Ketenimine Chemistry. Part 1. The Reaction of Triaryl Ketenimines with Arenesulphenyl Chlorides

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Benzenesulphenyl chloride reacts with diphenyl-*N*-*p*-tolylketenimine in diethyl ether solution to give *N*-(1-chloro-2,2-diphenyl-2-phenylthioethylidene)-*p*-toluidine (IV), *via* the attack of electrophilic sulphur on the terminal carbon of the ketenimine.

HYDROGEN SULPHIDE and thiols are known to add nucleophilically to the central atom of the ketenimines (I) to yield thioamides (II) and thioimidates (III), respectively.[1] We now report an investigation of the

$$Ar_2CH{\cdot}CS{\cdot}NHR \xleftarrow{H_2S} \underset{(I)}{Ar_2C{=}C{=}NR} \xrightarrow{R'SH} Ar_2CH{\cdot}C(SR){=}NR$$
(II) (III)

reaction of electrophilic divalent sulphur, in the form of benzenesulphenyl chloride, with triaryl ketenimines.

Diphenyl-*N*-*p*-tolylketenimine † (Ia; Ar = Ph, R = *p*-$CH_3C_6H_4$) was chosen as the main substrate on account of its relative ease of preparation. When mixed in diethyl ether solution at 20 °C in equimolar proportions, the ketenimine (Ia) and benzenesulphenyl chloride deposited crystals of the adduct (IV) in good yield after 6 days; use of an excess of the sulphenyl chloride resulted in an intractable tar.

$$\underset{(Ia)}{Ph_2C{=}C{=}N{\cdot}Tol\text{-}p} + PhSCl \xrightarrow{Et_2O} Ph_2C(SPh){\cdot}CCl{=}N{\cdot}Tol\text{-}p$$
(IV)

The i.r. spectrum of (IV) exhibited a strong absorption at 1 670 cm^{-1}, in agreement both with the literature value for imidoyl chlorides,[2] and with the chlorine adduct of the ketenimine (Ia), $PhCCl{\cdot}CCl{=}N{\cdot}Tol\text{-}p$.[3] Addition of sulphur to the central carbon atom of (Ia) would lead to the thioimidate, $Ph_2CCl{\cdot}C(SPh){=}N{\cdot}Tol\text{-}p$; however, as thioimidates absorb in the i.r. region at *ca.* 1 600 cm^{-1} [*viz.* 1 611 cm^{-1} for $PhC(SMe){=}NPh$,[4] and 1 598 cm^{-1} for $PhC(SPh){=}NPh$ [5]], the adduct (IV) clearly has the imidoyl chloride structure indicated.

Hydrolysis of the imidoyl chloride (IV) did not occur readily but was best achieved under acid conditions in aqueous ethanol to afford the amide (V); the imidate (VI) was obtained using sodium ethoxide in ethanol.

$$Ph_2C(SPh){\cdot}CO{\cdot}NH{\cdot}Tol\text{-}p \xleftarrow{H^+,\,H_2O} (IV) \xrightarrow{EtONa} Ph_2C(SPh){\cdot}C(OEt){=}N{\cdot}Tol\text{-}p$$
(V) (VI)

† Although the IUPAC approved name for such compounds would be *N*-diphenylvinylidene-*p*-tolylamines, for convenience, the ketenimine nomenclature has been retained.

Diphenyl(phenylthio)acetic acid was not obtained on attempted hydrolysis of the amide (V); forcing conditions led to cleavage of the phenylthio moiety resulting in the formation of diphenyl disulphide and, rather than the *p*-toluidide of benzilic acid, a compound shown by its mass spectrum to have double the molecular weight of the latter.

The reaction of benzilic acid and thiophenol is reported to afford diphenyl(phenylthio)acetic acid [6] and hence the synthesis of the amide (V) was attempted by similar treatment of the *p*-toluidide of benzilic acid. However, the literature route to this compound (V),[7] *viz.*, treating benzilic acid first with thionyl chloride then with *p*-toluidine followed by hydrolysis in aqueous acetone gave, instead, the *p*-toluidide of diphenyl(*p*-toluidino)-acetic acid (VII) (Scheme); prior protection of the α-hydroxy group enabled (V) to be synthesised, albeit in low yield.

$$Ph_2C(OH)CO_2H \xrightarrow{i} Ph_2CCl{\cdot}COCl \xrightarrow{ii} Ph_2CR{\cdot}COR \quad (VII)$$
$$\downarrow AcCl$$
$$Ph_2COAc{\cdot}CO_2H \xrightarrow[ii]{i} Ph_2C(OH)COR \xrightarrow{iii} (V)$$

SCHEME (R = *p*-MeC_6H_4NH)
Reagents: i, $SOCl_2$; ii, RH; iii, PhSH

The reaction of 2-nitro-, 4-nitro-, and 2,4-dinitrobenzenesulphenyl chlorides with the ketenimine (Ia) and of benzenesulphenyl chloride with the ketenimines (I; Ar = Ph, R = Ph or *p*-ClC_6H_4) afforded 1 : 1 adducts which defied isolation in an analytically pure state.

Electrophilic sulphur has thus been shown to attack the terminal carbon of the triarylketenimine (Ia) in contrast to nucleophilic sulphur which reacts at the central carbon; since this work was completed, Russian workers have reported briefly that benzenesulphenyl chloride adds to $(CF_3)_2C{=}C{=}NPh$ in the same orientation as it does to the ketenimine (Ia); [8] the i.r. absorption of the adduct is again at 1 670 cm^{-1}.

EXPERIMENTAL

N.m.r. spectra were determined with a Varian HA 100 machine (100 MHz) and a Perkin-Elmer R32 machine (90 MHz), i.r. spectra with a Perkin-Elmer 197 machine, and mass spectra with either an AEI MS 902 or an MS 45 machine.

All reactions were monitored by t.l.c., and those of the ketenimines also by observing the i.r. absorption at *ca.* 2 000 cm^{-1}.

N-p-Tolyldiphenylacetamide was prepared according to the method of Stevens and French,[7] and benzenesulphenyl chloride by the method of Lecher.[9]

Diphenyl-N-p-*tolylketenimine* (Ia).—The following procedure was modified from that given by Teichmann and Am.[10] *N-p*-Tolyldiphenylacetamide (5 g, 17 mmol), triphenylphosphine (5.66 g, 22 mmol), redistilled triethylamine (3.36 g, 33 mmol), and dry carbon tetrachloride (2.56 g, 17 mmol) were refluxed in absolute chloroform for 2 h. The solvent was removed under reduced pressure and the residue extracted (4 × 20-ml) with light petroleum (b.p. 30—40 °C) to give diphenyl-*N-p*-tolylketenimine (3.90 g, 81%), m.p. 76—78 °C (lit.,[7] 81—83 °C).

Reaction of the Ketenimine (Ia) with Benzenesulphenyl Chloride.—The ketenimine (Ia) (2 g, 7.1 mmol) was added to a solution of freshly prepared benzenesulphenyl chloride (1.02 g, 7.1 mmol) in dry diethyl ether (25 ml). After 6 d at 20 °C large white crystals had formed and were filtered off and recrystallised from light petroleum (b.p. 30—40 °C) to give *N*-(1-chloro-2,2-diphenyl-2-phenylthioethylidene)-*p*-toluidine (IV) (1.28 g, 42%), m.p. 106—108 °C (decomp.), *m/e* 427, 429 (M^+), and 391 (M − HCl); $\nu_{max.}$ 1 670 cm^{-1} (CCl=N); δ (CCl_4) 2.26 (3 H, s, Me), and 6.4—7.6 (19 H, complex, ArH) (Found: C, 75.5; H, 4.9; Cl, 7.9; N, 3.4; S, 7.6. $C_{27}H_{22}ClNS$ requires C, 76.0; H, 4.9; Cl, 8.3; N, 3.3; S, 7.5%).

Similar reaction of the following pairs of compounds yielded 1 : 1 adducts of similar spectral (i.r., n.m.r., and mass spec.) characteristics to those of (IV), but they could not be isolated in an analytically pure state without decomposition: diphenyl-*N-p*-chlorophenylketenimine and benzenesulphenyl chloride; *N*-biphenyl-2-yl(diphenyl)-ketenimine and benzenesulphenyl chloride; compound (Ia) and 2-nitrobenzenesulphenyl chloride; compound (Ia) and 2,4-dinitrobenzenesulphenyl chloride.

Hydrolysis of the p-*Toluidine Compound* (IV).—Compound (IV) (0.5 g, 1.2 mmol) was added to a mixture of 4M-hydrochloric acid (8 ml) and ethanol (4 ml), and the solution refluxed for 6 h. The solvent was removed under reduced pressure to give a pink syrupy residue which was dried in a vacuum desiccator and recrystallised [light petroleum (b.p. 60—80 °C)] to give white crystals of 2-phenylthio-*N-p*-tolyl(diphenyl)acetamide (V) (0.19 g, 42%), m.p. 109—111 °C, *m/e* 409 (M^+), 300 (M − PhS)$^+$, and 275 ($Ph_2\overset{+}{C}SPh$); $\nu_{max.}$ 3 325 (NH) and 1 670 cm^{-1} (C=O); δ (CCl_4) 2.26 (3 H, s, Me), 6.9—7.5 (19 H, complex, ArH) and 8.87 (1 H, s br, NH) (Found: C, 78.9; H, 5.5; N, 3.2; S, 7.9. $C_{27}H_{23}NOS$ requires C, 79.2; H, 5.6; N, 3.4; S, 7.8%).

Reaction of the p-*Toluidine Compound* (IV) *with Sodium Ethoxide.*—A saturated carbon tetrachloride solution of compound (IV) (0.5 g, 1.2 mmol) was added to a solution of sodium (0.1 g) in absolute ethanol (10 ml) and the mixture stirred for 2.5 h at 20 °C. The precipitate was filtered, dried, and dissolved in ethanol to remove sodium chloride, and then recrystallised from the same solvent to give *N*-(1-ethoxy-2,2-diphenyl-2-phenylthioethylidene)-*p*-toluidine (VI) (0.23 g, 44%), m.p. 166—167 °C, *m/e* 437 (M^+), 427 (M − PhSH)$^+$; $\nu_{max.}$ 1 660 cm^{-1} (C·OEt=N); δ (CCl_4) 1.86 (3 H, t, CH_2CH_3), 2.19 (3 H, s, $ArCH_3$), 3.63 (2 H, q, CH_2-CH_3), and 6.2—7.5 (19 H, complex, ArH) (Found: C, 78.7; H, 6.2; N, 3.3; S, 7.3. $C_{29}H_{27}NOS$ requires C, 79.6; H, 6.2; N, 3.2; S, 7.3%).

Hydrolysis of the Acetamide (V).—Compound (V) (1 g, 2.4 mmol) and 70% sulphuric acid were refluxed for 2.5 h. Water was cautiously added and the white suspension filtered and recrystallised from aqueous ethanol to yield a white solid (0.14 g), m.p. 270—272 °C, *m/e* 632 and 218 (Ph_2S_2) (Found: C, 83.2; H, 5.7; N, 4.3; S, 1.0%).

2-p-*Toluidino*-N-p-*tolyl*-2,2-*diphenylacetamide* (VII).—Benzilic acid (2 g, 8.8 mmol) and thionyl chloride (1 ml, 18 mmol) was refluxed for 2 h, and then the excess of thionyl chloride removed under reduced pressure. The residue was dissolved in diethyl ether and added to an ethereal solution of *p*-toluidine (1.03 g, 9.6 mmol) and pyridine (0.8 ml, 9.7 mmol). The mixture was allowed to stand overnight, the pyridine hydrochloride filtered off, and the solvent removed under reduced pressure to yield a solid (1.08 g), m.p. 100—102 °C; a solution of the solid (0.5 g) in ethanol (10 ml) was treated with 2N-sodium hydroxide (5 ml) and heated to 60 °C for 4 h. On cooling, the residue was collected and found to be 2-*p*-toluidino-*N-p*-tolyl-2,2-diphenylacetamide (VII) (0.30 g, 8%), m.p. 157—159 °C, *m/e* 406 (M^+) and 272 ($Ph_2\overset{+}{C}NHTol$-*p*); $\nu_{max.}$ 3 245 and 3 400 (NH), and 1 660 cm^{-1} (C=O); δ ($CDCl_3$) 2.08 (3 H, s, $ArCH_3$), 2.22 (3 H, s, $ArCH_3$), 5.00 (1 H, s, NH), 6.40 (2 H, d, ArH), 6.77 (2 H, d, ArH), 7.01 (2 H, d, ArH), 7.1—7.6 (12 H, complex, ArH) and 8.74 (1 H, s, CO·NH) (Found: C, 82.5; H, 6.3; N, 6.7. $C_{28}H_{26}N_2O$ requires C, 82.8; H, 6.4; N, 6.9%).

Synthesis of the Acetamide (V).—Benzilic acid (2 g, 8.8 mmol) and acetyl chloride (2.75 ml, 38 mmol) were warmed on a water-bath until the mixture became clear; the excess of acetyl chloride was distilled off, thionyl chloride (1.05 ml, 18 mmol) was added to the residue, and the mixture refluxed for 4 h. The excess of thionyl chloride was removed by distillation and the residue dissolved in diethyl ether and added to a solution of *p*-toluidine (1.03 g, 9.6 mmol) and pyridine (0.78 ml, 9.7 mmol) in diethyl ether (5 ml). The mixture was allowed to stand overnight, the precipitate collected and dissolved in chloroform (15 ml) to which thiophenol (0.6 g, 5.4 mmol) was then added. The solution was refluxed under nitrogen for 7 h, and then cooled to afford white crystals, which were washed with chloroform and found to be identical (i.r., m.p., and mixed m.p.) with a sample of the acetamide (V) prepared by hydrolysis of compound (IV) as above.

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