | 7.46, 7.47 (7.37) |
| 6 | $CH_3CH_2CC_6H_4$—Cl-*p* (=O) | | 66 | 41 | 59 | 113-116/3·10$^{-2}$ | $C_{17}H_{26}ClOSb$ | 50.15, 50.09 (50.50) | 6.76, 7.06 (6.50) |
| 7 | $CH_3CH_2CC_6H_4$—$CH_3$-*p* (=O) | 71 | | 19.5 | 80.5 | 95-97/3·10$^{-2}$ | $C_{18}H_{29}OSb$ | 56.33, 56.21 (56.43) | 7.47, 7.36 (7.63) |
| 8 | $CH_3CH_2CC_6H_4$—$OCH_3$-*p* (=O) | | 20 | 16 | 84 | 120-121/3·10$^{-2}$ | $C_{18}H_{29}O_2Sb$ | 53.81, 53.59 (54.17) | 7.53, 7.66 (7.32) |
| 9 | $(CH_3)_2CHCC_6H_5$ (=O) | | 58 | 100 | | 97-99/6·10$^{-2}$ | $C_{18}H_{29}OSb$ | 56.40, 56.05 (56.43) | 7.50, 7.51 (7.63) |
| 10 | $(CH_3)_2CHCC_6H_4$—$OCH_3$-*p* (=O) | | 32 | 100 | | 123-126/6·10$^{-2}$ | $C_{19}H_{31}O_2Sb$ | 55.48, 55.59 (55.21) | 7.53, 7.66 (7.57) |

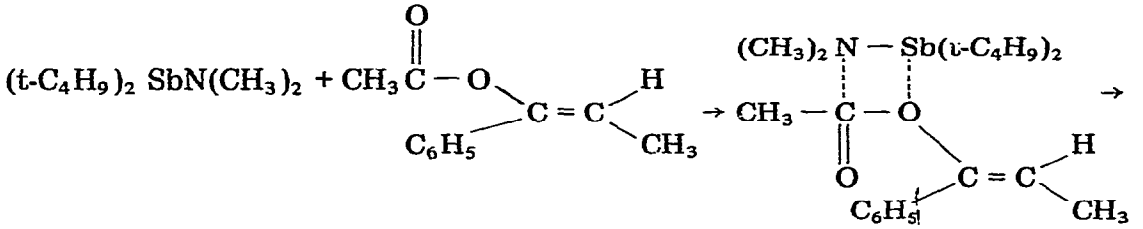
[a] The organo-antimony derivative of *p*-bromacetophenone was obtained from *p*-bromoacetophenone enol acetate [2] and di-tert-butyldimethylaminostibine. The yield was not measured. [b] Decomposes when distilled.

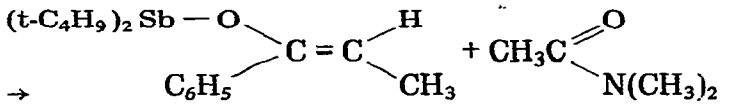
relative stability of the *O*-isomer rises and the isomer is observable in IR and PMR spectra.

Interconversions of the derivatives of propiophenone are worth discussing in more detail. The compound was obtained from propiophenone enol acetate and di-tert-butyl(dimethylamino)stibine. The starting enol acetate contained 95% *E* isomer. The reaction resulted in the *O*-derivative *E* isomer of propiophenone isolated by distillation. Thus, the configuration of the site

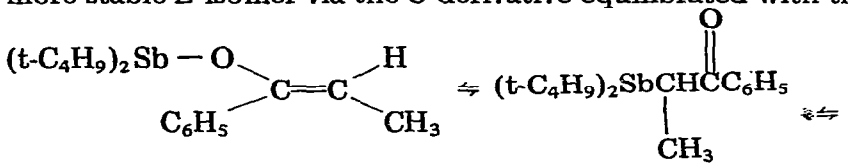


is retained in the reaction, shown below, which agrees with the four-centre mechanism proposed for reactions of enol acetates with nucleophilic alkoxy or dialkylamino derivates of elements [5]

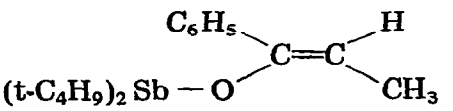




The *O*-*E*-derivative of propiophenone is thermodynamically unstable but it can be stored without decomposition for three month in the cold. Di-tert-butylchlorostibine (5% mol/mol) added to it converts (metal halides are known to accelerate metallotropic processes [1, 2]) the *O*-*E*-isomer into an equilibrium mixture containing 27% *O*-*Z*-isomer and 73% *C*-derivative of propiophenone. The conversion takes thirteen days at room temperature. The process was followed by PMR, to show that the *Z* isomer starts forming only after ca. 20% *C*-isomer has been accumulated. Consequently, the *E* isomer transforms to the more stable *Z* isomer via the *C*-derivative equilibrated with the *Z* isomer.



*E*-isomer *C*-isomer



*Z*-isomer

That the *Z* isomer of an organoelement phenylacetone enolate is thermodynamically more stable than is the *E* isomer (owing to the decrease in spatial hindrance to conjugation) has been noted previously [6].

The fact that the initial *E* enol acetates directly result in the organoantimony *O*-*E*-isomers was also demonstrated by us for the organoantimony derivatives of *p*-chloropropiophenone, *p*-methylpropiophenone, and *p*-methoxypropiophenone. The equilibrated mixtures were obtained by treating the *O*-*E*-isomers with di-tert-butylchlorostibine (5% mol/mol) for two weeks at room temperature. As with the propiophenone derivative, PMR spectra show that the less stable *E* isomers transform into the *Z*-isomers.

Di-tert-butylchlorostibine catalyst requires about two weeks to carry the equilibration to the end; we wanted to find the conditions that would accelerate the process.

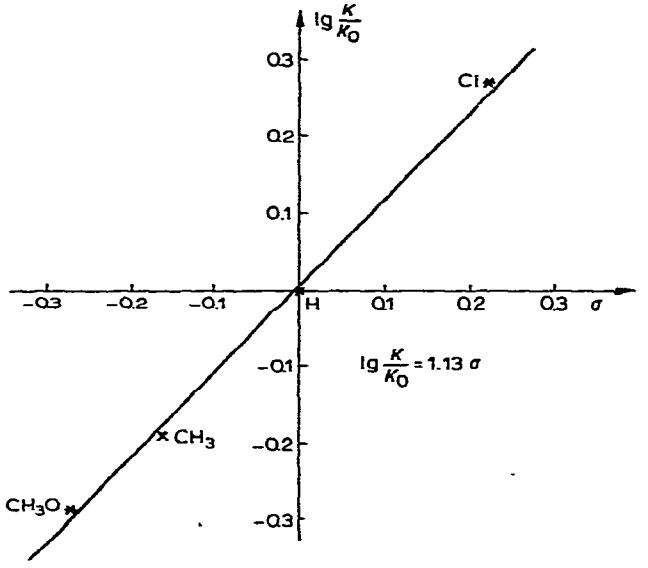
The equilibration was found to be unaffected by the application of benzene or hexamethyltriamidophosphate solvents. Mercuric dibromide is approximately as effective as di-tert-butylchlorostibine, but mercuric iodide only leads to tars in two days. In a striking manner, a good effect was achieved with carbon tetrachloride. Dissolving the organoantimony *O*-derivative of propiophenone in an equal volume of carbon tetrachloride gives the *O*/*C* equilibrium mixture in five days at room temperature, and in 1.5 h at 65°.

However, the stability of the equilibrated mixture is much decreased by carbon tetrachloride. For example, the mixture obtained from the thrice-distilled *E* species may be stored without decomposition in the cold, or even at room temperature in the absence of light, when di-tert-butylchlorostibine is the catalyst, whereas the solutions in carbon tetrachloride are tarred considerably even in two weeks. Heating the carbon tetrachloride solutions at 65° for two hours decomposes the compounds strongly. In the presence of mercuric dibromide at 85°, the decomposition is evident as early as eight hours. Therefore, temperature-dependencies of the equilibria defy almost any experimental approach. Nevertheless, the organoantimony propiophenone *O*-isomer content may be found to be temperature-insensitive at 20 to 85° within experimental error.

Let us collate the *O*- and *C*-isomer contents obtained for propiophenones substituted in the *para*-position (Table 2) with the data for germylated acetophenones [2]. In both the cases, the *O*-isomer content is higher for substituents of higher acceptor properties. For the organoantimony derivatives, however, the electronic factors in the organoantimony derivatives affect the equilibrium to a smaller extent that they do in the germylated acetophenones (the reaction constant is 1.67 for germanotropism [7], 1.13 for the antimony compounds, see Fig. 1).

Thus, Table 2 demonstrates that *C*-derivatives only were obtained for substituted acetophenones; introduction of a methyl in the α-position (i.e., replacing acetophenones by propiophenones) leads to tautomeric mixtures of *C*- and *O*-derivatives. The α, α-dimethyl compound (i.e. isobutyrophenone) yields the *O*-species exclusively. The *p*-methoxyisobutyrophenone organoantimony derivative, although it contains a group of a high + *M*-effect, gives no *C*-species either and is also an enolate.

When we compare the roles of spatial and electronic factors in the organo-




| Substituent | O-isomer, (%) | $K\frac{[O]}{[C]}$ | $\frac{K}{K_0}$ | $\lg\frac{K}{K_0}$ | σ |
|---|---|---|---|---|---|
| $CH_3O$ | 16.0 | 0.190 | 0.515 | −0.288 | −0.268 |
| $CH_3$ | 19.5 | 0.242 | 0.655 | −0.184 | −0.170 |
| H | 27.0 | 0.370 | 0 | 0 | 0 |
| Cl | 41.0 | 0.695 | 1.878 | 0.274 | 0.227 |

Fig. 1. The Hammett correlation for equilibrium constants.

antimony compounds studied we see that spatial factors are evidently predominant. Electronic factors operate in the same way as in organogermyl compounds, but more weakly.

## Experimental

### *General*

Chromatography was carried out on a Tsvet-1 instrument, column 500 × 0.4 cm packed with 10% SE-30 on Chromosorb W, carrier gas helium, heat conductivity detector. PMR spectra were recorded on an RS-60 machine with a hexamethyldisiloxane internal standard. IR spectra were taken in thin films on an IKS-22 two-beam spectrometer.

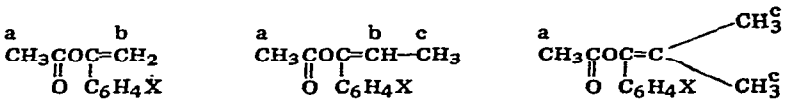
Spectral data are given in Tables 3 and 4.

### *1. α-Chloromercury(p-chloroacetophenone)*

*p*-Chloroacetophenone enol acetate [2] (21.1 g, 0.108 mol) was added dropwise to a vigorously shaken suspension of mercury acetate (34.2 g, 0.108 mol) in 60 ml water, placed in a cold water bath. The mixture was mechanically shaken for 4 h, the precipitate formed was triturated under the liquid layer to make it a uniform suspension, and a cold saturated solution of potassium chloride (8.02 g, 0.108 mol) in water was added dropwise thereto.

TABLE 3

PMR DATA FOR ENOL ACETATES AND ENOL TRIFLUOROACETATES OF ALIPHATIC-AROMATIC KETONES ($\delta$, ppm) [c]



| No. | Compound | | $H_a$ | $H_b$ | $H_c$ |
|---|---|---|---|---|---|
| 1 | $CF_3COCC_6H_5$ (O, $CH_2$) [b] | | | 5.00, 5.33 | |
| 2 | $CF_3COC-C_6H_4-Cl$-*p* (O, $CH_2$) [b] | | | 5.10, 5.40 | |
| 3 | $CF_3COC-C_6H_4-CF_3$-*m* (O, $CH_2$) [b] | | | 5.30, 5.64 | |
| 4 | $CH_3COCC_6H_5$ (O, $CHCH_3$) [c] | *E*-isomer | 1.98 | 5.75 | 1.45, 1.57 |
| | | *Z*-isomer | 1.83 | 5.37 | 1.50, 1.63 |
| 5 | $CH_3COC-C_6H_4-CH_3$-*p* (O, $CHCH_3$) [c] | *E*-isomer | 2.00 | 5.63 | 1.46, 1.60 |
| | | *Z*-isomer | 1.88 | 5.30 | 1.53, 1.70 |
| 6 | $CH_3COC-C_6H_4Cl$-*p* (O, $CHCH_3$) [c] | *E*-isomer | 2.06 | 5.70 | 1.45, 1.58 |
| | | *Z*-isomer | 1.93 | 5.37 | 1.50, 1.63 |
| 7 | $CH_3COC-C_6H_4-OCH_3$-*p* (O, $CHCH_3$) [c] | *E*-isomer | 2.10 | 5.66 | 1.46, 1.60 |
| | | *Z*-isomer | 1.93 | 5.56 | 1.53, 1.66 |
| 8 | $CH_3COCC_6H_5$ (O, $C(CH_3)_2$) | | 1.83 | | 1.58 |
| 9 | $CH_3COC-C_6H_4-OCH_3$-*p* (O, $C(CH_3)_2$) | | 1.90 | | 1.60 |
| 10 | $CF_3COC-C_6H_4-CH_3$-*p* (O, $CHCH_3$) [c] | *E*-isomer | | 5.80 | 1.46, 1.58 |
| | | *Z*-isomer | | 5.60 | 1.50, 1.63 |

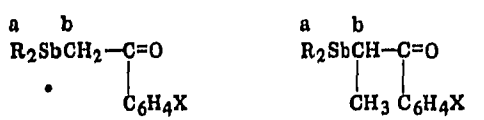
[a] Aromatic proton signals, a typical AA'BB' system, were found at 6.6 to 8.0 ppm for compounds no. 2, 5, 6, 7, 9, 10. [b] The vinyl protons are reflected by two doublets characteristic of AX spin systems [2]. [c] Chemical shifts of vinyl protons in isomeric enol acetates or enols with the cis-arrangement of the oxygen and hydrogen, i.e. in *E* isomers, are known [10] to lie in lower fields compared with the *Z* isomers.

The mixture was shaken for an hour more, white crystals of the product were filtered, washed with water, ether, and dried in vacuo over phosphorus pentoxide to give $\alpha$-chloromercury(*p*-chloroacetophenone), 35 g (83%), m.p. 152—153° (benzene). Found: C, 24.21, 24.27; H, 2.03, 2.19. $C_8H_6Cl_2OHg$ calcd.: C, 24.67; H, 1.54%.

*2. p-Chloroacetophenone enol trifluoroacetate*

Trifluoroacetyl bromide [3] (20 g. 0.113 mol) was bubbled through a sus-

TABLE 4. PMR AND IR DATA FOR ORGANOANTIMONY DERIVATIVES OF ALIPHATIC-AROMATIC KETONES[a]




R = t-C4H9

| No. | Compound | | PMR Spectra δ(ppm) | | | | IR Spectra ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | | $H_a$ | $H_b$ | $H_c$ | $H_d$ | C=C | C=O |
| 1 | $R_2SbCH_2COC_6H_5$ | | 1.26 | 3.16 | | | | 1660 |
| 2 | $R_2SbCH_2CO-C_6H_4-Cl$-p | | 1.20 | 3.10 | | | | 1660 |
| 3 | $R_2SbCH_2CO-C_6H_4-Br$-p | | 1.20 | 3.12 | | | | 1660 |
| 4 | $R_2SbCH_2CO-C_6H_4-CF_3$-m | | 1.23 | 3.14 | | | | 1665 |
| 5 | $R_2SbOCC_6H_5$ ‖ $CHCH_3$ | E-isomer | 1.20 | | 4.71 | | 1640 | |
| | | Z-isomer | 1.20 | | 4.63 | | | |
| 6 | $R_2SbCH(CH_3)COC_6H_5$ | | 1.21 | 2.90 | | | | 1680 |
| 7 | $R_2SbOC-C_6H_4-CH_3$-p ‖ $CHCH_3$ | E-isomer | 1.14 | | 4.80 | | | |
| | | Z-isomer | 1.14 | | 4.65 | | 1640 | |
| 8 | $R_2SbCH(CH_3)CO-C_6H_4-CH_3$-p | | 1.16 | 2.86 | | | | 1680 |
| 9 | $R_2SbOC-C_6H_4-Cl$-p ‖ $CHCH_3$ | E-isomer | 1.20 | | 4.80 | | 1640 | |
| | | Z-isomer | 1.20 | | 4.53 | | | |
| 10 | $R_2SbCH(CH_3)CO-C_6H_4-Cl$-p | | 1.20 | 2.73 | | | | 1670 |
| 11 | $R_2SbOC-C_6H_4-OCH_3$-p ‖ $CHCH_3$ | E-isomer | 1.20 | | 5.06 | | 1640 | |
| | | Z-isomer | 1.20 | | 4.66 | | | |
| 12 | $R_2SbCH(CH_3)CO-C_6H_4-OCH_3$-p | | 1.20 | 2.70 | | | | 1670 |
| 13 | $R_2SbOCC_6H_5$ ‖ $C(CH_3)_2$ | | 1.20 | | | 1.50 | 1640 | |
| | | | 1.26 | | | 1.83 | | |
| 14 | $R_2SbOC-C_6H_4-OCH_3$-p ‖ $C(CH_3)_2$ | | 1.13 | | | 1.46 | 1640 | |
| | | | 1.26 | | | 1.80 | | |

[a] Benzene ring proton signals lie at 6.8 to 7.8 ppm in all the compounds.

pension of α-chloromercury(*p*-chloroacetophenone) (51 g, 0.127 mol) in 70 ml absolute dichloroethane. The mixture was stirred for 3 h, and distilled to give 18.2 of *p*-chloroacetophenone enol trifluoroacetate.

*3. 2-Bromo-1-(m-trifluoromethylphenyl) diethyl ether*

1,2-Dibromo diethyl ether (82 g, 0.35 mole) was added to the Grignard reagent obtained from magnesium (9.6 g, 0.4 mol) and *m*-bromobenzotrifluoride (90 g, 0.4 mol) in 200 ml ether, the reaction flask being cooled by cold water. The reaction mixture was stirred for 2 h, decomposed with cold water, the ether layer was separated and dried over calcium chloride. Evaporation of the solvent followed by two distillations in vacuo gave 2-bromo-1-(*m*-trifluoromethylphenyl) diethyl ether, 80 g (77%), b.p. 81-82°/1.5 mm, $n_D^{20}$ 1.4775. Found: C, 44.15, 44.21; H, 3.97, 4.01. $C_{11}H_{12}BrF_3O$ calcd.: C, 44.50; H, 4.04%. NMR: δ 1.06(t), 3.1—3.5(m), 4.45(t), 7.3—7.7ppm (m).

*4. m-Trifluoromethyl- α-ethoxystyrene*

A mixture of 2-bromo-1-(*m*-trifluorophenyl) diethyl ether (80 g, 0.27 mol), potassium hydroxide (50 g), and 25 ml triethanolamine was refluxed at 180-190° for 4 h. All liquids were distilled off in vacuo, the residue was dissolved in water, twice extracted with ether, the distillate and the combined extracts were washed with water, and dried over magnesium sulphate. The solvent was evaporated, the residue distilled twice in vacuo, to give *m*-trifluoromethyl-α-ethoxystyrene, 41 g (70%), b.p. 87-90°/ 10 mm, $n_D^{20}$ 1.4625. Found, C, 61.43, 61.34; H, 5.28, 5.08. $C_{11}H_{11}F_3O$ calcd.: C, 61.09; H, 5.13%. NMR: δ 1.16(t), 3.64(q), 4.03(d), 4.50(d), 7.0—7.8ppm(m).

*5. Mercurybis(m-trifluoromethylacetophenone)*

A mixture of mercuric oxide (18.8 g, 0.087 mol), *m*-trifluoromethyl-α-ethoxystyrene (40 g, 0.184 mol), 40 ml methyl alcohol, 5 ml water, and 0.5 g mercuric acetate was shaken for 20 h. Mercuric oxide dissolved almost totally. The precipitate was filtered, washed with chloroform, the solvent was evaporated, and the residue was dried over $P_2O_5$ in vacuo to give 52.2 g (quantitative yield) of mercurybis(*m*-trifluoromethyl-acetophenone), light-yellow powder, m.p. 158° (ethanol). Found C, 37.41, 37.53; H, 2.04, 2.03. $C_{18}H_{12}F_6HgO_2$ calcd.: C, 37.60; H, 2.09%.

*6. m-Trifluoromethylacetophenone enol trifluoroacetate*

Trifluoroacetyl bromide [3] (23.5 g, 0.133 mol) was bubbled through a solution of mercurybis(*m*-trifluoromethylacetophenone) (50 g, 0.087 mol) in 100 ml dichloroethane. The mixture was stirred for 3h, and a white thin precipitate was filtered off and washed with ether. The filtrate was evaporated, the residue twice distilled in vacuo, to give 35 g of the compound desired.

Acetophenone enol trifluoracetate was obtained in a similar way [3], see Table 1.

*7. Propiophenone enol acetate*

A mixture of propiophenone (72 g, 0.5 mol), isopropenyl acetate (150 g, 1.5 mol) and 1 ml sulphuric acid was distilled on a 12-plate column. Acetone

(40 ml; the theoretical amount is 38 ml) was fractionated off in 10 h. The residue was distilled in vacuo, to give 80 g of a mixture of 80% the starting ketone and 20% the desired enol acetate. The enol acetate yield is 18%. It contains 66% *E* isomer, 34% *Z* isomer. The mixture was distilled on a 25 cm Vigreux column, the fraction collected at 71-86°/1 mm contained 83% enol acetate. The fraction collected at 68-71°/1 mm (propiophenone and ca. 7% enol acetate) was treated with isopropenyl acetate once more, the product was distilled in vacuo, the distillate contained about 70% enol acetate. Both the fractions enriched in tne enol acetate were distilled on a 25 cm Vigreux column to give propiophenone enol acetate, 16.7 g (19%), containing 87% *E* isomer and 13% *Z* isomer. Redistilling the product gave the enol acetate containing 95% *E* isomer.

The compounds 5 to 9 were obtained in a similar way, see Table 1.

*8. Di-tert-butylantimony derivative of acetophenone (method A)*

All operations with the organoantimony derivatives were carried out in a dry argon atmosphere.

Acetophenone enol trifluoroacetate (10.2 g, 0.047 mol) was added over 20 min to di-tert-butylmethoxystibine (10.3 g, 0.039 mol) with vigorous shaking at 0°. The mixture became slightly yellow. It was kept under ambient conditions for 2 h, all low-boiling products were distilled off in an oil-pump vacuum and collected in a trap cooled down to −78°. The contents of the trap were fractionated to give methyl trifluoroacetate, 9 g (88%), b.p. 41° (lit. [8] 41-43°), $n_D^{20}$ 1.3042 (lit. [8] 1.3053). The residue was rapidly (for 5 min) distilled from a small flask on an oil bath in a high vacuum. The flask was submerged into the oil down to the level of the thermometer bulb. Two distillations gave 10 g of α-di-tert-butylstibylacetophenone.

The compounds 2, 4, 7 (Table 2, method A) were obtained in a similar way.

*9. Di-tert-butylantimony derivative of propiophenone (method B)*

A mixture of di-tert-butyl(dimethylamino)stibine (16 g, 0.0572 mol) and propiophenone enol acetate (11.5 g, 0.0654 mol) was heated at 80-90° for 8 h until the reaction was complete (PMR follow-up). Low-boiling reaction products were distilled off in an oil-pump vacuum, the distillate was fractionated to give *N, N*-dimethylacetamide, 4.0 g (80%), b.p. 46-48°/3mm (lit. [9] 30°/2 mm), $n_D^{20}$ 1.4320 (lit. [9] 1.4308). The residue was distilled in a high vacuum (see Experiment No. 8). Two distillations gave 12 g of the di-tert-butylantimony derivative of propiophenone.

The compounds 6, 8 to 10 (Table 2, method B) were obtained analogously.

*10. Reaction of p-methylpropiophenone enol acetate with di-tert-butyl(dimethylamino)stibine*

*p*-Methylpropiophenone enol acetate (11.5 g, 0.0603 mol) was mixed with di-tert-butyl(dimethylamino)stibine (19.4 g, 0.055 mol). The mixture was kept for three days at room temperature, the reaction course was followed by PMR. No enamine signals were observed before the di-tert-butylstibyl-*p*-methoxypropiophenone formation became 30%. The mixture was kept at room tem-

perature for three days more, and the signals of the *p*-methylpropiophenone organoantimony derivative disappeared from, while the enamine signals appeared in, the spectrum. The mixture was distilled in vacuo to give a fraction boiling at 56-70° / 0.1 mm ( a mixture of the initial enol acetate with the enamine), and di-tert-butylstibine oxide, 7.3 g (55%), b.p. 96-97°/$10^{-2}$ mm. Found: C, 39.51, 39.84; H, 7.73, 7.73. $C_{16}H_{36}OSb_2$ calcd.: C, 39.40; H, 7.40%.

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