Chemical Property of 1-Dialkylamino-2-phenylthioethylene

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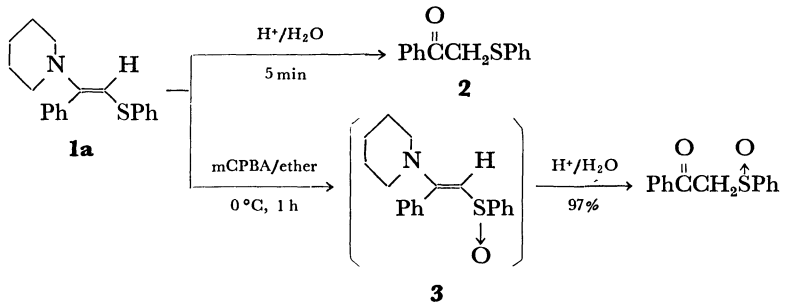
Synopsis. The olefins which are vicinally substituted by amino and phenylthio groups showed the reactivity as an enamine in the reactions with heterocumulenes and in cycloadditions with a 1,3-dipole and a 2-propenimine, giving a pyrazole derivative and a pyridine derivative, respectively.

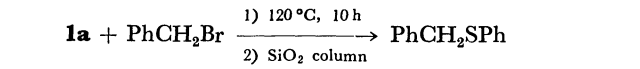
Hetero-atom substituted olefins such as enamines, vinyl sulfides, and nitrogen and sulfur analogs of ketene acetals are versatile synthons in organic synthesis. However, utility of vicinally dihetero-atom substituted olefins has not been known so well.[1] Recently we developed a new synthetic method for the ethylenes which are vicinally substituted by dialkylamino and phenylthio (or methylthio) groups.[2] To clarify their chemical properties, we report here several reactions of 1-dialkylamino-2-phenylthioethylenes **1**.

The olefins **1** are highly sensitive to hydrolysis and, for example, β-phenylthio-α-piperidinostyrene (**1a**) was easily converted to α-phenylthioketone **2** under acidic conditions.



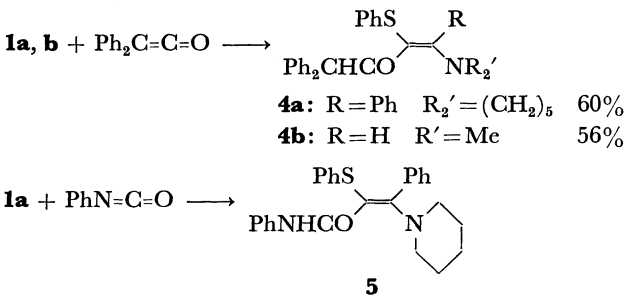
Oxidation of the olefin **1a** with *m*-chloroperbenzoic acid (mCPBA) gave β-phenylsulfinyl-α-piperidinostyrene (**3**) in 56% yield by NMR. It was difficult to isolate the sulfoxide **3** which was hydrolyzed to afford α-phenylsulfinylacetophenone.

Reaction of the olefins **1** with methyl iodide or benzyl bromide afforded salt-like materials which could be neither isolated nor identified. As a hydrolyzed product, benzyl phenyl sulfide was isolated by chromatographic treatment of the reaction mixture of **1a**

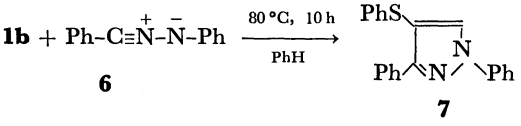


with benzyl bromide. The result implied a considerable extent of nucleophilic attack from the sulfur atom to the bromide. On the contrary, the reaction of **1a** with benzoyl chloride gave *N*-benzoylpiperidine in 34% yield as a hydrolyzed product, and 1-dimethylamino-2-phenylthioethylene (**1b**) gave *N*,*N*-dimethylbenzamide in 60% yield. Thus the reaction on the nitrogen atom is predominant in these reactions. However, no C–C bond forming reactions were observed for the reactions with the alkyl and acyl halides.

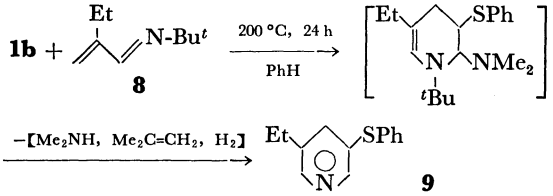
Diphenylketene is a highly reactive dipolarophile and smoothly reacted with the olefin **1a** at 20 °C to give the butenone derivative **4a** and with **1b** to give the butenone **4b**. Similarly, **1a** reacted with phenyl isocyanate to afford α-phenylthio-β-piperidinocinnamanilide (**5**) in 54% yield. These products are considered to be formed *via* 1:1 cycloadducts which rearrange to the linear 1:1 adducts.[3] Thus formation of the carbonyl compounds **4** and **5** would provide us a preparative method for highly functionalized olefins.



Cycloaddition reactions were also studied. The olefin **1b** reacted with the nitrilimine **6** to give the pyrazole derivative **7** in 40% yield. The formation of **7** is elucidated by elimination of dimethylamine from a 1:1 cycloadduct. As a dienophile the olefins



1 were not so reactive with cyclopentadiene and ethyl sorbate. However, **1b** reacted with a heterodiene, *N*-*t*-butyl-2-ethyl-2-propenimine (**8**), to give 3-ethyl-5-phenylthiopyridine (**9**) in 51% yield when heated at



200 °C for 24 h. The reaction is assumed to proceed *via* cycloaddition followed by elimination of dimethylamine and isobutylene and successive oxidative aromatization.

As these addition products **7** and **9** are suggested to be similar to 1:1 cycloaddition products of phenylthioacetylene with the 1,3-dipole **6** and the diene **8**, respectively, the olefins of type **1** are expected to become a reagent equivalent to arylthioacetylenes[4] in cycloadditions. In conclusion the olefins **1** show chemical property as an enamine rather than a vinyl sulfide but lower reactivity than usual enamines.

Experimental

Materials. Commercially available reagents were used unless otherwise noted. The olefins **1a** and **1b** were prepared by the reported method.[2] Diphenylketene was prepared by dehydrochlorination of diphenylacetyl chloride. The propenimine **8** was obtained by the reaction of *N-t*-butylmethanimine and 1-piperidino-1-butene at 150 °C for 6 h; bp 55—57 °C/4000 Pa; NMR ($CDCl_3$) δ 1.10(3H, t), 1.19(9H, s), 2.4(2H, m), 5.33(1H, broad s), 5.51(1H, m), 7.90(1H, s).

Hydrolysis. To a solution of **1a** (1.26 g, 4.3 mmol) in EtOH (5 ml) was added 12 mol dm^{-3} HCl (2 ml) and allowed to stand for 5 min. Extraction (ether), drying ($CaSO_4$), and concentration gave 725 mg (74%) of α-phenylthioacetophenone (**2**) which was identified with an authentic sample.

Oxidation. To a solution of **1a** (1.48 g, 5.0 mmol) in ether (5 ml) containing 1.06 g (10 mmol) of Na_2CO_3 was added mCPBA (1.08 g, 6.0 mmol) in ether (20 ml) and the mixture was stirred at 0 °C for 1 h. The reaction mixture was worked up as usual to give the crude oil containing the sulfoxide **3** (56% yield by NMR); IR (neat) 1580 (C=C) and 1030 cm^{-1} (S→O); NMR ($CDCl_3$) δ 5.4 (s, =CH). The oil (164 mg) was hydrolyzed in EtOH (5 ml) containing 12 mol dm^{-3} HCl (2 ml) to afford 97% of α-phenylsulfinylacetophenone which was identified with an authentic sample prepared by oxidation of **2**.

Reactions with Halides. A benzene solution (6 ml) of **1a** (1.48 g, 5.0 mmol) and benzyl bromide (0.85 g, 5.0 mmol) was heated at 120 °C for 10 h in a sealed tube. The reaction mixture was chromatographed (SiO_2–hexane) to give benzyl phenyl sulfide (0.35 g, 35%).

A solution of **1a** (5.0 mmol) and benzoyl chloride (703 mg, 5.0 mmol) in ether (10 ml) containing K_2CO_3 (2.0 g) was stirred for 20 h at 20 °C. Chromatographic treatment (SiO_2–benzene) of the filtrate gave 322 mg (34%) of *N*-benzoylpiperidine which was identified with an authentic sample. Similarly, 0.90 g (60%) of *N,N*-dimethylbenzamide was obtained from 1.79 g (10 mmol) of **1b**, the chloride (1.41 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) using DMF as a solvent.

Reactions with Diphenylketene and Phenyl Isocyanate. To a solution of **1** (5.0 mmol) in ether (10 ml) was added the ketene (0.97 g, 5.0 mmol) and the mixture was stirred for 3 h at 20 °C. A crystalline product was obtained by concentration in the case of **1a** and an oily product by column chromatography (SiO_2–EtOH) in the case of **1b**. 1,1,4-Triphenyl-3-phenylthio-4-piperidino-3-buten-2-one (**4a**): yield 1.47 g (60%); mp 163—164 °C; IR (Nujol) 1600 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.4—1.8 (6H, m), 2.9—3.3 (4H, m), 6.20 (1H, s), 6.8—7.5 (20H, m); MS *m/e* 489 (M^+). Found: C, 81.22; H, 6.25; N, 2.83; S, 6.31%. Calcd for $C_{33}H_{31}NOS$: C, 80.95; H, 6.38; N, 2.86; S, 6.53%. 4-Dimethylamino-1,1-diphenyl-3-phenylthio-3-buten-2-one (**4b**): yield 1.17 g (56%); IR (Nujol) 1640 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.10(6H, s), 6.13(1H, s), 6.9—7.3(15H, m), 8.18(1H, s); MS *m/e* 373 (M^+).

A mixture of **1a** (5.0 mmol) and the isocyanate (0.60 g, 5.0 mmol) in ether (10 ml) was stirred for 20 h at 20 °C. Concentration of the mixture gave solid material which was recrystallized from CH_2Cl_2 to give 1.12 g (54%) of β-phenylthio-α-piperidinocinnamanilide (**5**): mp 160 °C; IR (Nujol) 1620 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.4—1.9(6H, m), 3.0—3.5(4H, m), 6.9—7.6 (15H, m), 8.5—8.8(1H, broad s); MS *m/e* 414 (M^+).

*Reaction with N-Phenylbenzonitrilimine (**6**).* A mixture of **1b** (1.79 g, 10 mmol), *N*-anilinobenzimidoyl chloride[5] (2.3 g, 10 mmol) and triethylamine (3.0 g, 30 mmol) in benzene (20 ml) was heated at reflux for 10 h. The reaction mixture was chromatographed (SiO_2–benzene) to give 1.31 g (40%) of 1,3-diphenyl-4-phenylthiopyrazole (**7**): mp 80—82 °C; IR (Nujol) 1600 cm^{-1} (C=C, C=N); NMR ($CDCl_3$) δ 6.8—7.7(13H, m), 7.81(1H, s), 8.0—8.2(2H, m); MS *m/e* 328 (M^+). Found: C, 76.78; H, 4.75; N, 8.52; S, 9.66 %. Calcd for $C_{21}H_{16}N_2S$: C, 76.81; H, 4.91; N, 8.53; S, 9.75%.

*Reaction with the Propenimine **8**.* A mixture of **1b** (1.60 g, 8.9 mmol) and the imine (1.24 g, 8.9 mmol) in benzene (10 ml) was heated at 200 °C for 24 h in a sealed tube. The reaction mixture was extracted ($CHCl_3$), dried (Na_2CO_3), and chromatographed (SiO_2–benzene) to give 3-ethyl-5-phenylthiopyridine (**7**, 51%), whose analytical sample was obtained as a picrate: mp 141.5—142.5 °C (picrate); NMR ($CDCl_3$) δ 7.1—7.4 (5H, m), 7.45(1H, dd), 8.30 (1H, d), 8.37(1H, d); MS *m/e* 215 (M^+). Found: C, 50.71; H, 3.37; N, 12.64; S, 7.13%. Calcd for $C_{19}H_{16}N_4O_7S$ (picrate): C, 51.35; H, 3.63; N, 12.61; S, 7.20%.

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