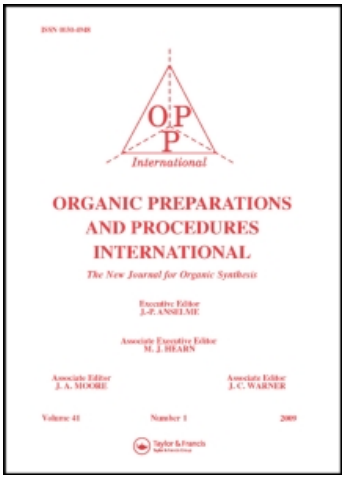

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Tsuge, O. , Shinkai, I. and Koga, M.(1972) 'STUDIES OF ACENAPHTHENE DERIVATIVES. XXVII. PREPARATION OF ACENAPHTHENEQUINONE MONOANIL N-OXIDES AND THEIR REACTIONS WITH ISOCYANATES', Organic Preparations and Procedures International, 4: 4, 169 — 177
To link to this Article: DOI: 10.1080/00304947209355543
URL: http://dx.doi.org/10.1080/00304947209355543

ORGANIC PREPARATIONS AND PROCEDURES INT. 4(4), 169-177 (1972)

STUDIES OF ACENAPHTHENE DERIVATIVES. XXVII.[1] PREPARATION OF ACENAPHTHENEQUINONE MONOANIL N-OXIDES AND THEIR REACTIONS WITH ISOCYANATES

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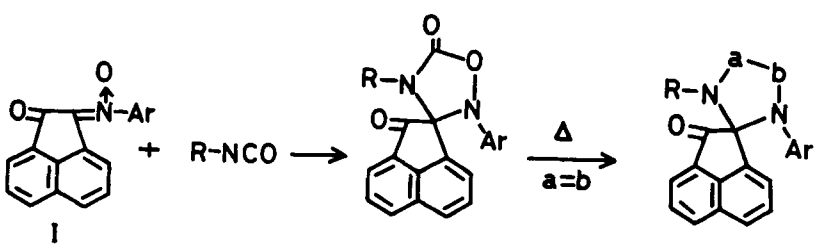
Recently, a great deal of interest has been focused on small ring heterocycles as precursors of dipolar intermediates in cycloaddition reactions.[3] As a continuation of our work[4] into the study of cycloelimination reaction of five-membered heterocycles, we anticipated that spiro-1,2,4-oxadiazolidin-5-ones would be obtained by the reaction of α-ketonitrones (I) with isocyanates.



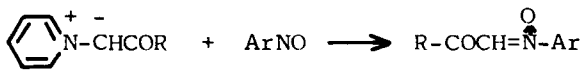
Scheme 1

Since little is known about the preparation of nitrones of type I and about the cycloelimination reaction of spiro-heterocycles, we have investigated a satisfactory method for the preparation of I and studied their reactions with iso-

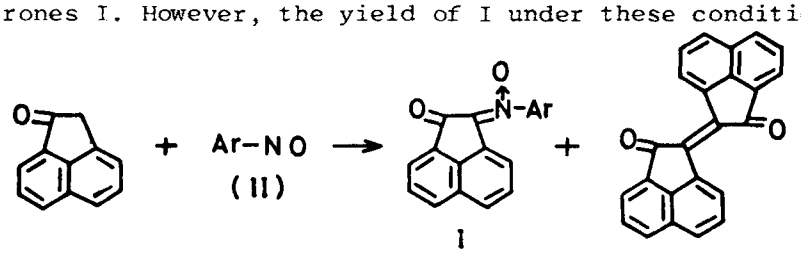
cyanate.

Preparation of α-Ketonitrones (I).

Although C-acylnitrones are easily obtained by the reaction of pyridinium ylids with nitroso compounds,[5] this method



is not applicable to the preparation of α-ketonitrones of type I.[6] It has been previously reported[7] that either the uncatalyzed or the base-catalyzed condensation of acenaphthenone with aromatic nitroso compounds (II) gave the corresponding acylnitrones I. However, the yield of I under these conditions is



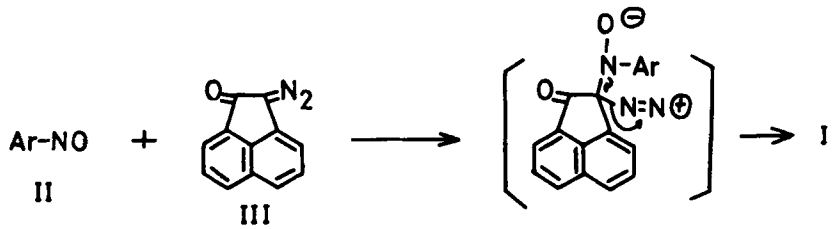
I

Scheme 2

poor and biacenedione is invariably a side-product; it presumably arises from the condensation of acenaphthenone with acenaphthenequinone, itself generated from the hydrolysis of I.

In the course of another study,[8] we have found that the reaction of 2-diazoacenaphthenone (III) with II affords I in excellent yields. When a xylene (or benzene) solution of III and nitrosobenzene (IIa) was heated at 130° (or at reflux in benzene) for 2 hr, Ia was obtained as pale yellow needles, mp 198-199° (dec.), in 85% yield. Its IR spectrum was superimposable upon that of authentic Ia.[7,9] Treatment of I with dil. hydrochloric acid gave a quantitative yield of acenaphthenequinone, mp 259-260°.[12] Upon standing at room temperature for

24 hr, a benzene solution of III and IIa yielded Ia in 84% yield.



a : Ar = Ph , b : Ar = p-ClC$_6$H$_4$, c : Ar = p-$(CH_3)_2$N-C$_6$H$_4$

Scheme 3

Under similar conditions (at 130° in xylene), p-chloro- (IIb) and p-N,N-dimethylaminonitrosobenzene (IIc) gave the corresponding nitrone (Ib) and (Ic). The elemental analyses and mass spectral data were in agreement with the proposed structures for I.

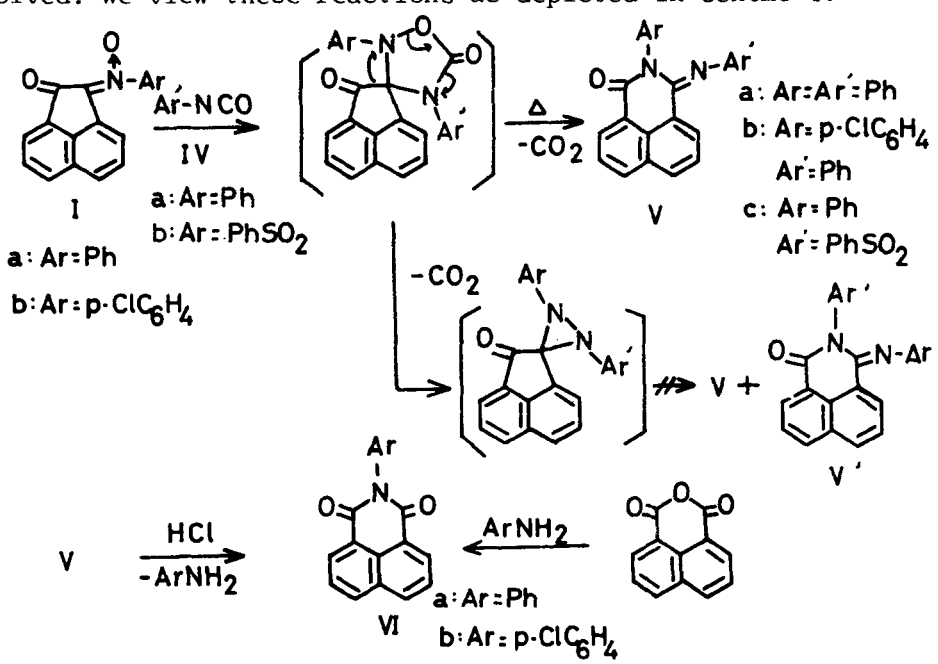
Cycloaddition Reaction of Nitrones (I) with Isocyanates (IV).

It was anticipated that the cycloadducts, 3-spiro-1,2,4-oxadiazolidin-5-ones, might act as precursors of azomethine imines in fashion similar to spiroisoxazolidines.[4]

When a xylene solution of Ia and phenyl isocyanate (IVa) was refluxed for 10 hr, a 72% yield of Va as orange yellow prisms, mp 256-257°, was obtained. The elemental analysis and mass spectral data (M^+ m/e 348) of Va did not agree with the expected spiro-1,2,4-oxadiazolidin-5-one, but fitted the molecular formula $C_{24}H_{16}N_2O$ which would arise from the elimination of carbon dioxide from a 1:1 adduct of Ia and IVa. The IR spectrum of Va showed the band at 1684 cm^{-1} ascribable to an amide I absorption.[13] The hydrolysis of Va with 15% hydrochloric acid in methanol afforded N-phenyl-1,8-naphthalimide (VIa) as colorless prisms, mp 203°, in 83% yield; it was

identified by comparison with an authentic sample prepared from the reaction of 1,8-naphthalic anhydride with aniline in acetic acid.

In order to clarify the reaction pathway, the reaction of Ib with IVa was investigated as two isomeric products might be formed in this case (Scheme 4). However, only Vb, mp 200-201°, could be isolated as yellow needles in 68% yield. The structure of Vb was established by its hydrolysis to N-(p-chlorophenyl)-naphthalimide (VIb), mp 274-275° (dec.). This result quite clearly shows that a spirodiaziridine intermediate was not involved. We view these reactions as depicted in Scheme 4.[14]



Scheme 4

The above pathway was supported by the following experiment. When a solution of Ia and benzene sulfonylisocyanate (IVb) in benzene was reacted at room temperature, Vc, mp 294-295° (dec.), was obtained as colorless prisms in 66% yield. Upon hydrolysis of Vc, VIa was obtained. Therefore, it seems

reasonable to assume that the cycloadducts, 3-spiro-1,2,4-oxadiazolidin-5-ones, are easily decomposed on heating and ring expansion reaction occurs; in all cases the substituent Ar of I is orientated in the imide nitrogen and the substituent Ar' of isocyanates IV in the exo imino nitrogen.

EXPERIMENTAL[16]

Materials.-- Nitrosobenzene (IIa),[17] p-chloronitrosobenzene (IIb),[18] p-N,N-dimethylaminonitrosobenzene (IIc)[19] and 2-diazoacenaphthenone (III)[20] were prepared by the reported methods. The isocyanates were purchased from Tokyo Kasei Co., Tokyo, Japan.

Preparation of α-ketonitrones (I).-- The general procedure used is illustrated with the reaction of III with IIa. A solution of III (900 mg) and IIa (500 mg) in dry xylene (30 ml) was warmed (oil bath temperature, 130°) for 2 hr, and then concentrated to about 15 ml in vacuo. The reaction mixture was then filtered to remove the precipitated crystals, which on recrystallization from ligroin (bp 80-110°) afforded 1.07 g (85%) of Ia, mp 198-199° (dec.), as pale yellow needles.

Anal. Calcd. for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13.
Found: C, 79.28; H, 3.62; N, 5.32.

IR: 1713 (C=O), 1296 cm^{-1} ($>C=\overset{+}{N}-\bar{O}$). Mass spectrum: m/e 273 (M^+).

Ib (Ar=p-ClC_6H_4): yield, 70%. Mp 215-216°. Yellow needles from EtOH.

Anal. Calcd. for $C_{18}H_{10}NO_2Cl$: C, 70.24; H, 3.26; N, 4.56.

Found: C, 70.10; H, 3.00; N, 4.81.

Mass spectrum: m/e 307 (M^+).

Ic (Ar=p-$(Me)_2NC_6H_4$): yield, 80%. Mp 182-183° (dec.). Reddish orange prisms from ligroin.

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86.

Found: C, 76.01; H, 5.34; N, 8.79.

Mass spectrum: m/e 316 (M^+).

A solution of Ia (50 mg) in methanol (20 ml) was refluxed for 2 hr with 1 ml of 15% hydrochloric acid. Filtration gave 29 mg (86%) of acenaphthenequinone, mp 258-260°.

Reaction of α-ketonitrones (I) with phenyl isocyanate (IVa).-- The general procedure used is illustrated with the reaction of Ia with IVa. A solution of Ia (300 mg) and IVa (260 mg) in dry xylene (20 ml) was refluxed for 10 hr. Evaporation of the solvent, followed by addition of 20 ml of petroleum benzine (bp 42-60°), and filtration gave yellow crystals, which on recrystallization from acetonitrile afforded 310 mg (72%) of Va, mp 256-257° (dec.), as orange yellow prisms.

Anal. Calcd. for $C_{24}H_{16}N_2O$: C, 82.74; H, 4.63; N, 8.04.

Found: C, 82.70; H, 4.40; N, 8.21.

IR: 1684 cm^{-1} (C=O). Mass spectrum: m/e 348 (M^+).

Vb (Ar=p-ClC_6H_4): yield, 68%. Mp 200-201° (dec.). Yellow needles from ethanol.

Anal. Calcd. for $C_{24}H_{15}N_2OCl$: C, 75.29; H, 3.92; N, 7.32.

Found: C, 75.41; H, 3.62; N, 7.52.

IR: 1690 cm^{-1} (C=O). Mass spectrum: m/e 382 (M^+).

Reaction of α-ketonitrone (Ia) with benzene sulfonylisocyanate (IVb).-- A benzene solution of Ia (300 mg) was slowly added to

10 ml of benzene solution of IVb (200 mg) with continuous stirring; heat was evolved. The mixture was stirred for 1 hr at room temperature, then the pale yellow crystals which had precipitated, were filtered and recrystallized from ligroin (bp 80-110°) to give 300 mg (66%) of Vc, mp 294-295° (dec.), as colorless prisms.

Anal. Calcd. for $C_{24}H_{16}N_2O_3S$: C, 69.90; H, 3.91; N, 6.79.
Found: C, 70.14; H, 3.69; N, 6.48.

Hydrolysis of V.-- A solution of Va (100 mg) in methanol (15 ml) was refluxed for 2 hr with 10 ml of 15% hydrochloric acid. After standing overnight, the precipitated product was collected and recrystallized from methanol to give 65 mg (83%) of N-phenyl-1,8-naphthalimide (VIa), mp 203° (dec.), as colorless needles; mass spectrum, m/e 273 (M^+). VIa was also obtained in 86% yield from the hydrolysis of Vc in ethanol. Similarly, the hydrolysis of Vb with conc. hydrochloric acid in ethanol, gave N-(p-chlorophenyl)-1,8-naphthalimide (VIb), mp 274-275° (dec.), as colorless needles.

Anal. Calcd. for $C_{18}H_{10}NO_2Cl$: C, 70.24; H, 3.26; N, 4.56.
Found: C, 70.64; H, 3.03; N, 4.68.

Mass spectrum:\m/e 307 (M^+).

These compounds VIa and VIb were identical with authentic samples prepared from the reaction of 1,8-naphthalic anhydride with corresponding aniline by reflux in acetic acid.

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(Received May 30, 1972; in revised form October 24, 1972)