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Studies of Acenaphthene Derivatives. XXVI.[1] The Thermal Cycloaddition of 2-Diazoacenaphthenone to Isocyanates

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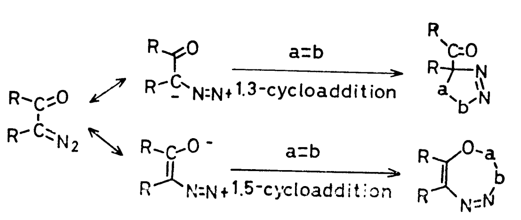
Although 2-diazoacenaphthenone did not react with phenyl isocyanate or phenyl isothiocyanate on prolonged reflux in toluene, it reacted with strongly electrophilic benzoyl and *p*-chlorobenzoyl isocyanates and thiobenzoyl isocyanate to give the corresponding spiro[acenaphthenone-2,5′-oxazolin-4′-one] and the spiro-thiazolin-4′-one in good yields. On the other hand, the reaction of the α-diazoketone with benzoyl isothiocyanate gave 8-benzoylacenaphtho[1,2-*d*]isoxazolin-9-thione, which on catalytic hydrogenolysis over PtO_2 gave the dihydro compound corresponding to reductive cleavage of N–O bond of the isoxazoline ring. Furthermore, the reaction of the α-diazoketone with benzenesulfonyl isocyanate gave two stereoisomeric bis-spiro-azetidinones. The mechanisms of these reactions are proposed.

In an earlier publication,[3] it was reported that the reaction of 2-diazoacenaphthenone (**1**) with olefins gave diastereoisomeric spiro-cyclopropanes under mild conditions. In contrast, acetylenes yielded spiro-3*H*-pyrazoles. The reaction of α-diazoketones has been extensively studied by Ried and his co-workers,[4] and it has been shown that the reactions of α-diazoketones with multiple bonds form 1,3-[5] or 1,5-cycloaddition products under rather mild conditions (Scheme 1). For example, the reaction of α-diazoketones with isothiocyanate[6] or thiophosgene[7] gave thiazoles. Recently, in order to prepare medium-sized heterocycles,



Scheme 1.

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1) Part XXV of this series: O. Tsuge and I. Shinkai, *Organic Preparations and Procedures (OPP) International*, in press (1972).

2) Author to whom correspondence should be directed.

3) O. Tsuge, I. Shinkai, and M. Koga, *J. Org. Chem.*, **36**, 745 (1971).

4) W. Ried and H. Lohwasser, *Ann.*, **683**, 118 (1965); for a review, see G. Pfundt and G. O. Schenck, "1,4-Cycloaddition Reactions," ed. by J. Hamer, Academic Press, New York and London (1967), p. 405.

5) For the 1,3-dipolar cycloaddition reaction of ketocarbenes generated from the thermolysis or photolysis of α-diazoketones, see R. Huisgen, G. Binsch, H. Konig, and H. J. Strum, *Angew. Chem.*, **73**, 368 (1961).

6) W. Ried and B. M. Beck, *Ann.*, **673**, 128 (1964).

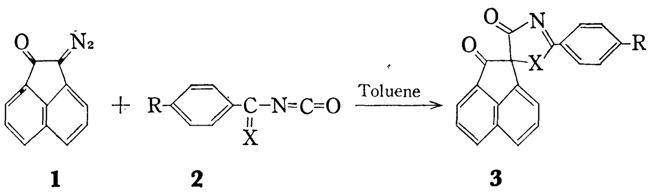
7) W. Ried and B. M. Beck, *ibid.*, **673**, 124 (1964).

the addition of 1,5-dipoles such as vinyldiazomethane,[8] vinylazide,[9] and other similar compounds,[10] has been investigated. However, the 1,5-dipoles cyclized intramolecularly to yield stable five-membered heterocycles rather than 1,5-cycloadducts.

Only the reaction of *o*-quinonediazide with ketenes[11] and ketenimines[12] resulted in 1,5-cycloaddition to yield the oxadiazepines. It would be expected that **1** might add to heterocumulene such as isocyanate to give the (2+5) cycloadduct, oxatriazepine. Since little information about the thermal cycloaddition reaction of **1** with isocyanates is available, we have investigated the reaction of **1** with several isocyanates under mild conditions, and now report our findings in this area.

Results and Discussion

It was previously reported[3] that thermolysis of α-diazoketone **1** did not take place in boiling toluene and the ketocarbene from **1** is not formed under such conditions. It has now been found that **1** did not react with phenyl isocyanate or isothiocyanate on prolonged reflux in toluene; **1** was recovered quantitatively. However, when a toluene solution of **1** and benzoyl isocyanate (**2a**) was refluxed for 30 hr, a 38.5% yield of **3a** was obtained as colorless needles, in addition to recovered **1**. The results of microanalysis and mass spectrum of **3a** fitted the molecular formula $C_{20}H_{11}NO_3$, which would arise from the elimination of nitrogen from a 1 : 1 adduct of **1** and **2a**. The IR spectrum of **3a** showed bands ascribable to carbonyl groups at 1762 and 1729 cm^{-1}. On the basis of the above observations, it may be deduced that **3a** is 2′-phenyl-spiro[acenaphthenone-2,5′-oxazolin-4′-one].



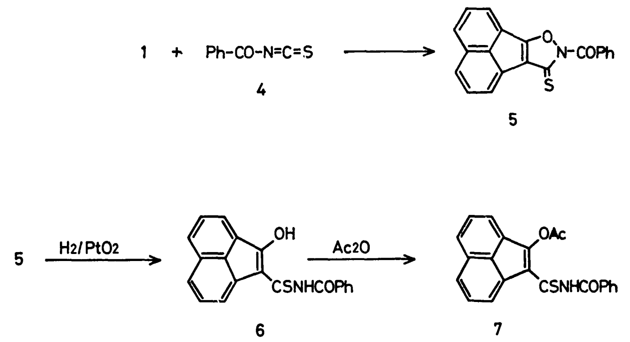
a: R=H, X=O; **b**: R=Cl, X=O; **c**: R=H, X=S

Under similar conditions, *p*-chlorobenzoyl (**2b**) and thiobenzoyl isocyanate (**2c**) gave the corresponding spiro-oxazolin-4′-one (**3b**) and spiro-thiazolin-4′-one (**3c**). The mass spectra of **3a**—**3c** were also compatible with the proposed structures.

It has been reported[13] that the C=N bond of isocyanate reacts easily with 1,3-dipoles, whereas the C–S bond of isothiocyanate is attacked predominantly. In order to compare with the reactivity of acyl isocyanates, the reaction of **1** with benzoyl isothiocyanate (**4**) was investigated.

When a toluene solution of **1** and **4** was refluxed for 10 hr, a 31% yield of a product **5** was obtained as yellow needles. The microanalysis and mass spectral data were in agreement with the molecular formula $C_{20}H_{11}NO_2S$ (M^+ m/e 329). Its IV spectrum exhibited a single carbonyl absorption at 1632 cm^{-1}. The thiocarbonyl test[14] was positive.

The hydrogenolysis of **5** over PtO_2 in dioxane at room temperature afforded a dihydro compound **6** as yellow needles. The IR spectrum of **6** showed the band ascribable to amide I absorption at 1645 cm^{-1}, and the NMR spectrum in carbon tetrachloride exhibited signals at δ 10.18 (1H, singlet, OH) and 14.15 ppm (1H, singlet, NH) besides aromatic protons. Treatment of the compound **6** with acetic anhydride afforded the *O*-acetylated derivative **7** as golden yellow needles.



Scheme 2.

On the basis of these observations, **5** and **6** were assigned as 8-benzoyl-acenaphtho[1,2-*d*]-Δ^4-isoxazolin-9-thione and 2-benzoylthiocarbamoyl-1-acenaphthylenol, respectively (Scheme 2).

Confirmatory evidence for the structure of **5** was provided by the mass spectrum; the spectrum of **5** showed no peak at *m/e* 226 which would arise by the elimination of benzonitrile from parent peak (M^+ *m/e* 329), while the fragment peaks (M^+- ArCN) appeared in the spectra of **3a**—**3c**.

These results show clearly that a ketocarbene intermediate was not involved. We view these reactions as depicted in Scheme 3. α-Diazoketone **1** would react with **2** to form intermediate **A** (X=Y=O or X=S, Y=O) which would cyclize to the triazoline, followed by the elimination of nitrogen and cyclization to **3**.

In contrast, the negative charge in the intermediate **A** (X=O, Y=S) formed from the reaction with **4** would be located on the sulfur atom, since diazomethane,[6] ketocarbenes[15] and epoxides[16] react predominantly

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8) I. Tabushi, K. Takagi, M. Okano, and R. Oda, *Tetrahedron*, **23**, 2621 (1967).

9) H. Reimlinger, *Chem. Ber.*, **103**, 1900 (1970).

10) H. Reimlinger, J. J. M. Vandewalle, G. S. D. King, W. R. F. Linger, and R. Merenyi, *ibid.*, **103**, 1918 (1970).

11) W. Ried and R. Dietrich, *Ann.*, **666**, 113 (1963); W. Ried and K. Wagner, *ibid.*, **681**, 45 (1965); W. Ried and R. Kraemer, *ibid.*, **681**, 52 (1965).

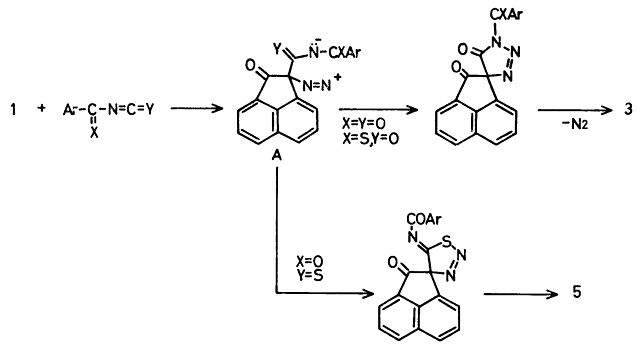
12) W. Ried and P. Junker, *ibid.*, **713**, 119 (1968).

13) E. Pfeil and K. Milzner, *Angew. Chem. Int. Ed. Engl.*, **5**, 667 (1966).

14) F. Feigl, "Spot Test in Organic Analysis," Elsevier Publishing Co., New York, N. Y. (1966), p. 84.

15) R. Huisgen, G. Binsch and H. König, *Chem. Ber.*, **97**, 2868 (1964).

16) K. Hartmann, *ibid.*, **98**, 1782 (1965).

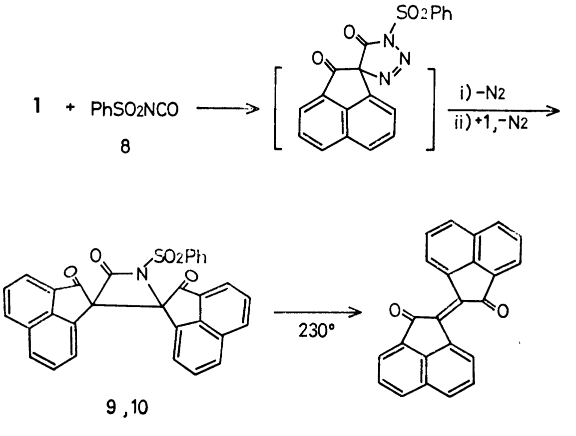


Scheme 3.

with the C=S bond of phenyl isothiocyanate. It would thus seem reasonable to assume that the betaine **A** would cyclize to the exo-double bonded thiadiazoline, followed by the elimination of nitrogen and ring closure to **5**.[17)]

Since the sulfonyl group does not enter into conjugative effects,[18)] products analogous to **3** would thus not be expected from the reaction of **1** with benzenesulfonyl isocyanate (**8**). The reaction of **1** with **8** in benzene at room temperature for 72 hr yielded two products **9** and **10** in 16 and 28.2% yields, respectively. Microanalyses of both **9** and **10** agreed with the molecular formula ($C_{31}H_{17}NO_5S$) derived from a 2 : 1 adduct of **1** and **8** with the elimination of nitrogen. The IR spectra of both **9** and **10** showed carbonyl bands at about 1800 cm^{-1}, which are assignable to carbonyl group in four-membered rings.[19)] Thermal decomposition of both **9** and **10** at 230°C gave biacenedione in 77.6 and 31% yields, respectively.

From a consideration of the high carbonyl frequency and the result of the thermal decomposition to biacenedione, **9** and **10** may be considered as stereoisomeric bis-spiro-azetidinone. However, their configurations have not been clarified (Scheme 4).



Scheme 4.

Recently, it has been reported that sulfonyl isocyanate reacted with diazofluorene to give bis-spiro-azetidinone which was converted thermally to bis-fluorenylidene.[20)] We also reported that biacenedione was obtained by thermal decomposition of *N*-phenyl-bis-spiro-pyrrolidine formed from the 1,3-dipolar cycloaddition of 2-benzylidenacenaphthenone to azomethine oxide.[2)]

On the basis of these results, it can be concluded that **1** does not react as a 1,5-dipole but rather as a 1,3-dipole incycloaddition to isocyanate, followed by cyclization to spiro-heterocycles.

Experimental

All melting points are uncorrected. The IR spectra were measured as KBr pellets and the NMR spectra were determined at 60 MHz with Hitachi R-20 NMR spectrometer using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer using a direct inlet and an ionization energy of 70 eV.

Materials. 2-Diazoacenaphthenone (**1**) was prepared by the reported method[22)] and purified by chromatography (alumina), mp 93—94°C (lit,[22)] mp 94°C); benzoyl (**2a**),[23)] *p*-chlorobenzoyl (**2b**),[23)] thiobenzoyl (**2c**),[24)] benzenesulfonyl isocyanate (**8**),[25)] and benzoyl isothiocyanate (**4**)[26)] were prepared by the methods described in the literatures respectively.

*Reaction of **1** with Isocyanates (**2**).* The general procedure used is illustrated with the reaction of **1** with **2a**.

A solution of 780 mg (4.0 mmol) of **1** and 730 mg (5.0 mmol) of **2a** in 30 m*l* of toluene was refluxed for 30 hr, the reaction mixture was then cooled and filtered to give crystals, which on recrystallization from benzene-petroleum benzine (bp 42—60°C) afforded 360 mg (38.5%) of 2′-phenyl-spiro[acenaphthenone-2,5′-oxazolin-4′-one] (**3a**), mp 246—247°C, as colorless needles.

Found: C, 76.48; H, 3.61; N, 4.52%. Calcd for $C_{20}H_{11}NO_3$: C, 76.67; H, 3.54; N, 4.47%. IR cm^{-1}: $\nu_{C=O}$ 1729, 1762.

Mass spectrum *m/e* (rel. intensity): 313 (M$^+$, 54.5), 210 (M$^+$−PhCN, 37.8), 182 (210$^+$−CO, 75.5) 154 (182$^+$−CO, 100), 126 (154$^+$−CO, 63.6).

The toluene filtrate was concentrated *in vacuo* and the residue was purified by chromatography on alumina to yield 480 mg (61.5%) of unreacted **1**.

Similarly, the reaction of **1** with **2b** and **2c** for 30 and 12 hr respectively afforded the corresponding spiro-oxazolin-4′-one **3b** and spiro-thiazolin-4′-one **3c**.

3b: mp 269—271°C, colorless prisms (benzene). Yield, 59%.

Found: C, 69.17; H, 2.71; N, 4.04%. Calcd for $C_{20}H_{10}NO_3Cl$: C, 69.06; H, 2.88; N, 4.03%. IR cm^{-1}: $\nu_{C=O}$ 1730, 1766.

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17) This reaction seems to be the same type as the decomposition of 4-acyltriazolones to form isoxazolines (K. H. Oehring, *Monatsch. Chem.*, **89**, 588 (1958)).

18) For the conjugation of anions to sulfonyl group, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y. (1965), p. 71.

19) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," ed. by G. A. Olah, Interscience Publishers, New York, N. Y. (1967), p. 195.

20) G. Lohaus, *Tetrahedron Lett.*, **1970**, 130.

21) O. Tsuge and I. Shinkai, *ibid.*, **1970**, 3847.

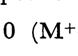
22) M. P. Cava, R. L. Litle, and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2257 (1958).

23) A. J. Speziale and R. L. Smith, *J. Org. Chem.*, **28**, 1805 (1963).

24) J. Goerdeler and H. Schenk, *Chem. Ber.*, **98**, 2954 (1965).

25) O. C. Billeter, *Ber.*, **37**, 690 (1904).

26) T. B. Johnson and L. H. Chernoff, *J. Amer. Chem. Soc.*, **34**, 164 (1912).

Mass spectrum *m/e* (rel. intensity): 349 (33.2), 347 (100) (M^+), 210 (M^+−Cl--CN, 57.5), 182 (210^+−CO, 44), 154 (210^+−CO, 88), 126 (154^+−CO, 36.4).

3c: mp 239—240°C, pale yellow prisms (benzene). Yield, 28%.

Found: C, 73.24; H, 3.29; N, 4.41%. Calcd for $C_{20}H_{11}NO_2S$: C, 72.94; H, 3.37; N, 4.25%. IR cm^{-1}: $\nu_{C=O}$ 1710, 1736.

Mass spectrum *m/e* (rel. intensity): 329 (M^+, 14), 226 (M^+−PhCN, 55), 198 (226^+−CO, 75), 170 (198^+−CO, 100), 126 (170^+−CS, 25.6).

In a similar fashion, 8-benzoylacenaphthol[1,2-*d*]-Δ^4-isoxazoline-9-thione (**5**), mp 215—217°C, was obtained in a 31% yield as yellow needles (from ligroin (bp 80—110°C)); a 33% yield of **1** was recovered.

Found: C, 73.14; H, 3.24; N, 4.15%. Calcd for $C_{20}H_{11}NO_2S$: C, 72.94; H, 3.37; N, 4.25%. IR cm^{-1}: $\nu_{C=O}$ 1632.

Mass spectrum *m/e* (rel. intensity): 329 (M^+. 100), 288 (8), 210 (288^+−CS, 4.4), 192 (6.6), 120 (5.2), 105 ($PhCO^+$, 66).

*Catalytic Hydrogenation of **5**.* Hydrogenation of 200 mg of 5 in 30 m*l* of dioxane with 100 mg of PtO_2 resulted in smooth absorption of one equivalent of hydrogen in about 5 hr at room temperature. The reaction mixture was filtered and the catalyst was washed with 5 m*l* of dioxane. Concentration of the filtrate *in vacuo* left a residue which on trituration with petroleum benzine (20 m*l*) gave 160 mg of yellow crystals. The crystals were recrystallized from acetonitrile to give 2-benzoylthiocarbamoyl-1-acenaphthylenol (**6**), mp 155—157°C, as yellow needles.

Found: C, 72.57; H, 3.81; N, 4.21%. Calcd for $C_{20}H_{13}NO_2S$: C, 72.50; H, 3.96; N, 4.23%. IR cm^{-1}: $\nu_{C=O}$ 1645.

NMR (in CCl_4) δ ppm: 7.4—8.3 (11**H**, multiplet, aromatic protons), 10.18, (1H, singlet, O**H**), 14.15 (1H, singlet, N**H**).

Mass spectrum *m/e*: 331 (M^+).

A solution of **6** in methanol containing trace amounts of pyridine was treated with acetic anhydride at room temperature for 10 min to give a quantitative yield of yellow crystals, which on recrystallization from benzene-petroleum benzine yielded *O*-acetyl derivative **7**, mp 152—153°C decomp.), as golden yellow needles.

Found: C, 70.76; H, 3.80; N, 3.91%. Calcd for $C_{22}H_{15}NO_3S$: C, 70.77; H, 4.05; N, 3.75%. IR cm^{-1}: $\nu_{C=O}$ 1693, 1715.

NMR (in $CDCl_3$) δ ppm: 2.63 (3H, singlet, COC**H**$_3$), 7.39—8.3 (11**H**, multiplet, aromatic protons), 13.36 (1H, singlet, N**H**).

Mass spectrum *m/e*: 373 (M^+).

*Reaction of **1** with **8**.* A solution of 1.55 g (8.0 mmol) of **1** and 1.83 g (10.0 mmol) of **8** in 50 m*l* of benzene was stirred for 72 hr at room temperature. The precipitated crystals were fractionally recrystallized several times from benzene to afford 190 mg (15%) of biacenedione, mp 294°C, identical with an authentic sample prepared from acenaphthenequinone and acenaphthenone, and 330 mg (16%) of bis-spiro-azetidinone **9**, mp 228—230°C (decomp.), as colorless prisms.

Found: C, 72.34; H, 3.71; N, 2.71%. Calcd for $C_{31}H_{17}NO_5S$: C, 72.23; H, 3.30; N, 2.72%. IR cm^{-1}: $\nu_{C=O}$ 1807, 1746, 1720.

The benzene filtrate was concentrated *in vacuo*; recrystallization of the residue from benzene-petroleum benzine gave 580 mg (28.2%) of isomeric bis-spiro-azetidinone **10**, mp 213—216°C (decomp.), as pale yellow needles.

Found: C, 72.09; H, 3.86; N, 2.54%. Calcd for $C_{31}H_{17}NO_5S$: C, 72.23; H, 3.30; N, 2.72%. IR cm^{-1}: $\nu_{C=O}$ 1806, 1738, 1710.

*Thermal Decomposition of **9**.* Forty miligrams of **9** were heated at 230°C for 5 min without solvent. After cooling, the resulting semicrystalline residue was chromatographed on alumina. Elution with chloroform afforded 20 mg (77.6%) of biacenedione, mp 294°C. Similarly, thermolysis of **10** at 230°C gave a 31% yield of biacenedione.