EXPERIMENTAL

Free radical (I) was dissolved in heptane, and then mineral oil was added down to a radical concentration of 10^{-3} mole/liter. The sample was carefully evacuated down to 10^3 torr by the freezing-thawing method in order to remove the heptane and dissolved oxygen. The spectra were measured on a Brüker Physik ER-200D spectrometer (Germany).

CONCLUSIONS

The HFS constants for the protons in positions 5-13 of the free radical 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl were determined by the DENR method.

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ACYLATION OF ARSENIC β-KETOYLIDES BY TRIFLUOROACETIC

ANHYDRIDE

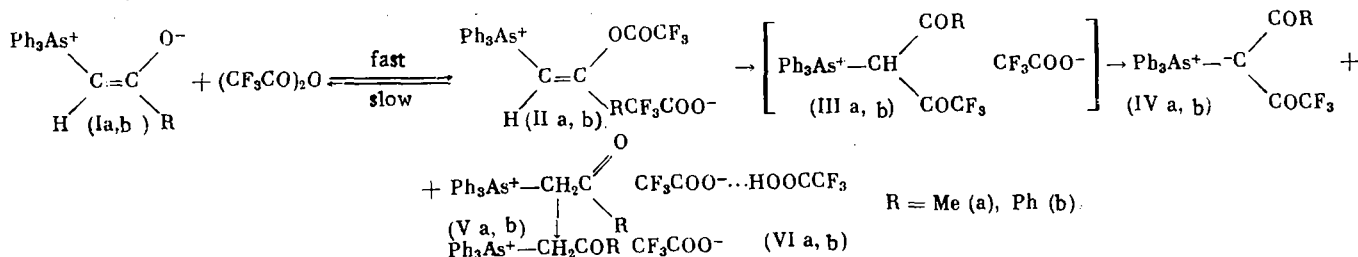N. A. Nesmeyanov, V. G. Kharitonov,   UDC 542.951.1:541.49:547.1'119
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Previously we had shown that the alkylation of ambident phosphorus ketoylides by CH_3I and $PhCH_2I$ first leads to the O-alkylated products, while on further heating the O → C rearrangement occurs, which consists in the reversible cleavage of alkyl iodide and in the slow but irreversible alkylation of the formed ylide at the C atom [1]. The reaction with trifluoroacetic anhydride (TFA) proceeds in a similar manner [2]. The mechanism of the O → C rearrangement is probably the same in this case. However, the arsenic ylides (I) of analogous structure are alkylated by the mentioned alkyl iodides simultaneously at both the O and C atoms, which we explain by the greater blocking of the ylide C atom by the triphenylphosphonium grouping. In this connection it was of interest to study the direction of the acylation of arsenic β-ketoylides by TFA and compare the properties of the products with their phosphorus analogs.

It proved that only one product (II) is formed when the reactants are mixed at −20°C in CH_2Cl_2 solution, and the IR spectrum of the reaction mixture is (ν, cm⁻¹): 1660 (C=C), 1690 (C=O of CF_3CO_2 anion), and 1815 (C=O). The absorption bands, corresponding to the rearrangement products, are absent initially. The rearrangement begins at 20°C and higher and leads to salt (III), which as a stronger acid ejects the trifluoroacetic acid (TFAA) molecule and is converted to ylide (IV).

The reaction mixture contains a large amount of the conjugated acid of the starting ylide (VI), which can be due not only to a partial hydrolysis of salt (II) by traces of moisture, but also to two other processes. First, if we correctly interpret the rearrangement

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mechanism, i.e. (II) migrates to (III) via ylide (I), then (I) can react not only with the cleaved anhydride, but also, as a base, with the TFAA that is cleaved from salt (III). Second, the TFAA, liberated as a result of the O → C rearrangement, is itself capable of cleaving ylides of the (IV) type.

Actually, a curious property of ylide (IV) is its ability to be cleaved when treated with strong acids. When an equimolar amount of TFAA is added to ylide (IV) the first to be formed is a complex via the H bond, the same as we had observed in the case of the phosphorus analog of (IV) [2]. Here, instead of the absorption bands of the $C=O$ groups of ylide (IV) at 1565 and 1620 cm^{-1}, appear bands at 1530 and 1650 cm^{-1}, which is explained by the fact that the TFAA is bonded by the H bond to the benzoyl, and not to the trifluoro-acetyl group.

When excess TFAA is added the ylide gradually decomposes to give salt (VI). An analogous cleavage of the CF_3CO group occurs when the ylide is treated with excess aqueous HBF_4 solution.

Such decomposition is probably explained by a weakening of the bonds at the central C atom, where three strong electron-acceptor groups are found. In one case the nucleophile, cleaving the CF_3CO group, is CF_3COO^-, and in the other case it is water. It is interesting that the phosphorus analogs of (IV) are not cleaved under the same conditions. This differ-ence is possibly related to the fact that only the keto form reacts, which in the case of the phosphonium salt should be substantially less. For example, acetylbenzoylmethyltri-phenylphosphonium chloride is 100% enolized [3], while the corresponding As salt, based on our data, contains the keto form along with the enol.

The decomposition of the (IV) ylides by HCl gas, with cleavage of the As—C bond and the formation of triphenylarsine oxide and the acyltrifluoroacetylmethane, proved unexpected.

$$(IV) \xrightarrow{HCl} \overset{\overset{\displaystyle \ominus Cl \quad H \oplus}{\diagdown \quad \diagup}}{Ph_3As^+\!\!-\!\!\underset{\diagdown COR}{\overset{\diagup H}{C}\!\!-\!\!COCF_3}} \quad Cl^- \longrightarrow \quad \begin{array}{c} [Ph_3AsCl_2] + CF_3CCH_2CR \\ \;\;\downarrow H_2O \qquad\quad \overset{\|}{O}\;\;\;\;\; \overset{\|}{O} \\ Ph_3AsO \end{array}$$

Probably, the nucleophile in the given case is the chloride ion, which is more inclined to attack the As, and not the C atom. The phosphonium analog of (IV) does not enter into this reaction, which can be explained by the greater energy of the P—C bond and smaller amount of the keto form.

<div align="center">EXPERIMENTAL</div>

All of the experiments were run in absolute solvents. The IR spectra were taken on a UR-20 instrument in CH_2Cl_2 solution, and the PMR spectra were taken on a Varian T-60 instrument in $CDCl_3$ solution. The separation of the products using preparative TLC was run on Al_2O_3 (activity II, Brockmann) in the system 3:2 benzene—acetone. The reaction course was checked via IR spectroscopy.

Reaction of Triphenylarsinoacetylmethylene (Ia) with TFA. To a solution of 1.3 g (3.6 mmoles) of ylide (Ia) in 10 ml of dichloroethane (DCE) was added 0.5 ml (3.6 mmoles) of TFA in 2 ml of DCE at —20°C. After 15 min, based on the IR spectra, the solution contained only salt (IIa). The reaction mixture was kept for 5 h at 20°C, the solvent was removed in vacuo, and the residual oil (1.91 g) was rubbed in hexane and then treated with ether. The ether solution was separated from the oil (residue (I)) and let stand for 15 h. The crystals of complex (V) (0.22 g) that deposited from the solution were filtered and washed with ether. Infrared spectrum (ν, cm^{-1}): 1720 ($C=O$), 1780 ($C=O$ of $CF_3CO_2^-$...$HOOCCF_3$ complex), mp 81.5-82.5°C. After distilling off the solvent from the ether filtrate the residual oil was treated with hexane and ether. We isolated 0.1 g of ylide (IVa). The residue after removing the solvents from the filtrate were combined with residue (I) and separated by preparative TLC. We isolated 0.25 g of ylide (IVa) and 0.67 g of (VIa).* The total yield of isolated (IVa) was 0.35 g (21.5%), mp 140-141°C. Found: C 60.35; H 4.12%. $C_{23}H_{18}AsF_3O_2$. Calculated: C 60.27; H 3.96%. Infrared spectrum (ν, cm^{-1}): 1565 ($C=O$ of CH_3CO group), 1620 ($C=O$ of

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*The isolation of salt (VIa), and not of the corresponding ylide, after separating the prod-ucts on Al_2O_3 is explained by the fact that ylide (Ia) and CF_3COOH are not separated under the conditions of isolating ylide (IVa).

CF_3CO group). PMR spectrum (δ, ppm): 2.4 s (3H), 7.5 m (15 H). The total yield of salt (VIa) was 0.85 g (49%). Infrared spectrum (ν, cm^{-1}): 1720 ($C=O$ of $COCH_3$ group), 1690 ($C=O$ of $CF_3CO_2^-$ anion). PMR spectrum (δ, ppm): 2.5 s (3H), 6.2 s (2H), 7.5 m (15 H).

Reaction of Ylide (Ib) with TFA. The reaction of 2.8 mmoles of ylide (Ib) and 3 mmoles of TFA proceeds the same as the preceding. To effect complete rearrangement the reaction mixture was refluxed for 3 h in DCE. After working up the reaction mixture like in the preceding experiment we isolated 0.66 g (45%) of ylide (IVb), mp 149-150°C (benzene—hexane). Found: C 65.21; H 3.77; As 14.32%. $C_{28}H_{20}AsF_3O_2$. Calculated: C 64.63; H 3.87; As 14.39%. Infrared spectrum (ν, cm^{-1}): 1565 ($C=O$ of PhCO group), 1620 ($C=O$ of CF_3CO group). After separation on Al_2O_3 we isolated 0.3 g (25%) of ylide (Ib).

Reaction of Ylide (Ia) with TFAA. To a solution of 0.3 g (0.083 mmole) of ylide (Ia) in 4 ml of CH_2Cl_2 was added 0.095 g (0.083 mmole) of CF_3COOH. Based on the IR spectral data, the formation of (VIa) is practically instantaneous (ν, cm^{-1}): 1690 ($C=O$ of $CF_3CO_2^-$ anion), 1720 ($C=O$ of CH_3CO group). Another 0.1 g (0.088 mmole) of the acid was added to the reaction mixture. Infrared spectrum (ν, cm^{-1}): 1720 ($C=O$ of $COCH_3$ group), 1750 and 1790 ($C=O$ of $CF_3CO_2^-$...$HOOCCF_3$ complex). After removal of the solvent the residual crystals were washed with hexane and reprecipitated from CH_2Cl_2 solution with hexane. The weight of complex (Va) was 0.37 g (76%), mp 79-80°C. Found: C 51.07; H 3.59%. $C_{25}H_{21}AsF_6H_5$. Calculated: C 50.86; H 3.58%. PMR spectrum (δ, ppm): 2.40 s (3H), 5.07 s (2H), 7.6 m (16H).

After adding ylide (Ia) to the (Va) complex in a 1:1 ratio only the conjugated acid of the starting ylide (VIa) is present in the reaction mixture. A similar complex could not be isolated for ylide (Ib).

Reaction of Ylide (IVb) with TFAA. To a solution of 0.2 g (0.38 mmole) of ylide (IVb) in 2 ml of CH_2Cl_2 was added 0.044 g (0.38 mmole) of TFAA. In the IR spectrum the $\nu_{C=O}$ of the COPh group is shifted to 1530 cm^{-1}, while the $\nu_{C=O}$ of the $COCF_3$ group is shifted to 1660 cm^{-1}. Another 0.09 g of the acid was added. After 20 min the solvent was removed in vacuo and the residue was separated on Al_2O_3. We isolated 0.09 g (45%) of ylide (IVb) and 0.08 g (39%) of salt (IVb). The reaction of (IVa) with TFAA proceeds in a similar manner.

Reaction of Ylide (IVb) with HBF$_4$. To a solution of 0.2 g (0.38 mmole) of ylide (IVb) in CH_2Cl_2 was added 0.2 g of 45% HBF$_4$ solution. After 0.5 h the organic layer was separated from the water and the solvent was vacuum-distilled. The residue (0.21 g) was separated by preparative TLC. We isolated 0.01 g (5%) of ylide (IVb) and 0.13 g (81%) of ylide (Ib). Mp of (IVb) 147-148°, and mp of (Ib) 168°C, cf. [5].

Decomposition of Ylide (IVb) by HCl Gas. An HCl stream was passed through a solution of 0.6 g (1.15 mmoles) of ylide (IVb) in 5 ml of CH_2Cl_2 until the absorption band at 1565 cm^{-1} disappeared in the IR spectrum. The solvent was vacuum-distilled, the residue was treated with ether, and the precipitate of triphenylarsine oxide was filtered. Weight 0.37 g (100%). After distilling off the solvent from the filtrate we obtained 0.21 g of a residue that was recrystallized from pentane to give 0.1 g (40%) of benzoyltrifluoroacetone, mp 38-38.5°C (cf. [4]). Its IR spectrum was identical with that of an authentic sample. The reaction of HCl gas with ylide (IVa) proceeds in a similar manner.

CONCLUSIONS

1. Ambident arsenic β-ketoylides are acylated by trifluoroacetic anhydride at the O atom of the carbonyl group to give diacyltriphenylarsinomethylenes.

2. In contrast to their phosphorus analogs, the diacyltriphenylarsinomethylenes are cleaved by strong acids with rupture of either the CF_3CO-C bond or the $As-C$ bond.

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