gas evolution. Titration[20] of this material showed it to be 83% hydroperoxide **16**.

It was purified by dissolving in anhydrous ether at 20°, filtering, adding *n*-hexane, and cooling to 0°. The solid, mp 119–120°, with gas evolution, analyzed as 98.6% hydroperoxide **16**: ir (KBr) 3470, 3450 (OH, NH), 1640 cm^{-1} (C=N); mass spectrum (70 eV) *m/e* (rel intensity) 394 (1, M$^+$), 361 (32), 360 (80), 197 (22), 186 (32), 181 (64), 180 (100), 149 (25), 105 (35), 93 (37), 77 (72).

Anal.[21] Calcd for $C_{26}H_{22}N_2O_2$: C, 79.15; H, 5.63; N, 7.10. Found: C, 78.92; H, 5.84; N, 7.00.

A 100-mg sample of **16** heated under vacuum at 150° for a few minutes decomposed with gas evolution. The product, recrystallized from methanol, gave 50 mg (55%) of benzil dianil identified by mixture melting point.

A solution of 1.56 g (0.0043 mol) of α,α'-dianilinostilbene (**11**) and 0.66 g (0.0086 mol) of anhydrous sodium acetate in 75 ml of THF was stirred overnight by a stream of dry O_2. Isolation of the hydroperoxide **16** was accomplished as previously described, 1.3 g, mp 110–120°, with gas evolution, identified by the ir spectrum.

Isomerization[4] of the Protonation Product.—The adduct **2** was protonated at −60° with 0.6 g (0.01 mol) of acetic acid and warmed to room temperature, and 35 ml of anhydrous DMF containing 100 mg of sodium cyanide was added. Nitrogen was bubbled through the mixture and the THF permitted to distil. The remaining solution was stirred by the nitrogen stream for 48 hr. The reaction was monitored by tlc (1:1 benzene–*n*-hexane) and during this time the fluorescent spot increased in size relative to the nonfluorescent spot.

Addition of water and extraction with ether and evaporation of the extracts provided the crude reaction product. Methanol (50 ml) was added and after 4 hr at 0°, 0.34 g (19%) of α,α'-dianilinostilbene were deposted and identified by its ir spectrum. Attempts to isolate anything further from the filtrates by evaporation and crystallization provided only 1.2 g (67%) of benzil dianil identified by mixture melting point.

Registry No.—**1**, 7510-33-0; **9**, 29954-13-0; **10**, 29954-14-1; **13**, 29954-15-2; **14**, 29954-16-3; **15**, 29954-17-4; **16**, 29954-18-5.

Acknowledgment.—The financial support of the National Research Council of Canada is gratefully acknowledged. The award of a Province of Ontario Graduate Fellowship to one of us (E. J. M.) is also appreciated.

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[20] R. L. Augustine, Ed., "Oxidation," Vol. 1, Marcel Dekker, New York, N. Y., 1969, p 222.

[21] We are grateful to Mr. W. Boos of the Uniroyal Research Laboratories, Guelph, Ontario, who arranged for the immediate analysis of this compound.

Reactions of Aryl Azides with Carbonyl-Stabilized Sulfonium Ylides

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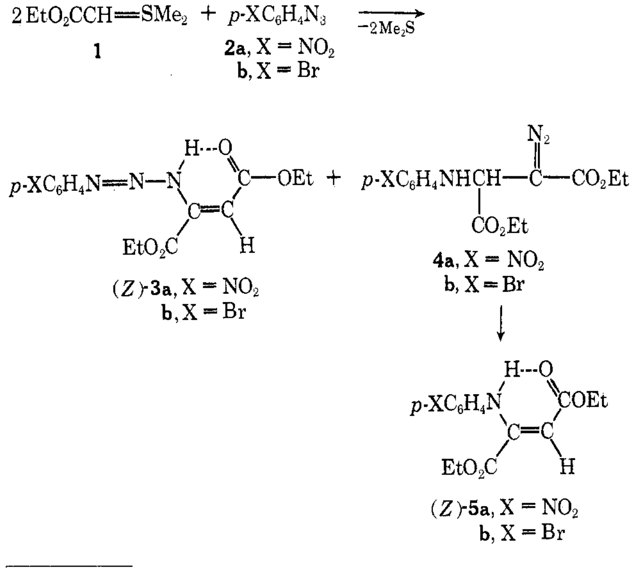
Aryl azides have been found to react with 2 equiv of carbethoxymethylenedimethylsulfurane to give a mixture of aryltriazenofumarates and anilinodiazosuccinates in various amounts depending on the solvent. Reaction of aryl azides with phenacylidenesulfuranes at room temperature produces 1-anilino-1,2-dibenzoylethylenes in addition to small amounts of 1-triazeno-1,2-dibenzoylethylenes (in equilibrium with the cyclic Δ^2-triazolines) and *trans*-1,2,3-tribenzoylcyclopropane. The stereochemistry of the reaction products is discussed as well as the mechanism of their formation.

Although phosphonium and sulfonium ylides are similar in structure, they have been found to react differently on several occasions. Johnson,[1] in reviewing the chemistry of both classes of ylides, clearly pointed out that the formation of a P=O bond (128 kcal/mol^{-1}) is the driving force in most *P*-ylide reactions, whereas *S*-ylides benefit from the sulfide leaving group. This principle is best illustrated by the synthesis of olefins and oxiranes by treating carbonyl compounds respectively with *P*- and *S*-ylides.

Different behavior is also observed in the reactions of nonstabilized phosphonium and oxysulfonium ylides with aryl azides, the former leading to imines[2] and the latter to triazenes and Δ^2-triazolines.[3] In recent studies, the reactions of carbonyl-stabilized phosphonium ylides with aryl azides led to triazoles or diazo compounds.[4] For comparison, in this paper we have investigated the reactions of the corresponding sulfonium ylides with aryl azides.[5]

Results

Carbethoxymethylenedimethylsulfurane (**1**) reacts smoothly with aryl azides **2a,b** at room temperature to give a mixture of aryltriazenofumarates (*Z*)-**3a,b**[6]



1

2a, X = NO$_2$
b, X = Br

(*Z*)-**3a**, X = NO$_2$
b, X = Br

4a, X = NO$_2$
b, X = Br

(*Z*)-**5a**, X = NO$_2$
b, X = Br

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[1] A. W. Johnson, "Ylid Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1966, p 331.

[2] H. Hoffmann, *Chem. Ber.*, **95**, 2563 (1962).

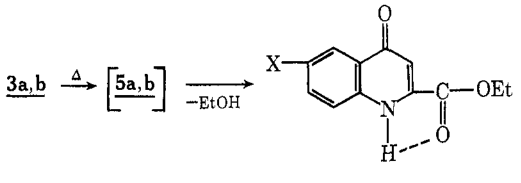
[3] G. Gaudiano, C. Ticozzi, A. Umani-Ronchi, and P. Bravo, *Gazz. Chim. Ital.*, **97**, 1411 (1967).

[4] G. R. Harvey, *J. Org. Chem.*, **31**, 1587 (1966). P. Ykman, G. L'abbé, and G. Smets, *Tetrahedron*, **25**, 5421 (1969); **27**, 845 (1971).

[5] For a preliminary report on this topic, see E. Van Loock, G. L'abbé, and G. Smets, *Tetrahedron Lett.*, 1693 (1970); see also Y. Hayashi, T. Watanabe, and R. Oda, *ibid.*, 605 (1970). This research was presented in part at the International Symposium on Ylides, Leicester, England, July 1970.

[6] (*Z*) and (*E*) are used to designate cis–trans isomers according to the sequence rule procedure; see "IUPAC Tentative Rules for the Nomenclature of Organic Chemistry. Section E. Fundamental Stereochemistry," *J. Org. Chem.*, **35**, 2849 (1970).

and anilinodiazosuccinates **4a,b**. Their structures were assigned on the basis of elemental analysis and spectral evidence. In particular, the ir and nmr spectra of (*Z*)-**3a,b** indicated intramolecular chelation as shown by the weak N–H absorption at 3190–3210 cm^{-1}, the two distinct C=O bonds at 1730 and 1670 cm^{-1}, and the large nmr δ value (*ca.* 12) for the N–H proton. The mass spectra of (*Z*)-**3a,b** displayed fragments corresponding to $M\cdot^+ - N_2$, $M\cdot^+ - CO_2Et$, $(XC_6H_4N_2)^+$, and $(XC_6H_4)^+$ in addition to the molecular ion peak $M\cdot^+$. Thermolysis of **3a** and **3b** in refluxing diphenyl ether affords the quinolones **6a** and **6b**, presumably *via* (*Z*)- and/or (*E*)-**5a,b**, and thus provides an extension of the Conrad–Limpach quinolone synthesis.[7]

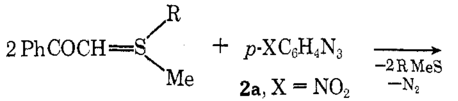


6a, X = NO$_2$
b, X = Br

The diazo compounds **4a,b** showed in the ir spectra a strong N–H band at *ca.* 3400 cm^{-1} and a diazo band at 2100 cm^{-1}. Their nmr spectra were also consistent with structure **4** and showed, *inter alia*, doublets at δ 5.58 and 5.10 (J = 6.5 Hz) for the N–H and tertiary protons. Deuterium exchange resulted in the disappearance of the former and collapse of the latter to a broad singlet at δ 5.10.

The nature of the solvent influences strongly the relative amounts of products **3a** and **4a**. A ratio of 80:20 (determined by nmr) is obtained in benzene solution, while this ratio is practically reversed in dichloromethane. In DMF, **3a** is formed in less than 10% yield and, furthermore, **4a** decomposes partially to (*Z*)-**5a** under the basic polar reaction conditions. An independent experiment showed that pure **4a** remained unchanged when treated with **1** in benzene or dichloromethane solution, but decomposed to (*Z*)-**5a** in DMF upon addition of a base such as **1** or diethylamine.

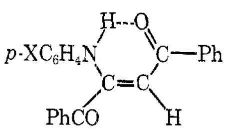
The reactions of the phenacylidenesulfuranes **7a** and **7b** with aryl azides **2a–d** in benzene at room temperature proceed with nitrogen evolution and produce enamines **8a–d** as the major products. They were isolated in the chelated (*Z*)-**8** form, with the exception of the reaction of **7a,b** with **2a** where both isomers of **8a** [60% of (*E*)-**8a** and 30% of (*Z*)-**8a**] were obtained. During the recrystallization process in ethanol or benzene, (*E*)-**8a** was transformed into (*Z*)-**8a**. Structural elucidation of the enamines **8a–d** was accomplished by spectral analysis (see Experimental Section) and confirmed by an independent synthesis from dibenzoylacetylene and arylamines. It is worthwhile to note here that the mass spectra showed a simple fragmentation pattern with characteristic peaks for $M\cdot^+$, $M\cdot^+ - COPh$, $PhCO^+$, and Ph^+.



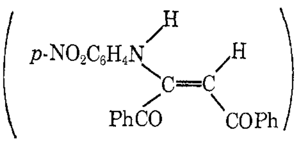
$$2\,PhCOCH{=}S\begin{smallmatrix}R\\Me\end{smallmatrix} + p\text{-}XC_6H_4N_3 \xrightarrow[-N_2]{-2RMeS}$$

7a, R = Me
b, R = Ph

2a, X = NO$_2$
b, X = Br
c, X = H
d, X = OMe

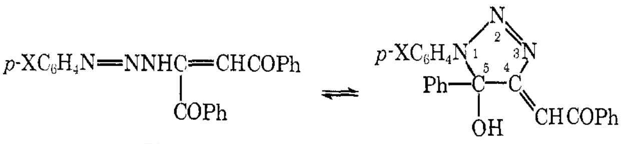


(*Z*)-**8a**, X = NO$_2$
b, X = Br
c, X = H
d, X = OMe



(*E*)-**8a**

In addition to the enamines **8a,b** the reactions of **7a,b** with **2a,b** furnish small amounts (2–5%) of triazenes **9a,b** in equilibrium with Δ^2-triazolines **10a,b**.

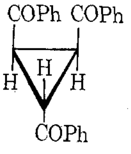


9a, X = NO$_2$
b, X = Br

10a, X = NO$_2$
b, X = Br

This type of ring–chain equilibrium has been described previously,[8] and it was shown that the equilibrium position depends on the nature of the substituents and the solvent used. In our particular case, the ir spectra (KBr) of the compounds in the solid state were interpretable in terms of **9a,b** and/or **10a,b** with a broad absorption in the region 3000–3500 cm^{-1} and further bands at 1665, 1620, 1380, and 945. The mass spectra were also consistent with **9a,b** and/or **10a,b** and showed peaks for $M\cdot^+$, $M\cdot^+ - N_2$, and $M\cdot^+ - COPh$. In DMSO solution, on the contrary, the nmr spectra indicated only one product consistent with the cyclic structure **10a,b**. Indeed, the phenyl protons in the 5 position of the Δ^2-triazolines **10a,b** gave rise to a singlet absorption as expected. Furthermore, the absorption pattern in the phenyl region resembled benzoin (PhCHOHCOPh) and not benzil (PhCOCOPh) or the enamines **8**.

A second side product isolated in the reactions of the keto ylides **7a,b** with aryl azides is *trans*-tribenzoylcyclopropane (**11**). Its structure was substantiated by spectral analysis (see Experimental Section) and its melting point.[9] Table I gives a summary of the reaction products.



11

Mechanism

A mechanism accounting for all observed products is outlined in Scheme I and involves three main intermediates **12**, **13**, and **14**. They result from the azide by successive addition of one, two, and three molecules of ylide. Stable products derived directly from intermediate **12** have not been isolated. For

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(7) M. Conrad and L. Limpach, *Ber.*, **20**, 994 (1887); **21**, 523, 1649 (1888). See also N. D. Heindel, P. D. Kennewell, and V. B. Fish, *J. Heterocycl. Chem.*, **6**, 77 (1969), and references cited therein.

(8) C. E. Olsen and C. Pedersen, *Tetrahedron Lett.*, 3805 (1968); R. Fusco and P. D. Croce, *ibid.*, 3061 (1970).

(9) G. Maier, *Chem. Ber.*, **95**, 611 (1962), and references cited therein.

SCHEME I

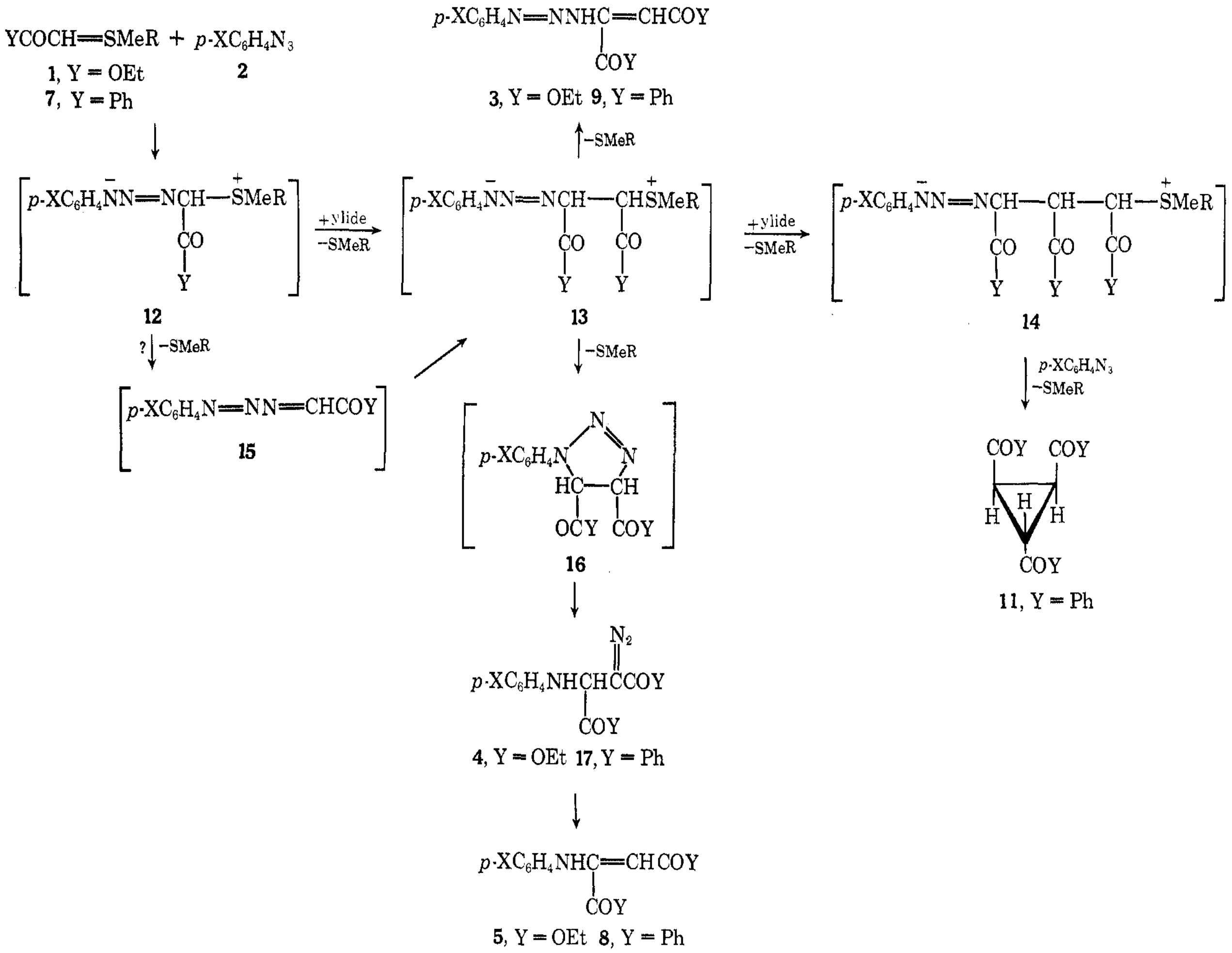

TABLE I
PRODUCT YIELDS FROM THE REACTIONS OF **7a,b** WITH **2a-d** IN BENZENE AT ROOM TEMPERATURE

Reagents	Enamine **8**, %	Triazene **9**, %	*trans*-Tribenzoylcyclopropane, %
7a,b + **2a**	90	4–5	
7a,b + **2b**	81	2–3	8–9
7a,b + **2c**	72		8–9
7a + **2d**	85		
7b + **2d**	40		20

instance, the reaction of equimolar amounts of ylide and azide failed to give the azoimine **15** but furnished instead products derived from intermediate **13** in addition to unreacted azide. Thus, if **15** is formed during the reaction, it must react immediately with another molecule of ylide in a manner analogous to imines.[10]

Stabilization of the intermediate **13** can occur in two ways, leading either to olefinic triazenes **3** and **9** by hydrogen shift, or to Δ^2-triazolines **16** by cyclization. The Δ^2-triazolines of type **16** are expected to be unstable in basic medium[11] and would decompose to diazo compounds **4** and **17**, and enamines **5** and **8**. This view is supported by our observation that, upon addition of ylide **7b**, triazoline **16c** underwent a fast and complete isomerization in less than 5 min to 3-benzoyl-3-anilino-2-diazopropiophenone (**17c**) followed by a slow decomposition (within 5 days) to 1-anilino-1,2-dibenzoylethylene (**8c**). (Triazoline **16c** was prepared from phenyl azide and dibenzoylethylene). By use of Et_2NH, a stronger base than **7b**, the process **16c** → **17c** → **8c** was too fast to be followed by nmr. Note also that the diazo esters **4a,b** were found to decompose by base to the enamines **5a,b** however, at much slower rate than the diazo ketones.[12]

The proposed mechanism *via* the intermediates **12** and **13** is believed to give a cis–trans mixture of the olefinic triazenes and the enamines. Isomerization to the most stable chelated (*Z*) configuration thus occurs in a later stage of the reaction. This is consistent with the isolation of (*E*)-**8a** and its subsequent conversion to (*Z*)-**8a** upon recrystallization.

The formation of *trans*-tribenzoylcyclopropane in *S*-ylide reactions has been the subject of several discussions in the literature.[13] The *S*-ylides **7a** and **7b**, namely, are stable at room temperature or on warming

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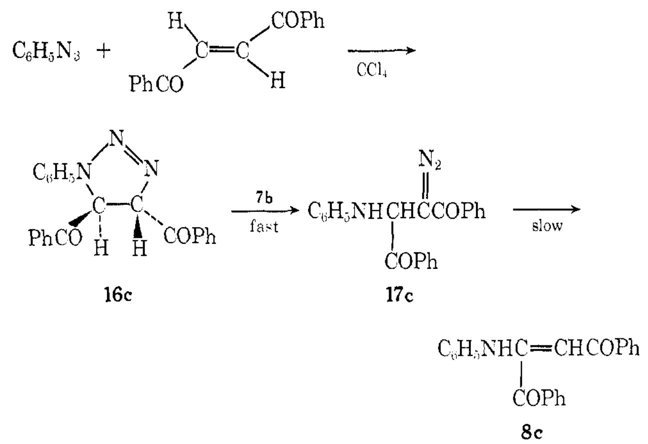
[10] A. J. Speziale, C. C. Tung, K. W. Ratts, and A. Yao, *J. Amer. Chem. Soc.*, **87**, 3460 (1965).

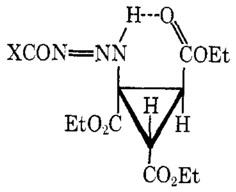
[11] R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, **99**, 475 (1966); G. Szeimies and R. Huisgen, *ibid.*, **99**, 491 (1966); W. Broeckx, N. Overbergh, C. Samyn, G. Smets, and G. L'abbé, submitted for publication.

[12] The alternative and attractive possibility that the enamines **8** arise from decomposition of the triazenes **9** is excluded by the fact that the latter are stable under the reaction conditions. For recent reviews on triazenes, see C. Süling in "Houben-Weyl. IV. Methoden der Organischen Chemie," Georg Thieme, Stuttgart, 1965, p 699; P. A. S. Smith "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, 1966, p 336.

[13] (a) F. Krollpfeiffer and H. Hartmann, *Chem. Ber.*, **83**, 90 (1950); (b) H. Nozaki, K. Kondô, and M. Takaku, *Tetrahedron Lett.*, 251 (1965); *Tetrahedron*, **22**, 2145 (1966); (c) B. M. Trost, *J. Amer. Chem. Soc.*, **88**, 1587 (1966); **89**, 138 (1967); (d) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969).



in the pure state, but decompose to **11** when some other product, such as phenacyl bromide or the sulfonium salt, is present. The same phenomenon seems to occur sometimes in the presence of azides. We interpret the formation of **11** in our reactions by Scheme I. Indeed, the intermediate **14**, produced from **13** by attack of a third molecule of ylide, can regenerate the azide and eliminate sulfide to yield the cyclopropane **11**. We were led to this interpretation by the observation that acyltriazenocyclopropanes **18** were isolated from the reactions of the *S*-ylides with acyl azides,[14] thereby proving the existence of an intermediate analogous to **14**.



18, X = OEt, *p*-MeOC$_6$H$_4$

Experimental Section

All melting points 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 spectrometer using TMS as an internal reference. Mass spectra were obtained with an AEI MS-12 instrument operating at an ionizing potential of 70 eV.

Sulfonium Ylides 1, 7a, and 7b.—The ylides were prepared by standard procedures[15] *via* the corresponding sulfonium salts. Carbethoxymethylenedimethylsulfurane (**1**) was obtained as a viscous pale yellow oil.[15] Benzoylmethylenedimethylsulfurane (**7a**) was recrystallized from benzene and dried carefully, mp 82–82.5° (lit.[13c] 78–79). Benzoylmethylenemethylphenylsulfurane (**7b**) was recrystallized repeatedly from benzene, mp 112–114° (lit.[13b] 113–114°).

Diethyl 2-(*p*-Nitrophenyltriazeno)fumarate [(*Z*)-3a].—Ylide **1** (0.02 mol) and *p*-nitrophenyl azide (0.01 mol) were allowed to react in benzene (100 ml) at room temperature, and the reaction was followed spectroscopically, being finished after 6 min. Removal of the solvent *in vacuo* left a red oil composed of **3a** and **4a** in a ratio of 80:20 (%) by nmr. The oil which solidified upon standing was washed with pentane and recrystallized from methanol (25 ml) to give yellow crystals of pure **3a** in 68% yield: mp 107–109°; ir (KBr) 3195 (chelated NH), 1730 (ester C=O), 1670 (chelated C=O), 1620 (C=C), 1515, and 1340 cm^{-1} (NO$_2$); nmr (CCl$_4$) δ 12.17 (1 H, NH), 8.27 (d, 2 H, J = 9 Hz, meta phenyl protons), 7.62 (d, 2 H, J = 9 Hz, ortho phenyl protons), and 5.45 (s, 1 H, C=CH); mass spectrum *m/e* (%) 336 (13, M$\cdot^+$), 308 (1.4, M$\cdot^+$ − N$_2$), 263 (13, M$\cdot^+$ − CO$_2$Et), 189 (9, 263 − EtOH) 150 (100, NO$_2$C$_6$H$_4$N$_2^+$), and 122 (100, NO$_2$C$_6$H$_4^+$).

Anal. Calcd for C$_{14}$H$_{16}$N$_4$O$_6$ (336): C, 50.00; H, 4.76; N, 16.66; O, 28.57. Found: C, 49.90; H, 4.75; N, 17.15; O, 28.35.

Diethyl 2-(*p*-Nitroanilino)-3-diazosuccinate (4a).—When ylide **1** (0.02 mol) and *p*-nitrophenyl azide (0.01 mol) were allowed to react in dichloromethane (100 ml) at room temperature and the solvent was removed *in vacuo*, the residual red oil was composed of 80% **4a** and 20% **3a** by nmr. The oil was triturated with pentane (25 ml) and fractionally crystallized from methanol to yield yellow crystals of pure **4a**: mp 92.5–94.5°; ir (KBr) 3400 (NH), 2100 (diazo), 1735 and 1690 (C=O), 1520 and 1320 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 8.15 (d, 2 H, J = 9 Hz, meta phenyl protons), 6.70 (d, 2 H, J = 9 Hz, ortho phenyl protons), 5.58 (d, 1 H, J = 6.5 Hz, NH), and 5.10 (d, 1 H, J = 6.5 Hz, CH).

Anal. Calcd for C$_{14}$H$_{16}$N$_4$O$_6$ (336): C, 50.00; H, 4.76; N, 16.66; O, 28.57. Found: C, 50.00; H, 4.75; N, 16.70; O, 28.35.

Diethyl 2-(*p*-Nitroanilino)fumarate [(*Z*)-5a].—When ylide **1** (0.02 mol) was allowed to react with *p*-nitrophenyl azide (0.01 mol) in DMF solution (100 ml) and the reaction followed by ir, the diazo compound **4a** was observed first but decomposed partially to **5a**. The nmr spectrum indicated a mixture of **3a**, **4a**, and **5a** in a ratio of 10:45:45. Compound **5a** was identical in all respects with an authentic sample prepared from diethyl acetylenedicarboxylate and *p*-nitroaniline.[16] Thus equimolar amounts (0.02 mol) of both substances were refluxed in methanol (40 ml) for 2 days. Cooling to −20° provided yellow crystals of (*Z*)-**5a**, yield 60%: mp 49.5–51.5°; ir (KBr) 3250 (chelated NH), 1730 (C=O), 1660 (chelated C=O), and 1610 cm^{-1} (C=C); nmr (CDCl$_3$) δ 9.8 (NH), 8.17 (d, 2 H, J = 9 Hz, meta phenyl protons), 6.90 (d, 2 H, J = 9 Hz, ortho phenyl protons), and 5.70 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 308 (2, M$\cdot^+$), 262 (2, M$\cdot^+$ − EtOH), 235 (8, 263 − 28), 207 (14, 235 − 28), 189 (35, 207 − H$_2$O), 162 (14, M$\cdot^+$ − 2CO$_2$Et).

Anal. Calcd for C$_{14}$H$_{16}$N$_2$O$_6$ (308): C, 54.54; H, 5.19; N, 9.09; O, 31.16. Found: C, 54.60; H, 5.20; N, 9.05; O, 31.35.

Diethyl 2-(*p*-Bromophenyltriazeno)fumarate [(*Z*)-3b].—A solution of ylide **1** (0.02 mol) and *p*-bromophenyl azide (0.01 mol) in benzene (100 ml) was kept in the dark at room temperature. The reaction, followed spectroscopically, was finished after 3 hr. Removal of the solvent left a red oil composed of **3b** and **4b** in a ratio of 80–90:10–20 (%) by nmr. The oil solidified upon standing and was recrystallized from methanol to give pale yellow crystals of pure (*Z*)-**3b**: mp 83–84°; ir (KBr) 3205 (chelated NH), 1730 (ester C=O), 1665 (chelated C=O), and 1610 cm^{-1} (C=C); nmr (CDCl$_3$) δ 12.0 (1 H, NH), 7.60 (d, 2 H, J = 9 Hz, meta phenyl protons), 7.40 (d, 2 H, J = 9 Hz, ortho phenyl protons), 5.45 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 369 and 371 (3, M$\cdot^+$), 341 and 343 (5, M$\cdot^+$ − N$_2$) 324 and 326 (1, M$\cdot^+$ − OEt), 296 and 298 (3, M$\cdot^+$ − CO$_2$Et), 183 and 185 (62, BrC$_6$H$_4$N$_2^+$), 155 (100), and 157 (95, BrC$_6$H$_4^+$).

Anal. Calcd for C$_{14}$H$_{16}$BrN$_3$O$_4$ (370): C, 45.40; H, 4.32; Br, 21.62; N, 11.35; O, 17.29. Found: C, 45.00; H, 4.30; Br, 21.90; N, 11.75; O, 17.45.

2-Carbethoxy-6-nitro-4(1*H*)-quinolone (6a).—This compound crystallized out in 40% yield when a solution of **3a** (0.5 g) in diphenyl ether (5 ml) was refluxed for 5 min and then cooled to room temperature. Recrystallization from methanol gave an analytical product: mp 296–297°; ir (KBr) 1725, 1630, and 1600 cm^{-1}; nmr (DMSO-d_6) δ 12.15 (1 H, NH) and 6.66 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 262 (85, M$\cdot^+$), 216 (17, M$\cdot^+$ − EtOH), 189 (14, M$\cdot^+$ − CO$_2$Et), 188 (100, 216 − CO), 142 (31, 188 − NO$_2$).

Anal. Calcd for C$_{12}$H$_{10}$N$_2$O$_5$ (262): C, 54.96; H, 3.81; N, 10.68; O, 30.53. Found: C, 54.95; H, 3.72; N, 10.65; O, 30.25.

2-Carbethoxy-6-bromo-4(1*H*)-quinolone (6b).—Triazene **3b** (0.1 g) was refluxed in diphenyl ether (5 ml) for 5 min. The solution was cooled to room temperature and treated with petroleum ether (5 ml) to crystallize the quinolone **6b**, yield 50%. Recrystallization from methanol and vacuum sublimation at 220° gave pure material: mp 249–251°; ir (KBr) 1730, 1620, and 1590 cm^{-1}; nmr (DMSO-d_6) δ 12.25 (1 H, NH) and 6.68 (s,

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[14] The reactions of acyl azides with carbonyl-stabilized sulfonium ylides will be reported in a forthcoming paper.

[15] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966); G. B. Payne, *ibid.*, **32**, 3351 (1967).

[16] See, for instance, R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966), and references cited therein.

1 H, C=CH); mass spectrum, *m/e* (%) 295 and 297 (70, $M^{\cdot +}$), 249 and 251 (12, $M^{\cdot +}$ − EtOH), 221 and 223 (100, $M^{\cdot +}$ − CO_2Et), 193 and 195 (10, 223 − CO), 142 (34, 223 − Br), and 114 (80, 142 − CO).

Anal. Calcd for $C_{12}H_{10}BrNO_3$ (296): C, 48.64; H, 3.37; Br, 27.02; N, 4.72; O, 16.21. Found: C, 48.77; H, 3.25; Br, 27.20; N, 4.70; O, 16.30.

Reaction of the Phenacylidenesulfuranes 7a and 7b with *p*-Nitrophenyl Azide.—Ylide **7a** or **7b** (0.02 mol) was treated with *p*-nitrophenyl azide (0.01 mol) in benzene (100 ml) at room temperature. A yellow precipitate was collected after 1 day and shown to be (*E*)-**8a**, yield 60%: ir (KBr) 3380 (NH), 1660, 1595, and 1575 cm^{-1} (C=O and C=C); nmr (DMSO-d_6) δ 10.10 (1 H, NH) and 7.00 (s, 1 H, C=CH). (*E*)-**8a** isomerized to (*Z*)-**8a** during the melting point determination or recrystallization process.

The mother liquor was left to stand for 1 month, during which period the orange triazene **9a** crystallized out, yield 4–5%: mp 172–175° (methanol); ir (KBr) 1665, 1620, and 1595 (CO and C=C) and 1380 cm^{-1} (N=N); nmr (DMSO-d_6) δ 8.52 (1 H, OH), 7.40 (s, 5 H, Ph), and 6.68 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 400 (0.3, $M^{\cdot +}$), 372 (6.5, $M^{\cdot +}$ − N_2), 295 (1.3, $M^{\cdot +}$ − COPh), 267 (68, 372 − COPh), 150 (6, $NO_2C_6H_4N_2^+$), 122 (17, $NO_2C_6H_4^+$), 105 (100, $PhCO^+$), and 77 (88, Ph^+).

Anal. Calcd for $C_{22}H_{16}N_4O_4$ (400): C, 66.00; H, 4.00; N, 14.00. Found: C, 66.00; H, 3.80; N, 14.45.

The resultant mother liquor was diluted with pentane (200 ml) and provided 30% (*Z*)-**8a**: mp 170–171° (methanol); ir (KBr) 1665, 1590, 1570, and 1555 cm^{-1}; nmr ($CDCl_3$) δ 12.85 (1 H, NH), 7.05 (d, 2 H, ortho phenyl protons), and 6.35 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 372 (27, $M^{\cdot +}$), 267 (100, $M^{\cdot +}$ − COPh), 189 (8, 267 − C_6H_6), 105 (64.5, $PhCO^+$), and 77 (52, Ph^+).

Anal. Calcd for $C_{22}H_{16}N_2O_4$ (372): C, 70.96; H, 4.30; N, 7.52; O, 17.20. Found: C, 70.66; H, 4.64; N, 7.31; O, 17.21.

Compound (*Z*)-**8a** was independently prepared in 75% yield by refluxing equimolar amounts (0.01 mol) of dibenzoylacetylene[17] and *p*-nitroaniline in ethanol (250 ml) for 4 hr.

Reaction of the Phenacylidenesulfuranes 7a and 7b with *p*-Bromophenyl Azide.—A solution of ylide **7a** or **7b** (0.02 mol) and *p*-bromophenyl azide (0.01 mol) in benzene (100 ml) precipitated *trans*-1,2,3-tribenzoylcyclopropane (**11**) within a few min, yield 8–9%, mp 221° (lit.[9] 215°); ir, nmr, and mass spectrum were consistent with the structure.

Anal. Calcd for $C_{24}H_{18}O_3$ (354): C, 81.35; H, 5.08; O, 13.55. Found: C, 81.24; H, 5.08; O, 13.70.

Treatment of the mother liquor with hexane (100 ml) gave a first crop of enamine (*Z*)-**8b**. The remaining enamine was isolated by evaporation of the solvent and treatment of the residue with ether (25 ml), total yield 81%: mp 167–169° (EtOH); ir (KBr) 1660, 1590, 1570, and 1550 cm^{-1}; nmr ($CDCl_3$) δ 12.60 (1 H, NH), 6.80 (d, 2 H, ortho anilino protons) and 6.15 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 405 and 407 (9, $M^{\cdot +}$), 300 and 302 (59, $M^{\cdot +}$ − COPh), 155 and 157 (5.5 $BrC_6H_4^+$), 105 (100, $PhCO^+$), and 77 (71, Ph^+).

Anal. Calcd for $C_{22}H_{16}BrNO_2$ (406): C, 65.02; H, 3.94; Br, 19.70; N, 3.44; O, 7.88. Found: C, 65.04; H, 4.01; Br, 19.65; N, 3.26; O, 7.87.

The triazene **9b**, contaminated with some enamine, was finally isolated from the ether solution by cooling to −20°. The crude material was washed with chloroform to remove the enamine and dried, yield 2–3%: mp 160–161°; ir (KBr) 1665, 1620, and 1580 (C=O and C=C) and 1380 cm^{-1} (N=N); nmr (DMSO-d_6) δ 8.50 (s, 1 H, OH) and 6.50 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 433 and 435 (0.5, $M^{\cdot +}$), 405 and 407 (2, $M^{\cdot +}$ − N_2), 328 and 330 (0.5, $M^{\cdot +}$ − COPh), 300 and 302 (4.5, 405 and 407 − COPh), 183 and 185 (7.5, $BrC_6H_4N_2^+$), 155 and 157 (11, $BrC_6H_4^+$), 105 (100, $PhCO^+$), and 77 (54, Ph^+).

Compound (*Z*)-**8b** was independently prepared in 90% yield by treating equimolar amounts (0.01 mol) of dibenzoylacetylene and *p*-bromoaniline in benzene (30 ml) at room temperature for 2 hr.

Reaction of the Phenacylidenesulfuranes 7a and 7b with Phenyl Azide.—Ylide **7a** or **7b** (0.02 mol) was allowed to react with phenyl azide (0.01 mol) in benzene (100 ml) at room temperature. After 24 hr the precipitated **11** was collected by filtration and the mother liquor was left to stand for 1 week. The solvent was then removed to give crude (*Z*)-**8c** in 72% yield. Recrystallization from methanol (40 ml) afforded yellow crystals (60%): mp 126–128°; ir (KBr) 1665, 1605, 1595, 1585, 1575, and 1550 cm^{-1}; nmr ($CDCl_3$) δ 12.5 (1 H, NH) and 6.05 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 327 (21, $M^{\cdot +}$), 222 (100, $M^{\cdot +}$ − COPh), 105 (50, $PhCO^+$), and 77 (64, Ph^+).

Anal. Calcd for $C_{22}H_{17}NO_2$ (327): C, 80.73; H, 5.19; N, 4.28; O, 9.78. Found: C, 80.95; H, 5.20; N, 4.20; O, 9.75.

Compound (*Z*)-**8c** was independently prepared in quantitative yield by heating at reflux equimolar amounts (0.01 mol) of dibenzoylacetylene and aniline in benzene (30 ml) for 2 hr.

Reaction of the Phenacylidenesulfuranes 7a and 7b with *p*-Methoxyphenyl Azide.—A solution of ylide **7a** (0.02 mol) and *p*-methoxyphenyl azide (0.01 mol) in benzene (100 ml) was allowed to stand at room temperature for 2 months. The solution was then diluted with hexane (100 ml) and cooled to 0°. The red crystals of (*Z*)-**8d** that precipitated were collected by filtration (85%) and recrystallized from ethanol, yield 50%: mp 127–129°; ir (KBr) 1670, 1585, 1570, 1550, and 1510 cm^{-1}; nmr ($CDCl_3$) δ 12.7 (1 H, NH), 6.98 and 6.68 (2 d, 4 aromatic protons), and 6.08 (s, 1 H, C=CH); mass spectrum, *m/e* (%) 357 (33.5, $M^{\cdot +}$), 252 (100, $M^{\cdot +}$ − COPh), 105 (52, $PhCO^+$), and 77 (30, Ph^+).

Anal. Calcd for $C_{23}H_{19}NO_3$ (337): C, 77.31; H, 5.32; N, 3.92; O, 13.44. Found: C, 77.30; H, 5.40; N, 3.90; O, 13.40.

When the ylide **7b** was used instead of **7a**, 20% **11** crystallized out after a few days. After 3 weeks, the solvent was removed and the residual oil was treated with methanol (30 ml) and crystallized at −20° to yield 40% (*Z*)-**8d**.

Compound (*Z*)-**8d** was also obtained in 98% yield by treating equimolar amounts (0.01 mol) of dibenzoylacetylene and *p*-methoxyaniline in benzene (50 ml) at room temperature for 2 hr.

Registry No.—**3a**, 29954-01-6; **3b**, 29954-02-7; **4a**, 30093-87-9; **5a**, 29954-03-8; **6a**, 30093-88-0; **6b**, 29954-04-9; (*E*)-**8a**, 29954-05-0; (*Z*)-**8a**, 29954-06-1; **8b**, 29954-07-2; **8c**, 29954-08-3; **8d**, 29954-09-4; **9a**, 29954-10-7; **9b**, 29954-11-8.

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[17] R. E. Lutz, *J. Amer. Chem. Soc.*, **48**, 2905 (1926).