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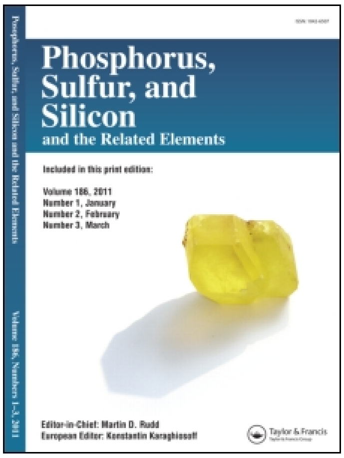

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REACTIONS OF ACETYLACETONE WITH ORGANOTELLURIUM(IV) CHLORIDES-C_1 BONDED ACETYLACETONATES OF TELLURIUM(IV)

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Abstract The reactions of acetylacetone (AcAc) with $ArTeCl_3$ (I), Ar_2TeCl_2 (II) and Ar_3TeCl (III) (where Ar = phenyl, 4-hydroxyphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 3-methyl-4-hydroxyphenyl and 3,4-dihydroxyphenyl) have been investigated. The I gives $ArTe(C_5H_7O_2)Cl_2$ (IV) type derivatives but II and III do not react even on prolonged refluxing in the presence of anhydrous $AlCl_3$. The structural features of the new acetylacetone derivatives (IV) have been explored by IR, PMR and CMR spectroscopy. The effect of phenyl ring substituents on the keto-enol tautomerism of IV has been found to be minor. The bond formation between Te and C_1 of AcAc and intramolecular secondary interaction between the oxygen of AcAc and Te have been inferred from the spectral data.

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INTRODUCTION

The β-diketonates of several metals and metalloids, except tellurium, are well documented in the literature[1]. Morgan and Drew[2-3] first studied the reactions of $TeCl_4$ with some β-diketones ($R\ C(O)CH_2C(O)R^1$) and obtained R_2TeCl_2 (R= β-diketonate group) type species having Te linked to terminal carbon of the dione when R or R^1 was methyl. In case of acetylacetone the second product identified[4a,b] latter as telluracyclohexane-3,5-dione dichloride was also noticed by Morgan and his coworkers. We have shown very recently that tellurium moieties can be bonded to carbonyl oxygen of β-diketones[5] as well as middle carbon atom (C_3) of acetylacetone[6]. The reactions of acetylacetone (AcAc) with organotellurium (IV) chlorides, unattended so far, seem to be interesting because the activation of expected products $Ar(C_5H_7O_2)TeCl_2$ and

$Ar_2(C_5H_7O_2)TeCl$ may result[7] easily the arylated acetylacetone otherwise difficult to synthesize. We have, therefore, studied such reactions of acetylacetone. The Ar_2TeCl_2 and Ar_3TeCl do not react on prolonged refluxing (48 h) in a variety of solvents. The anhydrous $AlCl_3$ also fails in catalyzing the reactions. The reaction of $ArTeCl_3$ gives C_1 bonded acetylacetonates, $Ar(C_5H_7O_2)$-$TeCl_2$ (IV) (where Ar = C_6H_5(a), 4-OH - C_6H_4(b), 4-$OCH_3C_6H_4$(c), 4-$OC_2H_5C_6H_4$(d), 3-CH_3-4-OHC_6H_3(e) or 2,4-$(OH)_2C_6H_3$(f). The results of preparative and spectral investigations on IVa to IVf are reported in the present paper.

EXPERIMENTAL

Physical Measurements

^1H and ^{13}C NMR spectra were recorded on a Jeol FX-100 FT-NMR spectrometer operating at 100 MHz and 25 MHz respectively. IR spectra in the region 4000-400 cm^{-1} were recorded on a Pye Unicam SP 1200 infrared spectrometer using KBr pellets. The FT-IR spectrometer Nicolet 5DX was used for the region 600-200 cm^{-1}. Mass spectra (70 eV) were recorded on a Varian AEI MS9 mass spectrometer at Aston University, U.K. The conductance measurements were carried on a Pye conductance bridge.

Analyses

Tellurium contents of the compounds were determined[8] by Pye Unicam SP 191 atomic absorption spectrophotometer. The chloride was estimated volumetrically[9]. For the determination of C and H, a Coleman carbon-hydrogen analyser model-33 was employed.

The literature methods were used for the preparation of phenyl-[10], (4-hydroxyphenyl)-[11], (4-methoxyphenyl)-[12], (4-ethoxyphenyl)-[12], (3-hydroxy-4-methylphenyl)-[13] and (3,4-dihydroxyphenyl)tellurium trichloride[11].

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General Procedure for Synthesis of IV

The IV (a to e) were prepared by refluxing the appropriate $ArTeCl_3$ (~5 mM) and acetylacetone (~30 mM) in 40 cm^3 benzene under nitrogen atmosphere till the evolution of hydrogen chloride ceased (6 to 8 h). The reaction mixture was filtered thereafter and reduced in volume to 5-6 cm^3. The 40 cm^3 petroleum ether (60-80°C) was added to this concentrate to separate the brown/grey solid which was washed with petroleum ether thrice, recrystallized from chloroform and dried under vacuum. For IVf, the reaction was carried out at room temperature and worked up as mentioned above.

RESULTS AND DISCUSSION

The $ArTeCl_3$ reacts with AcAc according to equation 1, as the results of elemental analyses (Table 1) of the products agree with the values calculated for $ArTe(C_5H_7O_2)Cl_2$.

$$ArTeCl_3 + C_5H_8O_2 \xrightarrow[C_6H_6, N_2]{\text{reflux}} ArTe(C_5H_7O_2)Cl_2 + HCl \qquad (1)$$

The molar conductivities of IVa to IVf in CH_3CN (1.45-8.68 ohm^{-1} cm^2 mol^{-1}) are in the range of nonelectrolyte, suggesting that these compounds behave as diorganyltellurium dichlorides, which is supported by their hydrolysis to corresponding $(ArTeO)_2O$ by 10% sodium carbonate solution. The concentrated hydrochloric acid can liberate AcAc from them (equation 2).

$$Ar(C_5H_7O_2)TeCl_2 + HCl \xrightarrow[\text{heat}]{CH_3CN} ArTeCl_3 + C_5H_8O_2 \qquad (2)$$

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TABLE I. Elemental analyses and physical properties

IV	Yield (%)	Colour (M.P.(d)°C)	Analyses (Found/Calcd. %) C	H	Te	Cl
a	65	Brown (123-125)	36.04 (35.24)	3.44 (3.20)	33.54 (34.07)	18.56 (18.75)
b	45	Dark brown (114-116)	32.98 (33.79)	3.52 (3.07)	31.42 (32.67)	17.85 (18.17)
c	90	Grey (115)	35.96 (35.50)	4.25 (3.69)	30.95 (31.45)	16.48 (17.50)
d	55	Brown (119-120)	36.25 (37.27)	4.02 (3.82)	29.12 (30.48)	15.56 (16.96)
e	70	Brown (110)	34.83 (35.58)	3.58 (3.54)	30.35 (31.58)	16.98 (17.55)
f	30	Brown (108)	31.95 (32.40)	3.20 (2.95)	30.05 (31.38)	16.95 (17.46)

The resorcinol exceptionally reacts with IVc, on heating them in 4:1 molar ratio in toluene at 80-90°C for 12 h, resulting highly hygroscopic $(\underline{p}\text{-}CH_3OC_6H_4)(2,4\text{-}(OH)_2C_6H_3)(C_5H_7O_2)TeCl$. On reduction of IVc and IVf with fused $Na_2S.9H_2O$ or $Na_2S_2O_5$ the elemental tellurium is precipitated whereas Ar_2Te_2 is obtained in other cases.

The chemical shifts observed in ^1H NMR spectra (Table II) suggest that in all the compounds (IVa to IVf) tellurium moiety is bonded with terminal carbon (C_1) atom of AcAc and the keto-enol tautomerism, as depicted in Scheme 1, exists in solution. Our assignments of CH_2-Te protons agree well with the literature reports[4a] for telluracyclohexane-3,5-dione, its dichloride and $(CH_3COCH_2COCH_2)_2TeCl_2$. The chemical shifts for protons of phenyl ring and its substituents were in agreement

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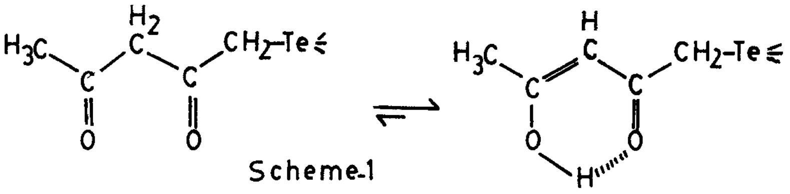
TABLE II Chemical shifts (δ, ppm)$^+$ in ^1H NMR spectra of IV at 25°C

IV	Enol form			Keto form		
	CH_3	CH	CH_2-Te	CH_3	CH_2	CH_2-Te
a	1.36	4.89	4.05	1.53	2.87	4.33
b	2.08	5.79	4.64	2.19	3.85	4.82
c	2.08	5.65	4.54	2.13	3.89	4.74
d	2.09	5.65	4.53	2.26	3.76	4.72
e	2.11	5.69	4.58	2.69	3.78	4.74
f	2.07	5.61	4.59	2.39	3.58	4.81

+ Solvent b,f - CD_3CN; a,c,d,e-$CDCl_3$



Scheme-1

with our earlier reports[11,13]. However, the OH resonance for IVb has been found merged in the phenyl signal. The % enol-form of AcAc increases to 95 when a hydrogen at C_1 is replaced by -Te(Ph)Cl_2 group. The substitution of an electron donating group on phenyl ring at position para to tellurium reduces the amount of enol form almost to the level of acetylacetone. The signals for phenyl protons of keto form could not be identified because of their merging in the phenyl signals of enol form except for IVb. In comparision to pure acetylacetone the CH_3 (δ 1.92/2.11 ppm) and CH/CH_2 resonances (δ 5.5/3.5 ppm) are observed to be shielded in the spectrum of IVa. This indicates that in IVa

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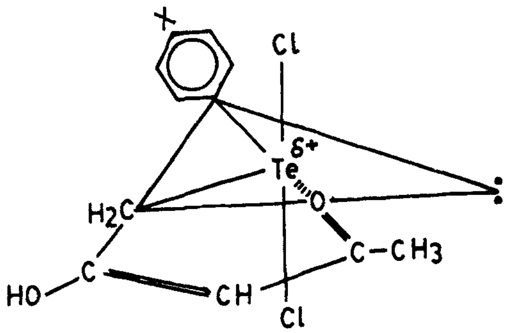

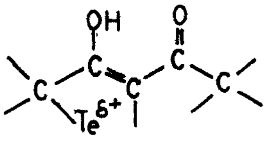
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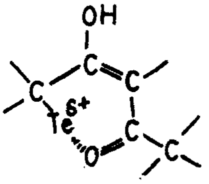
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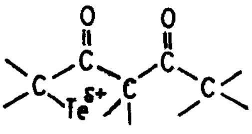
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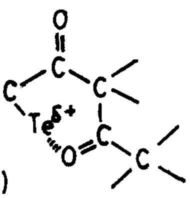
(E)

oxygen has significant secondary interaction with Te made positive by two electronegative chlorine atoms, which in turn brings the CH_3 protons under the influence of tellurium lone pair (structure A) and shields them. The shielding of CH/CH_2 also seems to result from the delocalization of electron density arising out of this interaction. When groups para to tellurium make it less positive, this secondary interaction breaks down and configuration B or D results which has CH/CH_2 proton in the vicinity $Te^{\delta+}$ and therefore, these protons are somewhat deshielded in comparision to configuration C and E. In absence of secondary interaction the positive charge on Te affects CH_2 group bonded directly to it more and thus that is also deshielded. The chemical shifts of CH_3 and CH/CH_2 protons observed for IVb to IVf are in general closer to the values of pure acetylacetone, which further support the hypothesis of intramolecular secondary interaction and its breaking.

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TABLE III Chemical shifts (δ, ppm)$^+$ in ^{13}C NMR spectra of IV at 25°C

IV	Acetylacetone				Phenyl carbon	Phenyl ring substituent's carbon
	C_1	C_3	C_2/C_4	C_5		
a	61.98 (44.24)	100.56 (64.76)	186.83 (188.59)	23.64 (31.20)	127.38-131.81	-
b	59.91 (57.91)	101.48 (63.96)	190.36	24.04	136.47 160.95 (C-OH)	-
c	60.61 (57.51)	100.48 (63.32)	185.97 (189.07)	23.75	119.45-135.24 162.30 (C-OMe)	55.45 (OMe)
d	64.11	101.97	191.25	24.74	116.81-135.50 161.80 (C-OEt)	14.68 (OEt) CH_2 merged in solvent
e	60.51 (57.51)	100.48 (63.32)	185.97 (189.06)	23.75	116.57-135.83 157.67 (C-OH)	15.89 (Me)
f	59.91 (57.90)	101.82 (63.92)	190.15	24.03	123.49-135.27 159.75 (C-OH)	-

\+ Solvent : b,f - CD_3CN a, c, d, e - $CDCl_3$

++ In parentheses the values are for keto form.

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^{13}C NMR spectra (Table III) support the linkage of tellurium moiety with C_1 of acetylacetone as well as the existence of keto-enol tautomerism in solutions of IVa to IVf. The variation in the position of methyl carbon (C_5) and C_1 signal with substitution on phenyl group is not much, suggesting the weak nature of tellurium oxygen interaction. It will be unwise to infer too much from small variations, even then small deshielding of C_5 in IVb-f with respect to IVa supports the possibility of above mentioned hypothesis of weak Te-O secondary interaction.

The IR spectra of these $Ar(C_5H_7O_2)TeCl_2$ type derivatives have broad bands assignable to ν_{OH}, between 3200-3600 cm^{-1} and ν_{CO} bands between 1585-1720 cm^{-1}. In pure acetylacetone also these bands are observed at similar positions, suggesting that tellurium is not bonded either to oxygen of acetylacetone or its C_3 carbon atom. This inference in conjunction with the occurrence of ν_{Te-CH_2} at 490-510 cm^{-1} and $\nu_{Te-C(phenyl)}$ at 205-265 cm^{-1} support the bonding of tellurium with C_1 atom of acetylacetone, keto-enol tautomerism resperesented in Scheme 1 and the predominance of enol form in solid state too.

The mass spectrum of IVa has a feature at m/e = 300, most probably due to tellurocyclohexane-3,5-dione dichloride ion, which further supports the bonding of tellurium moiety with C_1 of AcAc. The reaction of Ar_3TeCl with AcAc in accordance to equation 1 probably does not occur due to its ionic nature but the unreactivity of Ar_2TeCl_2 is surprising.

REFERENCES

1. R.C. Mehrotra, R. Bohra, and D.P. Gaur, "Metal-β-Diketonates and Allied Derivatives," (Academic Press, London, 1978).
2. G.T. Morgan, and H.D.K. Drew, J. Chem. Soc., 121, 922 (1922).
3. G.T.Morgan, and H.D.K. Drew, J.Chem. Soc.,117, 1456 (1920).
4. (a) D.H.Dewer, J.Fergusson, P.R.Hentschel, C.J.Wilkins, and P.P. Williams, J.Chem. Soc., 688 (1964); (b) R.L.Raston, R.J. Secomb and A.H. White, J.Chem. Soc., Dalton Trans.,2307 (1976).

5. B.L. Khandelwal, A.K. Singh, H.B. Singh, K.M. Prasad, N.S. Bhandari, and W.R. McWhinnie, J. Organometal. Chem., 291, 185 (1985).
6. B.L. Khandelwal, A.K. Singh, and N.S. Bhandari, J. Organometal. Chem., 320, 283 (1987).
7. J. Bergman in Proceedings Fourth International Conference on the Organic Chemistry of Selenium and Tellurium, Edited by F.J. Berry and W.R. McWhinnie (1983), p. 215.
8. P. Thavornyutikarn, J. Organometal. Chem., 51, 237 (1973).
9. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis, 3rd Edn. (Longmans, London, 1961).
10. R.C. Paul, K.K. Bhasin, and R.K. Chadha, J. Inorg. Nucl. Chem., 37, 2337 (1975).
11. B.L. Khandelwal, K. Kumar, and F.J. Berry, Inorg. Chim. Acta, 47, 135 (1981).
12. L. Reichel, and E. Kirschbaun, Ann., 523, 211 (1936).
13. B.L. Khandelwal, K. Kumar, and K. Raina, Synth. React. Inorg. Met.-Org. Chem., 11, 65 (1981).

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