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REACTIONS OF ETHYL AZIDOFORMATE AND SUBSTITUTED BENZOYL AZIDES WITH CARBONYL-STABILIZED SULFONIUM YLIDES

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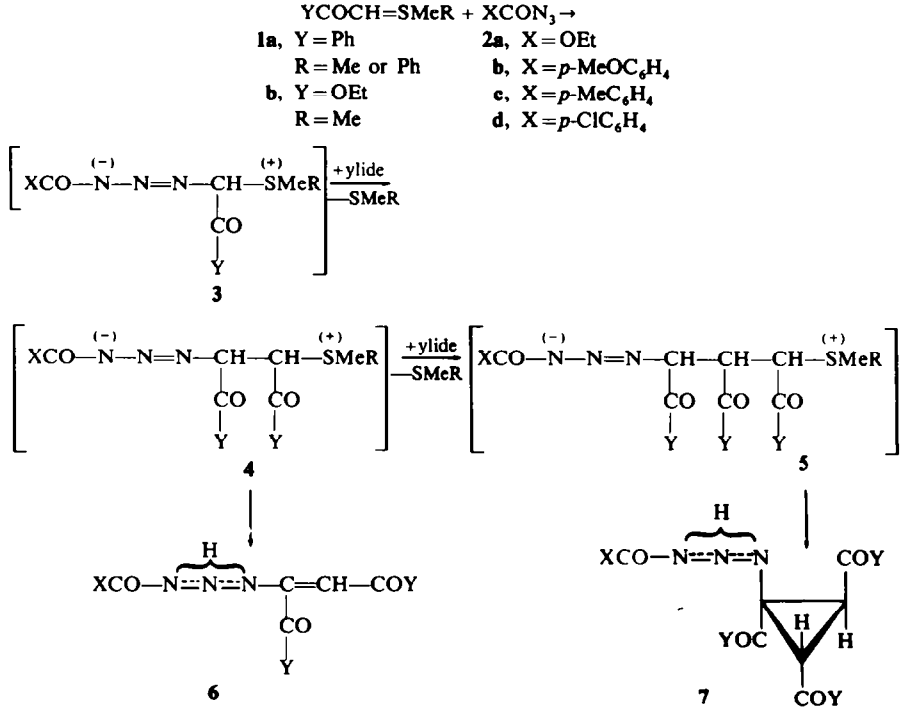
Abstract—The title reactions proceed by nucleophilic attack of the ylides either on the terminal nitrogen atom, or on the carbonyl function of the azides. The first pathway produces vinyl triazenes (**6**), cyclopropyl triazenes (**7**) or their presumed decomposition products, amides (**14** and **17**). In solution, several triazenes (**6a** and **7e–g**) exist in the Δ^2-triazoline form (**8** and **11e–g**), which can eventually decompose to N-acyl amides (**15**) when strong electron-withdrawing groups are attached to the N^1-nitrogen atom. The second pathway, leading to new stabilized sulphur ylides (**18**), is observed in the reactions of *m*- and *p*-nitrobenzoyl azide with carbethoxymethylenedimethylsulphurane. Spectral data which led to structure elucidation are discussed.

INTRODUCTION

TRIAZENES possess the interesting attribute of being converted to diazonium salts by acids and have as such found application in the manufacture of azo-dyes.[1] Aryl triazenes,

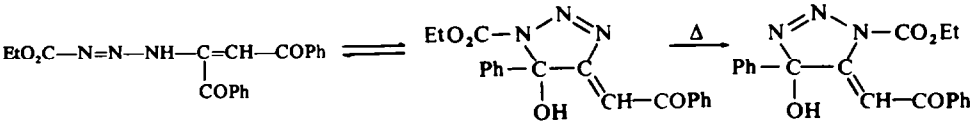
SCHEME 1



the best known representatives, are prepared either by reaction of diazonium salts with amines, or by treating aryl azides with Grignard reagents.[1] Recently, sulphur ylides have been found to react with azides according to several pathways, one of which leads to vinyl triazenes.[2-4] Their formation was rationalized by initial nucleophilic attack of the ylide on the terminal nitrogen atom of the azide. If the same mechanism were operating for the title reactions (scheme 1). vinyl triazenes of type **6** should be obtained. We have only isolated **6** in one particular case, since most of the reactions have led to cyclopropyl triazenes **7**. This indicates further nucleophilic attack of the ylide on intermediate **4** to give **5** which is stabilized by cyclization to **7**. In addition, two reactions have proceeded by attack of the ylide on the carbonyl function of the azide to produce new stable sulphur ylides. A detailed discussion is given in this paper.

RESULTS AND DISCUSSION

The phenacylidenesulfurane **1a** reacted with ethyl azidoformate (**2a**) in benzene at room temperature to give a product characterized as the vinyl triazene **6a** in the solid state*, but as the Δ^2-triazoline **8** in solution. The IR spectrum of the solid (KBr disc)



6a **8** **9**

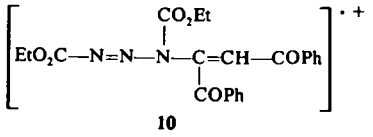
shows an NH band at 3420 cm^{-1}, C=O and C=C bands at 1745, 1660 and 1620 cm^{-1}, and a triazene N=N frequency[5] at 1400 cm^{-1}. Although the exact position of the NH hydrogen atom remains uncertain (either on the α or γ-nitrogen atom), the absence of a carbamate CNH absorption[6] in the region 1530–1540 cm^{-1} seems to favour structure **6a** over the other tautomer. Differentiation between the two, however, is not very significant since unsymmetrical disubstituted triazenes are known to tautomerize readily.[1,7]

In $CHCl_3$, acetone or DMSO solution, cyclization of **6a** to **8** has occurred. This is evident from the NMR absorption pattern in the phenyl region which resembles benzoin and not benzil. The phenyl group in the 5-position of **8** thus gives rise to a singlet absorption at τ 2·58 ($CDCl_3$) as expected. This type of ring-chain isomerism has been reported recently[4,8]

When heated in toluene for 1 hr, or kept in solution at room temperature for a longer period, **8** was irreversibly transformed into a new product of the same elemental composition. The latter displays IR and NMR spectral absorptions similar to, but distinct from **8** (experimental) and is therefore assigned structure **9**.[9] Noteworthy are the identical mass spectra of **6a** and **9**, showing a small molecular ion peak at *m/e* 351 and fragments at *m/e* 323, 278, 251, 250, 246 and 218. Loss of N_2 is the expected primary step of the fragmentation process of the two compounds in view of the facile decomposition of similar triazenes to enamines[4] and of triazolines to aziridines.[10] Further fragmentation of the $M^{\cdot+}$ — 28 ion of mass 323 is easily rationalized by the presence of the

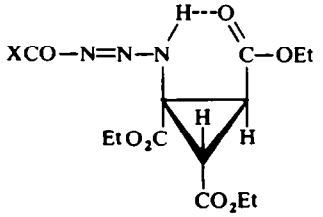
* Note added in proof: The IR spectrum of the compound in the solid state (KBr disc) is also interpretable in terms of **8** with a triazoline band at 928 cm^{-1}.

appropriate metastable peaks, and involves the loss of 45 (EtO), 73 (CO_2Et), 77 (Ph) and 105 (PhCO) mass units. The only difference observed in the mass spectra of **6a** and **9** is the presence of a small ion-molecule complex peak at *m/e* 423 in the spectrum of **6a** but not in that of pure **9**. This peak, whose intensity increases with higher operational temperature of the spectrometer (110→160°) is assigned to compound **10**.[9]



10

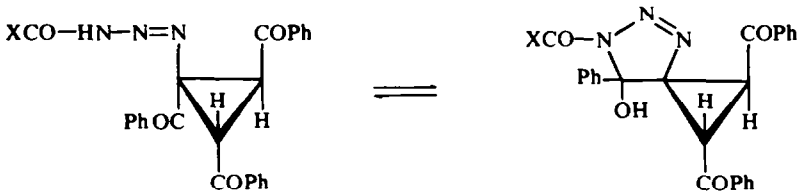
The 1:2 adduct **6a** was the only isolated product, even when the reactions were carried out with one or three equivalents of **1a**. In sharp contrast is the reaction of ethyl azidoformate (**2a**) with carbethoxymethylenedimethylsulfurane (**1b**) which always furnished the cyclopropyl triazene **7a**. Reactions of substituted benzoyl azides **2b–d** with **1b** likewise produced cyclopropyl triazenes **7b–d** instead of 1:2 adducts of type **6**. Their structures are fully supported by spectral examination, with typical IR absorptions for



7a, X=OEt
b, X=*p*-$MeOC_6H_4$
c, X=*p*-MeC_6H_4
d, X=*p*-ClC_6H_4

the C=O functions, the —N=N— function (at 1370–1390 cm^{-1})[5] and the ring deformation mode (at 1025–1030 cm^{-1}).[11] The NMR spectra ($CDCl_3$) show an AB pattern for the cyclopropyl *trans* hydrogens with doublets at τ 6·65 and 6·78 (J = 6 Hz) for **7a** and at τ 6·65 and 6·63 (J = 7·5 Hz) for **7b,c**. In the case of **7d**, both doublets have collapsed to a singlet at τ 6·65. The low τ-value at −0·4 → −0·8 for the NH proton indicates intramolecular chelation (in agreement with a broad and weak IR absorption at 3140–3180 cm^{-1}), thus proving the exact position of the triazene hydrogen atom. The mass spectra of **7b–d** show small molecular ion peaks, and degradation patterns consistent with loss of 28 (N_2 or $CH_2{=}CH_2$), 45 (EtO), 73 (CO_2Et) and 99 ($CH{=}CHCO_2Et$?) mass units. In the middle mass region, important fragments are found for $EtO_2C{-}CN_2{-}CH_2{-}CO_2Et^{+\cdot}$ (*m/e* 200), $XCONH_2^{+\cdot}$, XCO^+ (base peak) and X^+.

Reactions of substituted benzoyl azides **2b–d** with the phenacylidenesulfurane **1a** at room temperature also led to 1:3 adducts as shown by microanalysis. The IR spectra of the compounds in the solid state (KBr) exhibit a broad absorption at 3420–3440 cm^{-1}, a typical ring deformation mode at 1015–1025 cm^{-1} and other bands interpretable in terms of **7e–g** and/or **11e–g**. In $CDCl_3$ solution, on the contrary, the NMR spectra (100 MHz) indicate only one product of type **11** with doublets at τ 5·26 and 6·15 (J = 8 Hz) for the trans cyclopropyl hydrogens, and a singlet at τ 5·05 for the OH function (exchangeable with D_2O). Evidence for the presence of structures **11e–g** is also provided by the mass spectra showing peaks corresponding to the expected cleavage products **12** and **13**. Except for **7e**, the mass spectra were taken at or above the m.ps of the

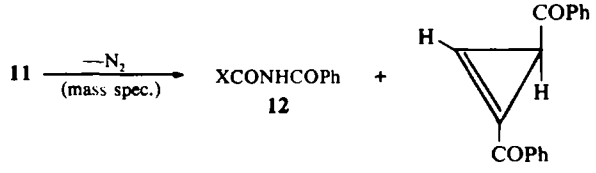


7e, X = *p*-$MeOC_6H_4$
f, X = *p*-MeC_6H_4
g, X = *p*-ClC_6H_4

11e, X = *p*-$MeOC_6H_4$
f, X = *p*-MeC_6H_4
g, X = *p*-ClC_6H_4

thermolabile products and lack molecular ion peaks. In the low mass region fragments are found for XCO^+ and $PhCO^+$.

Amides are the expected[1] decomposition products of triazenes of type **7**, and have been obtained when the ylides were allowed to react with those benzoyl azides which



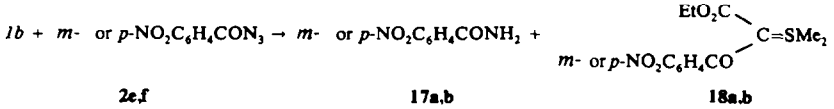
13

carry a strong electron-withdrawing group (Cl or NO_2) in the *para*-position. Thus the reaction of *p*-chlorobenzoyl azide **2d** with **1a** evolved N_2 and produced *p*-chlorobenzoyl amide (36%) in addition to **7g** (or **11g**). When *p*-nitrobenzoyl azide (**2e**) was treated with ylide **1a**, three products were isolated: *p*-nitrobenzoyl amide (**14**), N-benzoyl *p*-nitrobenzoyl amide (**15**) and di-(*p*)nitrophenyl urea (**16**). Compound **14** may result from decomposition of a triazene, and compound **16** is obviously the result of the Curtius rearrangement of the azide. The formation of compound **15** is a typical illustration of the fragmentation process **11** → **12**, which now occurs under the reaction conditions due to the strong electron-withdrawing N^1-substituent.

1a + *p*-$NO_2C_6H_4CON_3$ → *p*-$NO_2C_6H_4CONH_2$ + *p*-$NO_2C_6H_4CONHCOPh$ + (*p*-$NO_2C_6H_4NH)_2C{=}O$

2e **14** **15** **16**

Finally, the reactions of *m*- and *p*-nitrobenzoyl azide (**2e,f**) with the ester ylide **1b** were studied and led to the isolation of the benzoyl amides **17a,b**, in addition to the new stabilized sulfonium ylides **18a,b**. The formation of **18a,b** indicates that ylide **1b**, which is more nucleophilic than **1a**, is capable of attacking the carbonyl function of **2e,f** with



2e,f **17a,b** **18a,b**

elimination of N_3^-. A similar reaction has been reported by Gaudiano *et al.*[2] using the non-stabilized, and hence, stronger nucleophilic methylenedimethyloxysulphurane.

EXPERIMENTAL

All m.ps were obtained on a Leitz apparatus and are uncorrected. IR spectra were taken on a Perkin–Elmer 521 spectrometer. NMR spectra were recorded with a Varian A-60 or XL-100 spectrometer using TMS as internal reference. Mass spectra were obtained with an AEI MS-12 instrument operating at an ionising potential of 70 ev. The sulphonium ylides used in this work were described elsewhere.[4]

1-Carbethoxytriazeno-1,2-dibenzoylethylene (**6a**) and *1-carbethoxy-4-benzoylmethylene-5-phenyl-5-hydroxy-Δ^2-1,2,3-triazoline* (**8**). Ylide **1** (Y = R = Ph) (0·02 mol) and ethyl azidoformate **2a** (0·01 mol) were mixed in benzene (100 ml) at room temp. Monitoring by IR showed that 90% of the azide had disappeared after 24 hr. **6a** partially precipitated from solution and was collected after 3 days. Treatment of mother liquor with pentane gave the remaining **6a**, total yield 65%, m.p. 130–132° (MeOH); IR (KBr) 3420 (NH), 1745 and 1660 (C=O), 1620 (C=O and C=C) and 1400 cm^{-1} (N=N); IR ($CHCl_3$) 3520 (OH), 1717 and 1675 cm^{-1} (C=O); NMR ($CDCl_3$) τ 2·0–2·7 (m, 5 H), 2·58 (s, 5 H, Ph), 3·44 (s, 1 H, C=CH), 5·13 (br s, 1 H, OH), 5·68 (q, 2 H, J = 7 Hz, CH_2) and 8·75 (t, 3 H, J = 7 Hz, Me); NMR (acetone-d_6) τ 2·0–2·6 (m, 5 H), 2·52 (s, 5 H, Ph), 3·20 (br s, 1 H, OH) and 3·34 (s, 1 H, C=CH); NMR (DMSO-d_6) τ 1·98 (br s, 1 H, OH), 2·0–2·7 (m, 5 H), 2·57 (s, 5 H, Ph) and 3·33 (s, 1 H, C=CH); mass spectrum at 130°, *m/e* (%) 423 (0·03; **10**), 351 (2, $M^{\cdot+}$), 323 (13, $M^{\cdot+} - N_2$), 278 (2, 323 − OEt, m* at 239·2), 251 (3), 250 (3, 278 − CO, 323 − CO_2Et, m* at 193·5, $M^{\cdot+} - N_2 - CO_2Et$, m* at 178·0), 246 (2, 323 − Ph, m* at 172·4), 218 (19, 246 − CO, 323 − PhCO, m* at 147·1, 351 − N_2 − COPh, m* at 135·5), 105 (100, $PhCO^+$) and 77 (50, Ph^+); mass spectrum at 160°, *m/e* (%) 423 (0·37), 351 (2), 323 (4), 278 (2), 251 (5), 250 (2), 246 (2), 218 (8), 105 (100) and 77 (54). (Calc for $C_{19}H_{17}N_3O_4$ (351): C, 64·90; H, 4·86; N, 11·96; O, 18·23. Found: C, 64·86; H, 4·71; N, 11·98; O, 18·24%). The residue, after isolation of **6a** was distilled and gave methylphenylsulphide (60%).

1-Carbethoxy-4-phenyl-4-hydroxy-5-benzoylmethylene-Δ^2-1,2,3-triazoline (**9**). This compound was obtained in quantitative yield when **6a** (1 g) was refluxed in toluene (25 ml) for 1 hr. After removing solvent, the residue crystallized from MeOH to give an analytical product, m.p. 133–135°; IR (KBr) 3360 (br, OH), 1750 and 1665 (C=O) and 1625 cm^{-1} (C=C); IR ($CHCl_3$) 1745 and 1660 (C=O) and 1620 cm^{-1} (C=C); NMR ($CDCl_3$) τ 2·0–2·9 (m, 10 H), 2·25 (s, 1 H, C=CH), 3·60 (s, 1 H, OH), 5·76 (q, 2 H, J = 7 Hz, CH_2) and 8·84 (t, 3 H, J = 7 Hz, Me); mass spectrum at 110°, *m/e* (%) 351 (2), 323 (7), 278 (3), 251 (2), 250 (2), 246 (4), 218 (10), 105 (100) and 77 (40). (Calc for $C_{19}H_{17}N_3O_4$ (351): C, 64·90; H, 4·86; N, 11·96; O, 18·23. Found: C, 65·10; H, 4·80; N, 12·20; O, 18·35%).

trans-1-*Carbethoxytriazeno*-1,2,3-*tricarbethoxycyclopropane* (**7a**). Ylide **1b** (0·02 mol) was reacted with ethyl azidoformate **2a** (0·01 mol) in toluene (100 ml) at room temp. The reaction, followed spectroscopically, was complete after 3 min, leaving ½ unreacted azide. Solvent was removed after 1 day and the residual oil chromatographed on floresil with EtOAc—C_6H_6 as eluent. A yellow oil was obtained which failed to crystallize, yield 60% (2·2 g); IR (neat) 1725 with shoulder at 1680 (br, C=O), 1370 (—N=N—) and 1025 cm^{-1} (ring deformation); NMR ($CDCl_3$) τ −0·45 (br, 1 H, NH), 6·65 (d, 1 H, J 6 Hz) and 6·78 (d, 1 H, J 6 Hz). (Calc. for $C_{15}H_{23}N_3O_8$ (373): C, 48·25; H, 6·16; N, 11·26; O, 34·31. Found: C, 48·15; H, 6·05; N, 11·30; O, 34·50%).

trans-1-(p-*Methoxybenzoyltriazeno*)-1,2,3-*tricarbethoxycyclopropane* (**7b**). Ylide **1b** (0·02 mol) and azide **2b** (0·01 mol) were reacted in benzene (100 ml) at room temp to completion (30 min). Removal of solvent left a green- brown oil which fractionally crystallized (MeOH, 25 ml) at two temperatures. At −80°, unreacted azide was recovered in 30% yield. At −20°, **7b** crystallized out very slowly (2 months) in 25% yield (0·64 g), m.p. 110–113°; IR (KBr) 3180 (chelated NH), 1740, 1730 and 1670 (C=O), 1385 (—N=N—) and 1030 cm^{-1} (ring deformation); NMR ($CDCl_3$) τ − 0·58 (br, 1 H, NH), 6·63 (d, 1 H, J 7·5 Hz) and 6·65 (d, 1 H, J = 7·5 Hz); mass spectrum at 140° *m/e* (%) 435 (0·3, $M^{\cdot+}$), 407 (0·4, $M^{\cdot+}$ − 28), 390 (0·3, $M^{\cdot+}$ − OEt), 362 (1, $M^{\cdot+}$ − CO_2Et), 336 (0·8, $M^{\cdot+}$ − CH=$CHCO_2Et$), 200 (24, EtO_2C—CN_2—CH_2—CO_2Et), 151 (7, p-$MeOC_6H_4CONH_2^{\cdot+}$) and 135 (100, p-$MeOC_6H_4CO^+$). (Calc for $C_{15}H_{23}N_3O_8$ (435): C, 48·25; H, 6·16; N, 11·26; O, 34·31. Found: C, 48·15; H, 6·05; N, 11·30; O, 34·50%).

trans-1-(p-*Methylbenzoyltriazeno*)-1,2,3-*tricarbethoxycyclopropane* (**7c**). When ylide **1b** (0·03 mol) was treated with azide **2c** (0·01 mol) in CH_2Cl_2 (100 ml) at room temp, reaction proceeded to 80% completion within 24 hr. After 3 days, solvent was removed *in vacuo* and the residual oil crystallized from ether (10 ml) at −20° to give **7c** (57%, 2·4 g). Recrystallization from MeOH furnished an analytical sample, m.p. 123–126° (dec.); IR (KBr) 3140 (chelated NH), 1740, 1725 and 1670 (C=O), 1390 (—N=N—) and 1030 cm^{-1} (ring deformation); NMR ($CDCl_3$) τ − 0·60 (br, 1 H, NH), 6·65 (d, 1 H, J = 7·5 Hz) and 6·63 (d, 1 H, J = 7·5 Hz); mass spectrum at 130° *m/e* (%) 419 (0·1, $M^{\cdot+}$), 391 (0·1, $M^{\cdot+}$–

28), 374 (0·1, $M^{+\cdot} - OEt$), 346 (2, $M^{+\cdot} - CO_2Et$), 320 (2, $M^{+\cdot} - CH{=}CHCO_2Et$), 200 (13 $EtO_2C{-}CN_2{-}CH_2{-}CO_2Et$), 135 (9, p-$MeC_6H_4CONH_2^{+\cdot}$) and 119 (100, p-$MeC_6H_4CO^+$). (Calc for $C_{20}H_{25}N_3O_7$ (419): C, 57·27; H, 5·96; N, 10·02; O, 26·73. Found: C, 57·10; H, 6·05; N, 10·00; O, 26·80%).

trans-1-(p-*Chlorobenzoyltriazeno*)1,2,3-*tricarbethoxycyclopropane* (**7d**). Reaction of ylide **1b** (0·02 mol) and azide **2d** (0·0066 mol) in CH_2Cl_2 (100 ml) at room temp proceeded with gas evolution and was complete after 1 day. Removal of solvent and treatment of residue with ether (10 ml) yielded 32% (0·92 g) of **7d**, recrystallized from MeOH and decomposed at m.p. 114–118°; IR (KBr) 3150 (chelated NH), 1740, 1725 and 1670 (C=O), 1390 (—N=N—) and 1030 cm^{-1} (ring deformation); NMR ($CDCl_3$) τ −0·80 (br, 1 H, NH) and 6·65 (s, 2 H); mass spectrum, *m/e* (%) 439 (0·15, $M^{+\cdot}$), 411 (0·15, $M^{+\cdot} - 28$), 394 (0·15, $M^{+\cdot} - OEt$), 366 (3·5, $M^{+\cdot} - CO_2Et$), 340 (2, $M^{+\cdot} - CH{=}CHCO_2Et$), 200 (30, $EtO_2C{-}CN_2{-}CH_2{-}CO_2Et$), 155 (12, p-$ClC_6H_4CONH_2^{+\cdot}$), 139 (100, p-$ClC_6H_4CO^+$) and 111 (28, p-$ClC_6H_4^+$). (Calc for $C_{19}H_{22}ClN_3O_7$ (439): C, 51·87; H, 5·00; Cl, 8·07; N, 9·55; O, 25·48. Found: C, 51·85; H, 4·95; Cl, 8·05; N, 9·50; O, 25·50%).

trans-1-(p-*Methoxybenzoyltriazeno*)-1,2,3-*tribenzoylcyclopropane* (**7e**). Ylide **1a** (0·02 mol) was reacted with azide **2b** (0·01 mol) in CH_2Cl_2 (100 ml) at room temp. Reaction was complete after 3 days, leaving *ca* 30% unreacted azide. The solvent was removed and the residual oil crystallized from MeOH (30 ml) to yield **7e** in 45% (1·6 g), m.p. 161–163° (CH_2Cl_2 — pentane); IR (KBr) 3420 (br), 1670, 1650 and 1600 (C=O and C=C) and 1015 cm^{-1} (ring deformation); NMR (100 MHz, $CDCl_3$) τ 5·05 (s, OH), 5·26 (d, 1H, $J = 8$ Hz) and 6·15 (d, 1H, $J = 8$ Hz); mass spectrum, *m/e* (%) 531 (very weak, $M^{+\cdot}$), 503 (very weak, $M^{+\cdot} - N_2$), 398 (1, 503 − COPh, m* at 298·3), 352 (4, radical ion of 1,2,3-tribenzoylcyclopropene), 255 (5, p-$MeOC_6H_4CONHCOPh^{+\cdot}$), 248 (11, radical ion of **13**), 151 (2, p-$MeOC_6H_4CONH_2^{+\cdot}$), 135 (60, p-$MeOC_6H_4CO^+$), 105 (73, $PhCO^+$) and 28 (100). (Calc for $C_{23}H_{25}N_3O_5$ (531): C, 72·31; H, 4·70; N, 7·91; O, 15·06. Found: C, 72·74; H, 4·64; N, 7·71; O, 14·91%).

trans-1-(p-*Methylbenzoyltriazeno*)-1,2,3-*tribenzoylcyclopropane* (**7f**). Ylide **1a** (0·02 mol) was reacted with azide **2e** in CH_2Cl_2 (100 ml) at room temp. After 18 hr 76% of the azide had reacted (IR). Solvent was removed and the residual oil treated with ether (25 ml) at −20° to give **7f** (40%) (1·37 g). Recrystallization from MeOH gave an analytical product, m.p. 145–147°; IR (KBr) 3440 (br), 1680 shoulder at 1655, 1610 and 1600 (C=O and C=C) and 1020 cm^{-1} (ring deformation); NMR (100 MHz, $CDCl_3$) τ 5·08 (s, OH), 5·26 (d, 1 H, $J = 8$ Hz) and 6·15 (d, 1 H, $J = 8$ Hz); mass spectrum at 145°, *m/e* (%) 248 (90, radical ion of **13**), 239 (42, p-$MeC_6H_4CONHCOPh^{+\cdot}$), 119 (100, p-$MeC_6H_4CO^+$) and 105 (76, $PhCO^+$). Calc for $C_{32}H_{25}N_3O_4$ (515): C, 74·54; H, 4·85; N, 8·15; O, 12·42. Found: C, 74·75; H, 4·70; N, 8·25; O, 12·45%).

trans-1-(p-*Chlorobenzoyltriazeno*)-1,2,3-*tribenzoylcyclopropane* (**7g**). Ylide **1a** (0·02 mol) reacted readily with azide **2d** (0·0066 mol) in CH_2Cl_2 (100 ml) at room temp (87% conversion of azide after 7 hr). Solvent was removed and the residual oil treated with ether (25 ml) to give p-chlorobenzoyl amide (36%, 0·36 g), m.p. 179°. The ether of the mother liquor was replaced by MeOH (25 ml) and yielded **7g** in 20% (0·72 g), m.p. 139–141° (MeOH); IR (KBr) 3430 (br), 1675 shoulder at 1655, and 1600 (C=O and C=C) and 1025 cm^{-1} (ring deformation); mass spectrum at 160° *m/e* (%), 352 (0·1, radical ion of 1,2,3-tribenzoylcyclopropene), 259 (31, p-$ClC_6H_4CONHCOPh^{+\cdot}$), 248 (56, radical ion of **13**), 139 (42, p-$ClC_6H_4CO^+$) and 105 (100, $PhCO^+$). (Calc for $C_{31}H_{22}ClN_3O_4$ (535): C, 69·46; H, 4·10; N, 7·84; O, 11·95. Found: C, 69·35; H, 3·95; N, 7·75; O, 11·95%).

Reaction of phenacylidenesulfurane **1a** *with* p-*nitrobenzoyl azide* (**2e**). When ylide **1a** (0·02 mol) was reacted with azide **2e** (0·01 mol) in benzene (100 ml) at room temp (65% conversion of azide after 1 hr), p-nitrobenzoyl amide **14** (m.p. 202°) precipitated (38%, 0·6 g). Treatment of the mother liquor with hexane precipitated **15**, contaminated with **16**. Recrystallization from EtOH furnished pure **15** (10%, 0·3 g), m.p. 172·5–174°. Compound **16** precipitated when the mixture was allowed to stand for a few months. It is formed by slow decomposition of azide **2e**, followed by partial hydrolysis and combination of the resulting amine and isocyanate. The IR, NMR, mass spectra and microanalyses were in accordance with the structures.

α-(p-*Nitrobenzoyl*) *carbethoxymethylenedimethylsulfurane* (**18a**). Ylide **1b** (0·02 mol) with p-nitrobenzoyl azide (0·01 mol) in benzene (100 ml) at room temp evolved N_2 and precipitated p-nitrobenzoyl amide (35%, 0·6 g) after 2 days. Addition of hexane (50 ml) to the mother liquor yielded ylide **18a** (35%, 1·0 g), m.p. 169·5–170°, characterized by spectral analyses and independent synthesis from ylide **1b** and p-nitrobenzoyl chloride.[12]

α-(m-*Nitrobenzoyl*) *carbethoxymethylenedimethylsulfurane* (**18b**). Ylide **1b** (0·02 mol) and *m*-

nitrobenzoyl azide **2f** (0·0066 mol) were reacted in CH_2Cl_2 (100 ml) to completion, solvent was removed and the residual oil dissolved in toluene (20 ml), and *m*-nitrobenzoyl amide **17b** crystallized out (30%, 0·26 g), m.p. 142–143°. Replacement of toluene by a mixture of ether —CCl_4 (20/10 ml) furnished ylide **18b** in 25% yield (0·4 g), m.p. 127–128°, characterized by spectral analyses and independent synthesis from ylide **1b** and *m*-nitrobenzoyl chloride.[12]

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