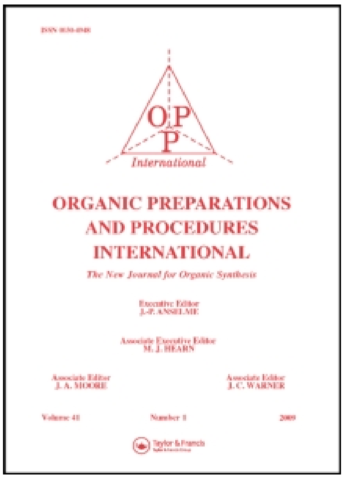


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

STUDIES OF ACENAPHTHENE DERIVATIVES. XXIX. THE REACTION OF CARBONYL-STABILIZED SULFONIUM AND PHOSPHONIUM YLIDES WITH 2-DIAZOACENAPHTHENONE

Otohiko Tsuge[a]; Masahiro Koga[ab]
[a] Research Institute of Industrial Science, Kyushu University, Fukuoka, Japan [b] Central Research Institute, Teizin Co., Ltd, Hino, Tokyo

To cite this Article Tsuge, Otohiko and Koga, Masahiro(1975) 'STUDIES OF ACENAPHTHENE DERIVATIVES. XXIX. THE REACTION OF CARBONYL-STABILIZED SULFONIUM AND PHOSPHONIUM YLIDES WITH 2-DIAZOACENAPHTHENONE', Organic Preparations and Procedures International, 7: 4, 173 — 177

To link to this Article: DOI: 10.1080/00304947509355141

URL: http://dx.doi.org/10.1080/00304947509355141

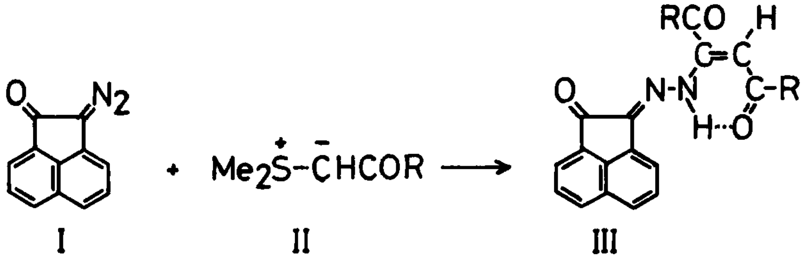
ORGANIC PREPARATIONS AND PROCEDURES INT. 7(4), 173-177 (1975)

STUDIES OF ACENAPHTHENE DERIVATIVES. XXIX.[1]

THE REACTION OF CARBONYL-STABILIZED SULFONIUM AND PHOSPHONIUM YLIDES WITH 2-DIAZOACENAPHTHENONE

Otohiko Tsuge* and Masahiro Koga**
Research Institute of Industrial Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812, Japan

We have recently shown[2] that the reactions of 2-diazoacenaphthenone (I) with olefins and with aroyl isocyanates under mild conditions proceed via a 1,3-cycloaddition of the diazomethane moiety of I to the unsaturated bonds, followed by the elimination of nitrogen and concurrent recyclization to afford spiro-cyclopropanes and spiro-oxazolidinones respectively. Thus, in the cycloaddition reaction not involving the ketocarbene, I behaves exclusively as a 1,3-dipole. It thus was of interest to study the reaction of I with carbonyl-stabilized sulfonium and phosphonium ylides.

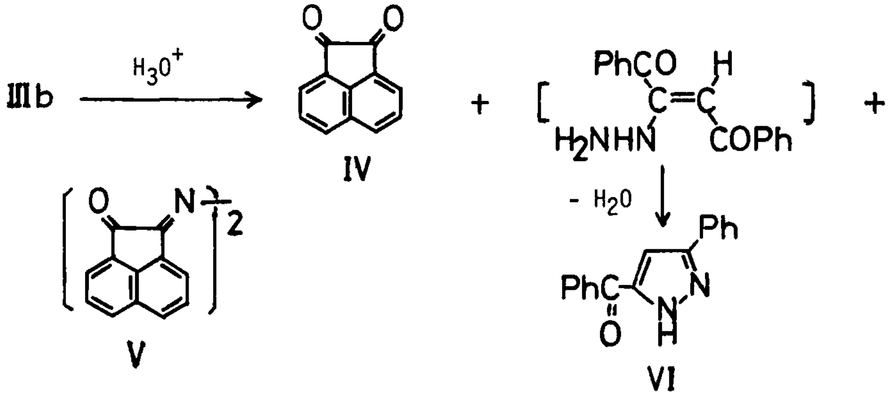


(1)

a: R = OEt; b: R = Ph; c: R = p-BrC$_6$H$_4$

Diazoketone I reacted with two moles of ethyl (dimethylsulfuranilidene)acetate (IIa) to give a product IIIa, mp 148-149°, as green yellow needles in a 73% yield. Even when equimolar IIa was used, only a low yield of IIIa was obtained. The molecular formula of IIIa and its spectral data agreed with that of the compound derived from a 1:2 adduct of I and IIa with the elimination of two moles of dimethylsulfide. From these observations, IIIa was assumed to be acenaphthenequinone N-1,2-bis(ethoxycarbonyl)vinyl monohydrazone whose configuration can be reconciled only with that depicted in equation 1. Similarly, the reaction of I with dimethylsulfonium phenacylide (IIb) and p-bromophenacylide (IIc) afforded the corresponding hydrazone IIIb and IIIc in 65 and 67% yields, respectively.

Hydrolysis of IIIb with hydrochloric acid in tetrahydrofuran gave a mixture of acenaphthenequinone (IV) and acenaphthenequinoneketazine (V) and 3(5)-benzoyl-5(3)-phenylpyrazole (VI). The formation of IV and VI from IIIb supported strongly the proposed structure for IIIb as illustrated below, although ketazine V appeared to be formed by the condensation of IV and acenaphthenequinone monohydrazone. Similarly, the reaction of diazoketone I with ethoxycarbonyltriphenylphosphonium methylide (VIIa) and triphenylphosphonium phenacylide (VIIb) afforded the corresponding hydrazones IIIa and IIIb, respectively.



$$\mathrm{I} \quad + \quad \underset{\mathrm{VII}}{\mathrm{Ph_3\overset{+}{P}\text{-}\overset{-}{C}HCOR}} \longrightarrow \mathrm{III}$$

a: R = OEt; b: R = Ph

EXPERIMENTAL

All the melting points are uncorrected. The NMR spectra were determined at 60 MHz with a 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 at 70 eV. The IR spectra were measured as KBr pellets.

Reaction of Diazoketone I with Carbonyl-stabilized Ylide II. The procedure used is illustrated with the reaction of I with ethyl (dimethylsulfuranilidene)acetate (IIa).

A solution of ylide IIa was prepared by the following procedure. To a stirred suspension of dimethylethoxycarbonylsulfonium bromide (3.5 g, 1.5 x 10^{-2} mol) in 50 ml of THF, sodium hydride (1.0 g, 2 x 10^{-2} mol) was added a 50% mineral oil dispersion in one portion. After the mixture was then stirred at room temperature for 6 hr, it was filtered to remove the sodium bromide, thus giving a yellow solution of IIa.

The solution of IIa was added to a solution of diazoketone I[3] (1.16 g, 6 x 10^{-3} mol) in 30 ml of THF at -60°, and the mixture was warmed to room temperature and then stirred for 1.5 hr. The mixture was evaporated *in vacuo* to leave a residue, which was triturated with ethanol to give 1.6 g (73%) of greenish yellow crystals, mp 137-140°. Recrystallization from petroleum ether (bp 80-110°) afforded pure hydrazone IIIa, mp 148-149°, as greenish yellow needles.

Anal. Calcd for $C_{20}H_{18}N_2O_5$: C, 65.56; H, 4.95; N, 7.65.

Found: C, 65.83; H, 4.87; N, 7.59.

Mass spectrum m/e : 366 (M^+). IR cm^{-1}: 3140 (NH), 1745, 1695, 1680 (C=O). NMR ($CDCl_3$) δ: 1.32, 1.45 (each 3H, t, $C\underline{H}_3$), 4.35, 4.45 (each 2H, q, $C\underline{H}_2$), 5.28 (1H, s, =C$\underline{H}$), 7.5-8.2 (6H, m, aromatic protons), 14.47 (1H, broad, N$\underline{H}$).

Similarly, I reacted with 2.5 equivalents of ylides IIb and IIc, generated from the corresponding bromide[4] and sodium hydride, to give the hydrazones IIIb and IIIc in 65 and 67% yields respectively.

IIIb: mp 182-183°, orange needles.

Anal. Calcd for $C_{28}H_{18}N_2O_3$: C, 78.12; H, 4.22; N, 6.51.
Found: C, 78.17; H, 4.22; N, 6.53.

Mass spectrum m/e: 430 (M^+). IR cm^{-1}: 1690, 1670 (C=O). NMR ($CDCl_3$) δ: 6.34 (1H, s, =CH), 7.3-8.3 (16H, m, aromatic protons), 15.77 (1H, broad, NH).

IIIc: mp 252-253°, greenish yellow needles. IR cm^{-1}: 1698, 1690 (C=O).

Anal. Calcd for $C_{28}H_{16}N_2O_3Br_2$: C, 57.14; H, 2.72; N, 4.76.
Found: C, 57.38; H, 2.55; N, 4.84.

Hydrolysis of IIIb. After IIIb (0.3 g) was refluxed with conc. HCl (5 ml) in 20 ml of THF for 1 hr, the mixture was evaporated *in vacuo* to leave a residue. The residue was triturated with conc. HCl (15 ml), and filtration afforded 70 mg of yellow crystals, which were found to be a mixture of acenaphthenequinone (IV) and acenaphthenequinoneketazine (V) by the IR spectrum.

The filtrate was poured into water to give 60 mg of colorless crystals, mp 168-170°. Recrystallization from petroleum ether (bp 80-110°) afforded 3(5)-benzoyl-5(3)-phenylpyrazole (VI), mp 170-171°, lit.[5] mp 169.5-170.5°, identical with an authentic sample.[5]

Reaction of I with triphenylphosphonium phenacylide (VIIb). After a solution of I (0.67 g, 3.45 x 10^{-3} mol) and ylide VIIb[6] (1.4g, 3.7 x 10^{-3} mol) in 50 ml of benzene was refluxed for 10 hr, the mixture was evaporated *in vacuo* to leave a residue. The residue was extracted with 20 ml of carbon tetrachloride to leave 0.29 g of unreacted I. The extract was evaporated *in vacuo* and then a solution of the residue was chromatographed on silica gel to give 0.4 g of I and 0.44 g (29.6%) of IIIb.

Similarly, I (0.75 g, 3.75 x 10^{-3} mol) reacted with ethoxycarbonyltriphenylphosphonium methylide (VIIa)[7] (1.55g, 4.58 x 10^{-3} mol) to afford 0.35 g of I and 0.1 g (7%) of IIIa.

REFERENCES

*To whom inquiries should be addressed.

**Present address: Central Research Institute, Teizin Co., Ltd. Hino, Tokyo.

1. Part XXVIII: O. Tsuge, M. Koga, and I. Shinkai, Tetrahedron, 29, 259 (1973).
2. O. Tsuge, I. Shinkai, and M. Koga, J. Org. Chem., 36, 745 (1971); Bull. Chem. Soc. Japan, 45, 3657 (1972).
3. M. P. Cava, R. L. Little, and D. R. Napier, J. Am. Chem. Soc., 80, 2257 (1958).
4. K. W. Ratts and A. N. Yao, J. Org. Chem., 31, 1185 (1966).
5. D. G. Farnum and P. Yates, J. Am. Chem. Soc., 84, 1399 (1962).
6. F. Ramirez and S. Dershowitz, J. Org. Chem., 22, 41 (1957).
7. D. B. Denney and S. T. Ross, ibid., 27, 998 (1962).

(Received May 19, 1975; in revised form July 11, 1975)