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SYNTHESES AND NUCLEOPHILIC REACTIONS OF N-ALKYLDIPHENYLSULFILIMINES

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Abstract—N-Alkyldiphenylsulfilimines, $Ph_2S^+N^-R$, were prepared by treating diphenylsulfilimine with alkyl halides in refluxing chloroform. Reactions of N-benzyldiphenylsulfilimine with activated olefins and acetylenes were investigated and found to give products consistent with nucleophilic attack of $^-NCH_2Ph$ followed by S–N bond cleavage with or without hydrogen transfer. In general, the reaction conditions had a pronounced effect on the product distribution.

It has become increasingly apparent that the sulfilimines, which have the generalized structure $R^1R^2S^+N^-R$, are highly useful as intermediates in organic systhesis.[1] A variety of efficient synthetic methods of the sulfilimines have also been developed.[2] In continuation of our previous studies directed toward exploring the synthetic potential of the sulfilimines,[1g-i] we have now prepared a series of N-alkyldiphenylsulfilimines (**3**)[3] and investigated their reactions with activated olefins and acetylenes.

Preparation. N-Benzyldiphenylsulfilimine (**3a**) was first obtained when a solution of equimolar amounts of diphenylsulfilimine[2b,c] (**1**) and benzyl bromide (**2a**) in chloroform was refluxed for 20 hr. However, the yield of **3a** was only 10% and the major products were benzylamine and diphenyl sulfide. This appears to be ascribed to the inherent instability of **3a** to acid (HBr is generated in this reaction). Compound **3a** was found to be prepared in a satisfactory yield by using 2 molar equiv of **1**. Thus, after refluxing a chloroformic solution of 2 molar equiv of **1** and 1 mole equiv of **2a** for 5 hr, the mixture was chromatographed to give **3a** in 77% yield as colorless crystals. In this manner, sulfilimines **3b-d** were obtained as oils from the reaction of **1** with the corresponding primary alkyl bromides (**2b-d**).

$$\underset{\mathbf{1}}{Ph_2S^+N^-H} + \underset{\mathbf{2a\text{-}g}}{RX} \rightarrow \underset{\mathbf{3a\text{-}g}}{Ph_2S^+N\ R} \xrightarrow{\text{conc HCl}} \underset{\mathbf{4a\text{-}g}}{RNH_3Cl^-}$$

a, R = CH_2Ph; **b**, R = n-C_6H_{13}; **c**, R = CH_2CH_2Ph; **d**, R = 1-naphthylmethyl; **e**, R = CHMePh; **f**, R = $CHMeCO_2Et$; **g**, R = $CHEtCO_2Et$

The reaction of **1** with activated secondary alkyl bromides such as 1-phenethyl bromide (**2e**), ethyl 2-bromopropionate (**2f**), and ethyl 2-bromobutylate (**2g**) proceeded without any difficulty to give the corresponding sulfilimines (**3e-g**). However, the reaction with cyclohexyl bromide was very slow and gave a complex mixture consisting of the starting materials, cyclohexylamine, and diphenyl sulfide after prolonged heating.

†High resolution mass measurements were accurate to within 4 mili mass units of the required values.

‡Diphenylsulfoxide was also obtained in 20–30% yields from **3f** and **3g**.

The structures of **3** were confirmed by the spectral data and chemical transformation. All the mass spectra gave the corresponding molecular ions, whose compositions were determined by high resolution mass spectrometry.† The most important primary fragmentation process of N-alkyldiphenylsulfilimines is α-cleavage of the molecular ion. Thus sulfilimines **3a-d** give a common fragment ion *a* at *m/e* 214, and **3e** gives two possible ions *b* and *c* at *m/e* 290 and *m/e* 228 in a ratio of *ca.* 7:1. In the mass spectra of **3f** and **3g**, only loss of ethoxycarbonyl radical from the molecular ion (ions *c* and *d*, respectively) was observed. Another common fragment ion is diphenyl sulfide ion radical *e* (*m/e* 186). In the mass spectra of **3a**, **3c** and **3d**, an ion represented by *f* (*m/e* 200) was observed.

$Ph_2S^+\text{-}N{=}CHR$ $\quad$ Ph_2S^+ (*e*) $\quad$ $Ph_2S^+\text{-}N$ (*f*)

a, R = H;
b, R = Ph;
c, R = Me;
d, R = Et

In the IR spectra, all the compounds showed a strong band in the region 1060–1135 cm^{-1} which is expected for the S–N stretching band of N-alkylsulfilimines.[2h]

Final confirmation of the structures was obtained by S–N bond cleavage of **3** into the hydrochlorides **4** of the corresponding amines and diphenyl sulfide‡ upon refluxing **3** in conc. hydrochloric acid.

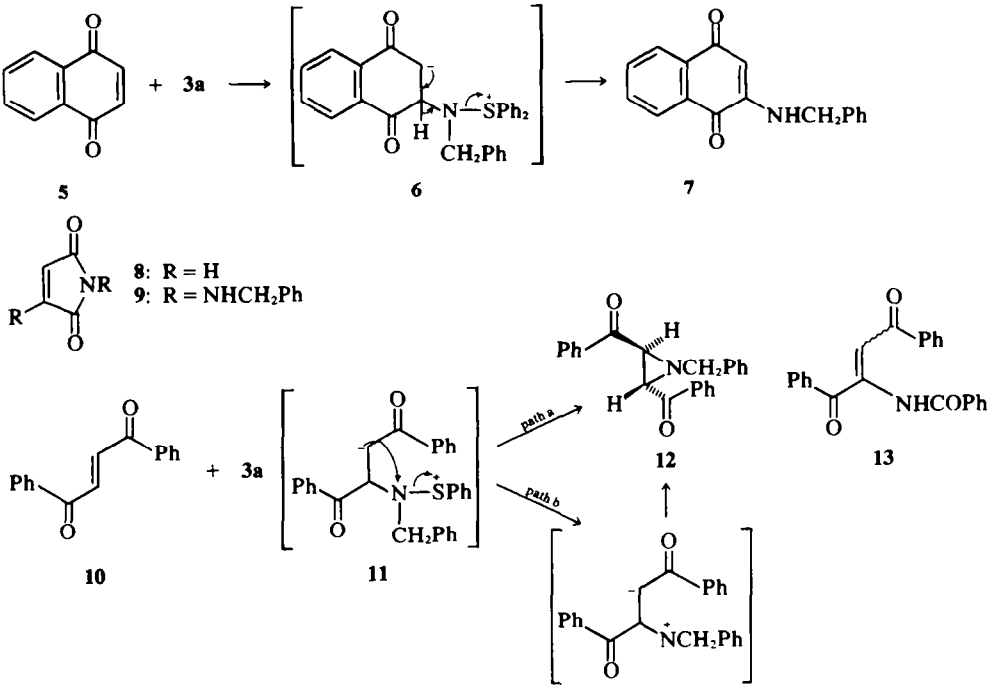
Reactions with activated olefins. As a sulfilimine, N-benzyldiphenylsulfilimine (**3a**) was chosen because it was easy to purify. Reaction of **3a** with 1,4-naphthoquinone (**5**) occurred in methanol, chloroform, or benzene at room temperature to give 2-benzylamino-1,4-naphthoquinone (**7**)[4] in 56, 66, 74% yields, respectively. Similarly, **3a** reacted with N-phenylmaleimide (**8**) in chloroform to give 2-benzylamino-N-phenylmaleimide (**9**) in 79% yield, whose structure follows from its elemental and spectral analysis (Experimental). The formation of **7** and **9** may involve a hydride transfer from carbon to nitrogen in an intermediate like **6**. This behavior of **3a** is analogous to that of diphenylsulfilimine **1**.[1g]

Reaction of **3a** with *trans*-1,2-dibenzoylethylene (**10**) in chloroform was very slow at room temperature. After 1 week (60–70% completion), the reaction gave 1-benzyl-

trans-2,3-dibenzoylaziridine (**12**)[5] and 1-benzylamino-1,2-dibenzoylethylene (**13**)[5] in 27 and 18% yields, respectively. However, it was found that the reaction conditions have a pronounced effect on the proportions of **12** and **13**; the reaction in refluxing chloroform was complete after 5 hr and afforded only the aziridine **12** in 78% yield. The same reaction in refluxing methanol gave a mixture of **12** and **13** in 60 and 22% yields, respectively. Since both **12** and **13** are stable under these reaction conditions, **12** is not a precursor of **13** and *vice versa*; an internal displacement reaction in an intermediate **11** either by a concerted process (path a) or by a stepwise process (path b) may account for the formation of **12**. Although the formation of the aziridine ring appears to be a kinetically favored reaction course as shown in the reaction of **10** with **3a**, this process may become less favorable in the cases of **5** and **8** due to the ring strain resulting from the 6–3 or 5–3 ring system. Consequently, the exclusive formation of **7** and **9** would be anticipated from **5** and **8**, respectively.

In sharp contrast to the reaction of **3a** with **14** in methanol, the same reaction in an aprotic solvent such as chloroform or benzene produced a crystalline product **22** (53% yield) and diphenyl sulfide (55% yield), along with a small amount of an unidentified product. The structure of the major product **22** was established by combination of the spectral and chemical evidence. The elemental analysis and mass spectrometry confirmed the molecular formula $C_{28}H_{24}N_2$. The IR spectrum showed a strong band at 1615 cm^{-1} (C=N) and the NMR spectrum demonstrated the presence of four phenyl groups and four benzylic methylene protons at δ 4·56 (singlet). The mass spectrum showed a fragment peak at *m/e* 194 corresponding to a half of the molecule. The remaining important peaks are *m/e* 297 (M^+-$C_6H_5CH_2$) and 91 ($C_6H_5CH_2^+$). Acid hydrolysis of **22** gave benzil **23**.

A possible mechanistic rationalization for the formation of **22** is based on the premise that the initially formed carbanion **16** undergoes an internal displacement reaction



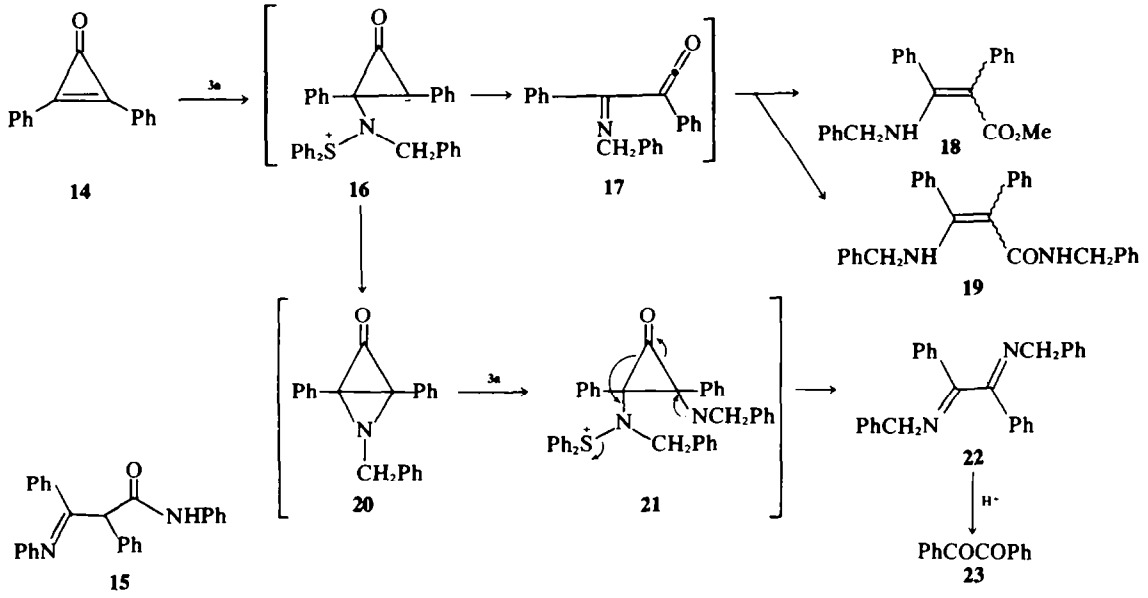
Reaction of **3a** with tetracyanoethylene in refluxing chloroform resulted in the formation of only an intractable mixture, and with benzalacetophenone, and maleic anhydride practically no reaction took place even after refluxing in chloroform for more than 12 hr.

Diphenylcyclopropenone (**14**), considered as a strong electrophile, is known to react with ylides to give a ketene intermediate which undergoes further transformation reactions.[6] For example, Rees and coworkers[1f] have recently reported the formation of **15** as one of products from the reaction between **14** and N-phenyldimethylsulfilimine. We also found that 2 molar equiv of **3a** reacted with 1 mole equiv of **14** in methanol at room temp to give two oily products **18** and **19** in 30 and 35% yields, respectively, in addition to diphenyl sulfide. The structures were deduced from their spectral data (Experimental). The formation of both compounds **18** and **19** can be rationalized in terms of the ketene intermediate **17**.

to give a bicyclic intermediate **20**. This step is then followed by ring opening by nucleophilic attack of another molecule of **3a** to give **21**, which undergoes fragmentation with elimination of carbon monoxide and diphenyl sulfide to **22**. However, the role of the solvent is not clear at present.

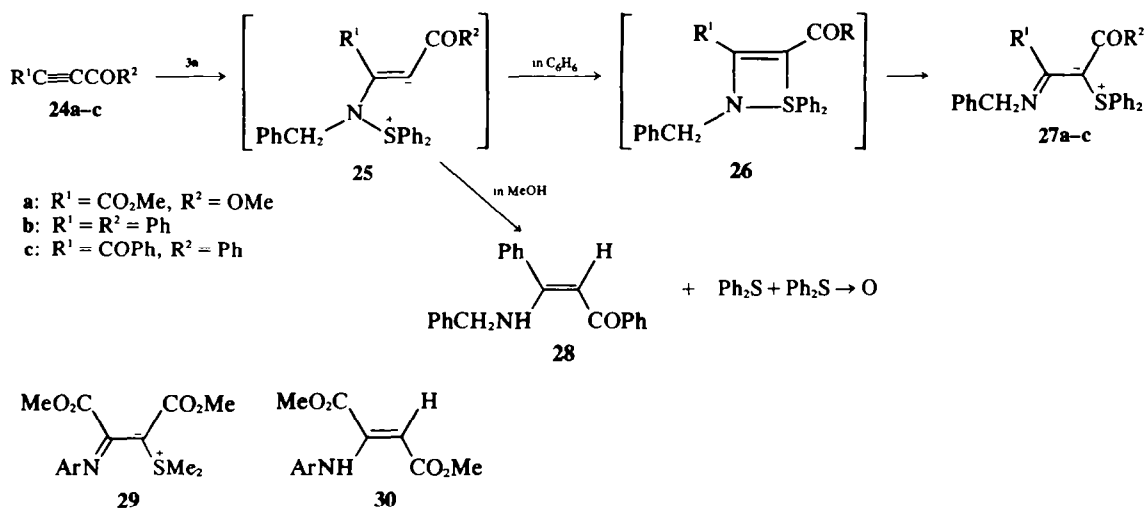
Reaction with activated acetylenes. Sulfilimine (**3a**) reacted slowly with dimethyl acetylenedicarboxylate (**24a**) in chloroform or benzene at room temp. The reaction was complete after 1 day (by TLC). It gave a pale yellow crystalline product **27a**, whose structure was assigned by the IR and mass spectrum. The IR spectrum showed strong bands at 1730 and 1710 cm^{-1}, and the mass spectrum showed the correct molecular weight and a strong peak at *m/e* 328 corresponding to loss of $C_6H_5CH_2N$ from the molecular ion.

Similar treatment of **3a** with benzoylphenylacetylene (**24b**) and dibenzoylacetylene (**24c**) in benzene gave sulfonium ylides **27b** and **27c**, respectively. This reaction



was again found to be solvent dependent. When reaction of **3a** with **24b** was carried out in methanol, **28**, diphenyl sulfide, and diphenylsulfoxide were obtained.

In progress of our work, Hayashi *et al.*[7] reported a similar reaction of N-aryldimethylsulfilimines with **24a** to give a sulfonium ylide **29** and an N-arylaminofumarate **30**, depending upon the solvents used, and proposed the reaction mechanism as shown below. The reaction of diphenylsulfilimine (**3a**) with **24** appears to be less sensitive to moisture than in the case of dimethylsulfilimine.



EXPERIMENTAL

M.ps are uncorrected. NMR spectra were determined with a JEOL-MH-100 and a Hitachi R-20A spectrometer (TMS as internal standard in $CDCl_3$). IR spectra were recorded with a Hitachi EPI-G3 spectrophotometer. UV spectra were recorded with a Shimazu UV-200 spectrophotometer. Low and high resolution mass spectra were obtained with a Hitachi RMU-6D (70 eV) and a JEOL-JMS-01SG instrument (32 or 75 eV) with a direct inlet system, respectively. Preparative TLC was carried out on Alumina PF_{254}.

N-Alkyldiphenylsulfilimines (**3**). A soln of 10 mmole of **1** and 5 mmole of **2** in 15 ml $CHCl_3$ was refluxed until the starting material disappeared (by TLC) (0·5–5 hr). After evaporation of the solvent *in vacuo*, the residual oil was chromatographed on 30 g of alumina (300 mesh). Elution with ether gave a small amount of diphenyl sulfide and compound **3**, and further elution with chloroform gave unreacted **1**. Compounds **3a–g** were prepared by this procedure. Attempts to prepare the hydrochlorides or picrates of the oily compounds **3b–g** were unsuccessful: the S–N bond cleavage took place.

N-Benzyldiphenylsulfilimine (**3a**) was obtained from **1** and **2a** in 77% yield, m.p. 62–64° (from petroleum benzin–benzene) (lit.[2a] m.p. 65·5–66·5°); $\nu_{max}^{CHCl_3}$ 1090 (s), 1060 (s) (S–N) cm^{-1}; NMR δ 7·1–7·6 (15H, m, aromatic protons), 4·10 (2H, s, $N-CH_2Ph$); *m/e* (75 eV) (rel. int.), 291 ($C_{19}H_{17}NS$, M^+, 13), 214 ($C_{13}H_{12}NS$, *a*, 7),

N-n-Hexyldiphenylsulfilimine (**3b**) was obtained from **1** and **2b** in 51% yield as a viscous oil; $\nu_{max}^{liq.film}$ 1095 (s) (S–N) cm^{-1}; NMR δ 7·2–7·7 (10H, m, aromatic protons), 2·88 [2H, t, J = 5·5 Hz, $NCH_2(CH_2)_4CH_3$], 0·95–1·75 (8H, m, $NCH_2(CH_2)_4CH_3$), 0·82 (3H, t, J = 3 Hz, CH_3); *m/e* (32 eV) (rel. int.) 285 ($C_{18}H_{23}NS$, M^+, 31), 214 ($C_{13}H_{12}NS$, *a*, 77), 186 ($C_{12}H_{10}S$, *e*, 100).

N-2-Phenylethyldiphenylsulfilimine (**3c**) was obtained from **1**

and **2c** in 54% yield as a viscous oil, $\nu_{max}^{liq\ film}$ 1095 (s) (S–N) cm^{-1}; NMR δ 7·41 (10H, s, aromatic protons), 7·2 (5H, s, aromatic protons), 3·0–3·2 (2H, m, NCH_2CH_2Ph), 2·7–2·9 (2H, m, NCH_2CH_2Ph); *m/e* (75 eV) (rel. int.) 305 ($C_{20}H_{19}NS$, M^+, 20), 290 ($C_{19}H_{16}NS$, 35), 214 ($C_{13}H_{12}NS$, *a*, 97), 200 ($C_{12}H_{10}NS$, *f*, 28), 186 ($C_{12}H_{10}S$, *e*, 100).

N-(1-*Naphthylmethyl*)*diphenylsulfilimine* (**3d**) was obtained from **1** and **2d** in 74% as a viscous oil; $\nu_{max}^{CHCl_3}$ 1085 (s) (S–N) cm^{-1}; NMR δ 7·2–8·0 (17H, m, aromatic protons), 4·55 (2H, s, NCH_2–); *m/e* (75 eV) (rel. int.) 341 ($C_{23}H_{19}NS$, M^+, 71), 214 ($C_{13}H_{12}NS$, *a*, 52), 200 ($C_{12}H_{10}NS$, *c*, 76), 186 ($C_{12}H_{10}S$, *e*, 100).

N-1-*Phenylethyldiphenylsulfilimine* (**3e**) was obtained from **1** and **2e** in 71% yield as a viscous oil; $\nu_{max}^{liq.film}$ 1090 (s) (S–N) cm $^{-1}$; NMR δ 7·1–7·7 (15H, m, aromatic protons), 4·36 (1H, q, J = 7·0 Hz, $NCHCH_3Ph$), 1·45 (3H, d, J = 7·0 Hz, $NCHCH_3Ph$); *m/e* (75 eV) (rel. int.) 305 ($C_{20}H_{19}NS$, M^+, 11), 290 ($C_{19}H_{16}NS$, *b*, 53), 228 ($C_{14}H_{14}NS$, *c*, 8), 186 ($C_{12}H_{10}S$, *e*, 100).

N-1-*Ethoxycarbonylethyldiphenylsulfilimine* (**3f**) was obtained from **1** and **2f** in 54% yield as an oil; $\nu_{max}^{liq\ film}$ 1730 (s) (C=O), 1120 (s) (S–N) cm $^{-1}$; NMR δ 7·25–7·9 (10H, m, aromatic protons), 3·99 (1H, q, J = 7·0 Hz, $NCHCH_3CO_2Et$), 3·90 (2H, q, J = 7·0 Hz, OCH_2CH_3), 1·4 (3H, d, J = 7·0 Hz, $NCHCH_3CO_2Et$), 1·04 (3H, t, J = 7·0 Hz, OCH_2CH_3); *m/e* (75 eV) (rel. int.) 301 ($C_{17}H_{19}NO_2S$, M^+, 8), 228 ($C_{14}H_{14}NS$, *c*, 38), 186 ($C_{12}H_{10}S$, *e*, 100).

N-1-*Ethoxycarbonylpropyldiphenylsulfilimine* (**3g**) was obtained from **1** and **2g** in 38% yield as an oil; $\nu_{max}^{liq\ film}$ 1735 (s) (C=O), 1190 (s) (C–O), 1135 (s) (S–N) cm^{-1}; NMR δ 7·2–7·85 (10H, m, aromatic protons), 3·91 (2H, q, J = 7·5 Hz, OCH_2CH_3), 3·71 [1H, t, J = 7·5 Hz, $NCH(CH_2CH_3)CO_2Et$], 1·4–2·1 [2H, m, $NCH(CH_2CH_3)CO_2Et$], 1·06 (3H, t, J = 7·5 Hz, OCH_2CH_3), 0·93 (3H, t, J = 7·5 Hz, $NCH(CH_2CH_3)CO_2Et$], *m/e* (75 eV) (rel. int.) 315 ($C_{18}H_{21}NO_2S$, M^+, 4), 242 ($C_{15}H_{16}NS$, *d*, 4), 186 ($C_{12}H_{10}S$, *e*, 100).

Alkylamines (**4a–g**) *from* **3**. A soln of **3** (5 mmole) in 10 ml conc HCl and EtOH (1:4) was heated at 80° for 3–4 hr. The solvent was removed *in vacuo* and 4 ml of benzene was added to the residue. An insoluble solid of hydrochloride of a primary amine was collected, purified by recrystallization and identified by comparison of the m.p. and IR spectrum with those of an authentic sample. Hydrochlorides of **4a** (87%), **4b** (71%), **4c** (82%), **4d** (91%), **4e** (74%), **4f** (41%) and **4g** (42%) were obtained by this procedure. Diphenyl sulfide was obtained in quantitative yield from the benzene layer. Diphenylsulfoxide was also isolated from the reaction mixture of **3f** and **3g** in 20–30% yields.

Reaction of **3a** *with* 1,4-*naphthoquinone* (**5**). A soln of **3a** (291 mg) and **5** (158 mg) in 5 ml $CHCl_3$ was allowed to stand at room temp. for 2 days. The red mixture was concentrated and submitted to preparative TLC (alumina/benzene) to give red needles of **7** in 66% yield, m.p. 154–156° (from benzene-n-hexane) (lit.[4] 156°), and diphenyl sulfide in 70% yield. Replacing the solvent with MeOH or benzene gave **7** in 56 and 74% yields, respectively.

Reaction of **3a** *with* N-*phenylmaleimide* (**8**). By a similar method to that described for **7**, **9** was obtained from **3a** (291 mg) and **8** (173 mg) in $CHCl_3$ in 79% yield, m.p. 117–118° (from benzene-n-hexane); ν_{max}^{KCl} 3330 (m) (NH), 1705 (s) (C=O), 1630 (s) (C=C) cm^{-1}; λ_{max}^{EtOH} 234 (log ϵ 4·26), 263 (3·95), 365 nm (3·50); NMR δ 7·1–7·5 (10H, m, aromatic protons), 5·8–6·15 (1H, bt, NH), 4·98 (1H, s, olefinic proton), 4·45 (2H, d, J = 6 Hz, benzylic protons); *m/e* (70 eV) 278 (M^+). (Found: C, 73·37; H, 5·26; N, 9·91. $C_{17}H_{14}N_2O_2$ requires: C, 73·36; H, 5·07; N, 10·07%).

Reaction of **3a** *with* trans-1,2-*dibenzoylethylene* (**10**). (Procedure A) A soln of **3a** (291 mg) and **10** (236 mg) in 10 ml $CHCl_3$ was allowed to stand at room temp for 1 week. The solvent was evaporated and the residue was submitted to preparative TLC (alumina/benzene-n-hexane) to give diphenyl sulfide (64%), **12** (27%), m.p. 132–134° (lit.[5] 134°) **13** (18%), m.p. 98° (lit.[5] 98–101°), and unreacted **10** (25%). (Procedure B) A soln of **3a** (291 mg) and **10** (236 mg) in 10 ml $CHCl_3$ was refluxed for 5 hr, and the solvent was removed. Work up as described for procedure A gave only **12** in 78% yield. (Procedure C) A soln of 146 mg of **3a** and 118 mg of **10** in 5 ml of MeOH was refluxed for 5 hr. Work up as described for Procedure A gave **12** (60%) and **13** (22%).

Reaction of **3a** *with diphenylcyclopropenone* (**14**). (Procedure A) A soln of **3a** (291 mg) and **14** (103 mg) in 10 ml MeOH was allowed to stand at room temp for 2 days. The solvent was evaporated and the residue was submitted to preparative TLC (alumina/benzene-n-hexane) to give **18** (30%), **19** (35%), and diphenyl sulfide (76%).

Compound **18**: an oil; $\nu_{max}^{CHCl_3}$ 3260 (m) (NH), 1640 (s) (C=O) cm^{-1}; λ_{max}^{EtOH} 241 sh (log ϵ 3·87), 306 nm (4·05); NMR δ 6·6–7·4 (15H, m, aromatic protons), 4·15 (2H, d, J = 7 Hz, benzylic protons), 3·63 (3H, s, OCH_3); *m/e* (75 eV) 343 (M^+, $C_{23}H_{21}NO_2$).

Compound **19**: an oil; $\nu_{max}^{CHCl_3}$ 3420 (m) (NH), 3350 (m) (NH), 1675 (s) (C=O), 1520 (s) (C=C) cm^{-1}; λ_{max}^{EtOH} 246 (log ϵ 4·15), 306 nm (3·72); NMR δ 10·35 (1H, b, NH), 7·2 (10H, s, aromatic protons), 7·01 (10H, bs, aromatic protons), 5·4 (1H, b, CONH), 4·43 (2H, d, J = 6 Hz, benzylic protons), 4·06 (2H, d, J = 6·5 Hz, benzylic protons); *m/e* (75 eV) 418 (M^+, $C_{29}H_{26}N_2O$). (Procedure B) A soln of 291 mg of **3a** and 103 mg of **14** in 10 ml of chloroform (or benzene) was allowed to stand at room temp. for 2 days. Work up as described above gave N,N′-dibenzylbenzildianil (**22**) in 53% yield, m.p. 91–93° (from n-hexane), in addition to diphenyl sulfide (55%); ν_{max}^{KCl} 1615 (s) (C=N) cm^{-1}; λ_{max}^{EtOH} 251 nm (log ϵ 4·05); NMR δ 7·65–8·0 (4H, m, aromatic protons), 6·9–7·5 (16H, m, aromatic protons), 4·56 (4H, s, benzylic protons); *m/e* (70 eV) (rel. int.) 388 (M^+, 8), 386 (8), 311 (10), 297 (17), 295 (9), 194 (12), 91 (100), 89 (12). (Found: C, 86·49; H, 6·01; N, 7·18. $C_{28}H_{24}N_2$ requires: C, 86·56; H, 6·23; N, 7·21%).

Benzil from **22**. A soln of **22** (39 mg) in 1 ml $CHCl_3$ containing 0·1 ml conc. HCl was refluxed for 2 hr. Evaporation of the solvent gave **23** (20 mg), m.p. 92–93°.

Reaction of **3a** *with dimethyl acetylenedicarboxylate* (**24a**). A soln of **3a** (291 mg) and **24a** (142 mg) in 10 ml benzene (or $CHCl_3$) was allowed to stand at room temp. for 1 day. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (alumina/benzene) to give pale yellow crystals of **27a** in 90% yield, m.p. 105–106·5° (from ether); $\nu_{max}^{CHCl_3}$ 1730 (s) (C=O), 1710 (s) (C=O) cm^{-1}; λ_{max}^{EtOH} 241 (log ϵ 4·19), 280 (3·99), 355 nm (3·79); NMR δ 6·7–7·7 (15H, m, aromatic protons), 4·88 (2H, s, benzylic protons), 3·62 (3H, s, OCH_3), 3·42 (3H, s, OCH_3); *m/e* (70 eV) (rel. int.) 433 (M^+, 13), 328 (13), 292 (29), 201 (15), 162 (15), 142 (13), 121 (64), 91 (100). (Found: C, 69·27; H, 5·24; N, 3·29. $C_{25}H_{23}NO_4$ requires: C, 69·27; H, 5·35; N, 3·23%).

Reaction of **3a** *with benzoylphenylacetylene* (**24b**). Using a procedure similar to that described for **27a**, **27b** was obtained in 78% yield from **3a** (291 mg) and **24b** (206 mg) in benzene as a yellow oil; $\nu_{max}^{CHCl_3}$ 1665 (s) (C=O) cm^{-1}; λ_{max}^{EtOH} 257 (log ϵ 4·30), 284 sh (4·13), 408 nm (3·71); NMR δ 7·4–7·7 (20H, m, aromatic protons), 4·82 (2H, s, benzylic protons); *m/e* (70 eV) (rel. int.) 497 (M^+, 11), 388 (26), 180 (85), 105 (100). (Found: C, 82·17; H, 5·59; N, 2·69. $C_{34}H_{27}NOS$ requires: C, 82·06; H, 5·47; N, 2·81%). (Procedure B) A soln of **3a** (291 mg) and **24b** (206 mg) in 5 ml MeOH was allowed to stand at room temp. for 30 min. After evaporation of the solvent, the residue was chromatographed on silicagel. Elution with n-hexane gave **28** (79%), m.p. 96–98° (lit.[6] 98–99°), diphenyl sulfide (42%), and diphenylsulfoxide (16%).

Reaction of **4a** *with dibenzoylacetylene* (**24c**). Using a procedure similar to that described for **27a**, **27c** was obtained in 38% yield from **3a** (291 mg) and **24c** (234 mg) in benzene as a yellow solid, m.p. 139–141° (from petroleum ether–benzene); $\nu_{max}^{CHCl_3}$ 1670 (s) (C=O), 1640 (s) (C=O) cm^{-1}; λ_{max}^{EtOH} 248 (log ϵ 4·35), 284 sh (4·16), 4·22 nm (3·69); NMR δ 6·8–8·1 (25H, m, aromatic protons), 4·85 (2H, s, benzylic protons); *m/e* (70 eV) (rel. int.) 525 (M^+, 8), 182 (25), 181 (13), 121 (11), 105 (100). (Found: C, 79·94; H, 5·23; N, 2·70. $C_{35}H_{27}NO_2S$ requires: C, 79·97: H, 5·18; N, 2·66%).

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