Cycloaddition of *N*-Arylketenimines to Thiobenzophenones. Formation of 4*H*-3,1-Benzothiazine and 2-Iminothietan Derivatives

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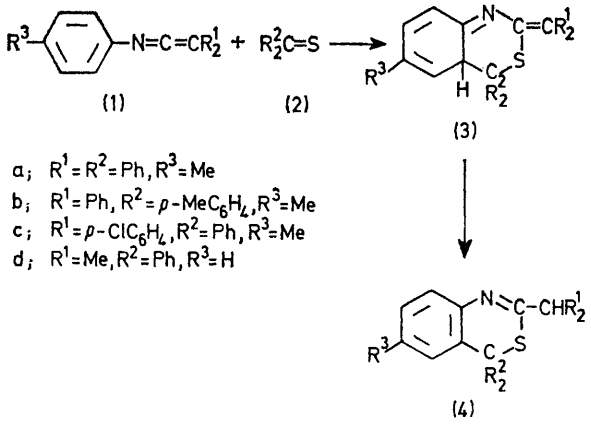
Summary *N*-*p*-Tolyl and *N*-phenylketenimines (**1**) react with thiobenzophenones (**2**) by a formal 4 + 2 cycloaddition to give substituted 4*H*-3,1-benzothiazines (**4**) whose structures have been confirmed by an *X*-ray diffraction study, whereas the *N*-mesitylketenimine (**5**) leads to the 2-iminothietan (**6**) by a 2 + 2 cycloaddition.

KETENIMINES have been shown to take part as 2π-electron components in thermally and photochemically induced cycloaddition reactions with various multiple bond systems and give 1 : 1 adducts either utilising the cumulene C=C or the C–N linkage.[1] We now report that *N*-arylketenimines (**1**) prefer to react with thiobenzophenones (**2**) as a 4π system, giving as final products the 4*H*-3,1-benzothiazines (**4**) by cyclisation across the C=N bond and the C=C of the *N*-aryl ring. A formally similar cycloaddition has been reported to occur between ketenimines and ynamines.[2]



Equimolar mixtures of the ketenimines[1] (**1**) (*ca.* 0·1 M) and thioketones[3] (**2**) in cyclohexane or tetrahydrofuran (THF) (3—5 days, 30 °C, sealed phial *in vacuo* or under CO_2) gave, by filtration or on chromatographic work-up (silica, dichloromethane–light petroleum 1 : 3), the corresponding 1 : 1 adducts (**4**) in 80—85% yield: (**4a**), m.p. 234—239 °C decomp. [from dimethylformamide (DMF)], *m/e* 481 (M^+), 314 ($M - Ph_2CH$), and 167 ($M - C_{21}H_{16}NS$); (**4b**), m.p. 149—154 °C decomp. (from dichloromethane–light petroleum), *m/e* 509 (M^+), 342 [$M - (MeC_6H_4)_2CH$], and 167 ($M - C_{23}H_{20}NS$); (**4c**), m.p. 195—198 °C decomp. (from benzene–light petroleum), *m/e* 549 (M^+), 314 [$M - (ClC_6H_4)_2CH$], and 165 [$M - (C_{21}H_{17}NS - Cl_2)$]; (**4d**), m.p. 143—146 °C decomp. (from dichloromethane–light petroleum), *m/e* 343 (M^+) and 300 ($M - Me_2CH$); in all cases analytical data were satisfactory. The ^1H n.m.r. spectra ($CDCl_3$, Me_4Si) of (**4a—c**) exhibited besides aromatic and methyl resonances, a broad methine signal at δ 5·1 ($CHPh_2$) and the spectrum of (**4d**) showed a septet centred at δ 2·7 ($CHMe_2$) and a doublet centred at δ 1·05 (CMe_2), J 6·8 Hz.

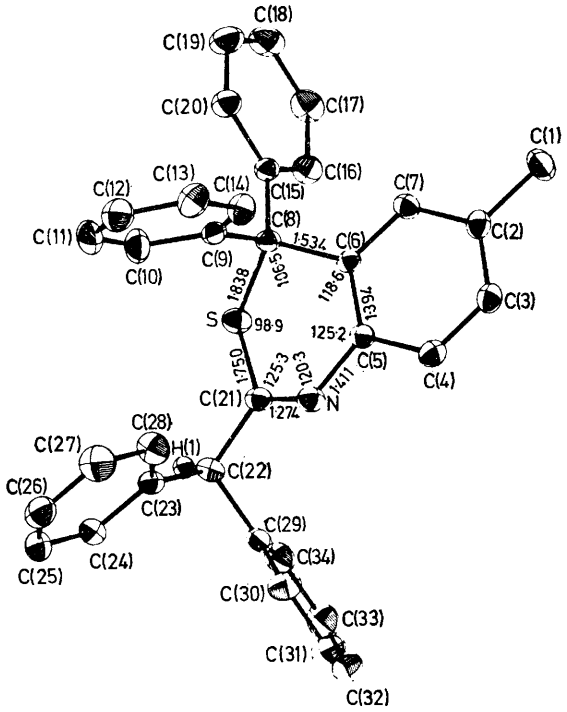


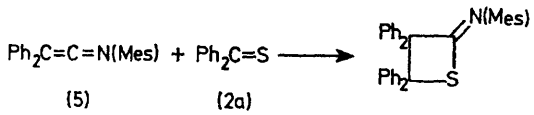
FIGURE. Structure of 2-diphenylmethyl-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine (**4a**) (average e.s.d.'s for bond lengths and angles are 0·005 Å and 0·4°).

Conclusive evidence for the 4*H*-3,1-benzothiazine structure was provided by a single-crystal *X*-ray study of (**4a**). The structure was solved by direct methods using MULTAN[4] and refined by least-squares to $R = 0{\cdot}038$. The Figure shows a perspective view of the molecule with selected bond lengths (Å) and angles (°). The heterocyclic ring is non-planar, the major deviations from the least-squares plane through the C(2)–C(7) phenyl ring being those of sulphur (−1·05 Å) and C(21) (−0·62 Å) whereas nitrogen (−0·12 Å) and C(8) (0·14 Å) lie almost in the plane.

The cycloaddition between (**1**) and (**2**) provides a simple route (good yields, mild conditions, easily available starting materials) to substituted 3,1-benzothiazines which are not readily accessible by conventional methods.[5] The reaction can be envisaged as a formal 4 + 2 addition of the ketenimine to the thione to give an initial adduct (**3**), whose aromatisation by 1,5 H shift to the ethylenic carbon would give the observed product (**4**). The mechanism of this reaction,

however, remains to be explored, particularly with respect to the step(s) which may precede the formation of (**3**), in order to identify its possible precursor, *i.e.* a stabilised 1,4-dipole similar to that proposed for the cycloaddition with ynamines,[2] and/or other transient species.

The observed cyclisation to a six-membered heterocycle appears to be a particularly favourable reaction pathway for the ketenimine–thioketone cycloaddition. Four-membered 1 : 1 adducts which could derive from a concerted supra–antara[6] or a stepwise 2 + 2 cycloaddition were not isolated in the cases described above. However, a 2 + 2 cycloadduct was obtained from diphenyl-*N*-mesitylketenimine (**5**) and (**2a**) which after 40 days at 30 °C in THF gave the 2-iminothietan (**6**) (30%), m.p. 156—159 °C. The structure of (**6**) was assigned on the basis of spectral data: i.r. (CCl_4), ν_{max} 1655 cm^{-1} (C=N);[7] ^1H n.m.r. δ (CCl_4, Me_4Si), 2·05 (6H, s, 2Me), 2·2 (3H, s, 1 Me), and 6·6—7·4 (22H, m, ArH); the ^{13}C n.m.r. spectrum ($CDCl_3$, Me_4Si) exhibited two quaternary carbon resonances at δ 66·9 and 83·4 p.p.m. corresponding to the non-equivalent carbon atoms of the thietan ring. The mass spectrum showed, in addition to M^+ at *m/e* 509, the tetraphenylethylene‡ (*m/e* 332) and ketenimine (**5**) (*m/e* 311) fragments arising from the two possible ways of fragmentation of the molecule into halves. By contrast, bis(methylsulphonyl)-*N*-methylketenimine[1] which also could behave only as a 2π-electron component, appeared quite unreactive toward (**2a**) and was recovered almost entirely unaltered (80%) under the above conditions.



(5) (2a) (6)

Mes = mesityl

In conclusion, the variable regiochemistry of the ketenimine–thioketone cycloaddition offers some points of interest on both synthetic and mechanistic grounds.

(*Received*, 6*th October* 1976; *Com.* 1133.)

† Prepared by dehydration (C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, 1964, **29**, 34) of *N*-mesityldiphenylacetamide and purified by chromatography (silica, dichloromethane–light petroleum 1 : 3); obtained as a yellow oil, and characterized by i.r., n.m.r., and mass spectroscopy.

‡ Metastable ions analysis proved that this fragment was derived directly from M^+.

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