A Convenient One-Pot Synthesis of Acenaphthenequinones from 1-Acenaphthenones by NBS-DMSO Oxidation

Jiro TATSUGI,* Shigeo OKUMURA, and Yasuji IZAWA
Department of Applied Chemistry, Aichi Institute of Technology, Yakusa, Toyota 470-03
(Received February 3, 1986)

Synopsis. Acenaphthenequinone was obtained in 95% yield when the reaction of 1-acenaphthenone with *N*-bromosuccinimide was carried out in dimethyl sulfoxide at room temperature. Under similar conditions, several acenaphthenequinones were prepared from the corresponding 1-acenaphthenones in good yields.

Acenaphthenequinones are interesting with regard to photochemistry,[1] synthetic photochemistry,[2] and versatile synthetic intermediates to polycyclic hydrocarbons[3] and heterocyclic compounds.[4] The most widely used methods for the preparation of acenaphthenequinones are the oxidation of acenaphthenes with various oxidizing agents[5] and the Friedel-Crafts reaction of naphthalenes with oxalyl dichloride.[6] However, the yields of acenaphthenequinones by these methods are low due to the formation of by-products such as naphthalic anhydrides and 1,1′-biacenaphthylidene-2,2′-diones. In the course of our studies on the chemistry of 1-acenaphthenones, we found that the reaction of 1-acenaphthenones with *N*-bromosuccinimide (NBS) in dimethyl sulfoxide (DMSO) gave the corresponding acenaphthenequinones in good yields. We now report on a convenient preparation of acenaphthenequinones using NBS in DMSO.

1-Acenaphthenones (**1**) and NBS were dissolved in anhydrous DMSO. The mixture was stirred at room temperature under nitrogen atmosphere until all the substrate had been consumed to give the corresponding acenaphthenequinones (**2**) in good yields. The oxidation products were identified by their melting points, and by IR, ^{1}H NMR, and MS spectra.

The reaction of **1** with NBS in DMF gave only 5-bromo-1-acenaphthenone in 84% yield and with *N*-chlorosuccinimide (NCS) in DMF gave only 5-chloro-1-acenaphthenone in 47% yield. By contrast, 5-halo-1-acenaphthenone could not be isolated at all when the reaction was carried out in DMSO at room temperature. The results of the reaction of **1** with several halogenating agents, such as NBS, *N*-bromoacetamide (NBA), 2-oxopyrrolidinium tribromide (OB), phenyltrimethylammonium perbromide (PTAB), pyridinium tribromide (PB), 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (TCD), iodine, bromine, and NCS in DMSO at room temperature are summarized in Table 1. As shown in Table 1, the reactions gave **2** in good to excellent yields except for that with NCS. The chlorination of DMSO took place exclusively when the reaction of **1** with NCS was carried out in DMSO at room temperature. This result suggests that NCS reacts with DMSO faster than with **1**.[7] The reactions of **1** with various molar ratios of NBS were carried out in order to find the most suitable reaction conditions for the preparation of **2**. The results are summarized in Table 2. The optimum yield was achieved when the reaction was carried out using an equivalent of NBS to **1** at room temperature for 24 h. The oxidation of some substituted 1-acenaphthenones (**1a—l**) to the corresponding acenaphthenequinones (**2a—l**) was carried out under similar conditions. The results are summarized in Table 3. As shown in Table 3, the compounds **1a—l** were oxidized into **2a—l** in good yields. In the cases of **1j**, **1k**, and **1l**, however, the corresponding 1,1′-biacenaphthyliden-2-ones were produced as by-products in 22, 5, and 6% yields, respectively.

Table 1. Raction of 1-Acenaphthenone with Several Halogenating Agents in DMSO at Room Temperature

Halogenating agents	Yield[a] of **2**/%
NBS	95
NBA	95
OB[b]	96
PTAB[c]	94
PB[d]	98
TCD[e]	77
I_2	82
Br_2	93
NCS	0

a) Isolated yield. b) 2-Oxopyrrolidinium tribromide. c) Phenyltrimethylammonium perbromide. d) Pyridinium tribromide. e) 2,4,4,6-Tetrabromo-2,5-cyclohexadien-1-one.

Table 2. Reaction of 1-Acenaphthenone with Various Molar Ratios of NBS in DMSO

1	NBS	Reaction		Yield[a] of **2**/%
mmol	mmol	Temp/°C	Time/h	
5	5	r.t	24	95
5	2.5	r.t	48	88
5	1.25	r.t	110	21
5	1.25	50	24	75
5	1.25	100	5	81
5	0.63	r.t	110	6

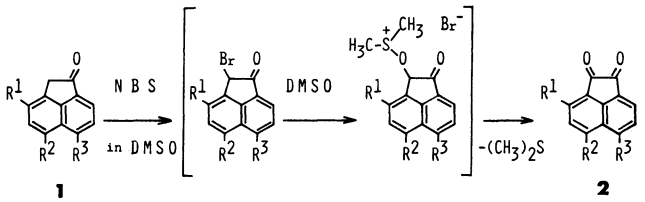
a) Isolated yield.

To ascertain the reaction pathways leading to the quinones, the DMSO-oxidation of 2-bromo-1-acenaphthenone was carried out. The reaction of **1** with NBS in dichloromethane gave 2-bromo-1-acenaphthenone[12] in 59% yield, and the reaction of the resulting 2-bromo-1-acenaphthenone with DMSO at room temperature for 24 h afforded **2** in quantitative yield. On the basis of these facts and the results for related reactions,[13] it is clear that the course of the reaction involves α-bromination of **1** with NBS and then oxidation[14] of the resultant 2-bromo-1-acenaphthenones with DMSO to (2-oxo-1-acenaphthenyloxy)sulfonium bromides which then decomposes to give **2** and dimethyl sulfide as shown in Scheme 1.

Table 3. Reaction of 1-Acenaphthenones with NBS in DMSO at Room Temperature

1	R^1	R^2	R^3	Yield[a] of 2/%	Mp(θ_m/°C) (lit.)	
a	H	H	H	95	259—260	(260—261)[5]
b	CH_3	H	H	85	204—206	
c	H	CH_3	H	74	192—194	
d	C_2H_5	H	H	75	128—129	
e	H	H	C_2H_5	77	131—132	(117—119)[8]
f	H	Cl	H	90	216—217	(212—213)[9]
g	H	H	Cl	88	216—217	(212—213)[9]
h	H	Br	H	93	244—246	(246)[10]
i	H	H	Br	94	244—246	(246)[10]
j	H	NO_2	H	67	214—215	(218)[11]
k	H	CN	H	83	258—260	
l	H	H	CN	84	258—260	

a) Isolated yield.



1 2

Scheme 1.

In conclusion, the advantages of the present preparation of **2** using NBS in DMSO are: 1) the yields of 2 are satisfactory, 2) the experimental set up and work up are exceedingly simple, 3) the reactions are performed under mild conditions, 4) the reagents are easy to handle and are commercially available, and 5) there is no need to isolate the α-bromo ketone intermediate, which is somewhat unstable, from the reaction mixture.

Experimental

Melting points are uncorrected. IR, ^{1}H NMR, and MS spectra were recorded on a shimadzu IR-440, a JEOL JNM-PMX 60SI, and a Hitachi M-80B spectrometers, respectively.

Materials. DMSO was fractionated over CaH_2. NBS was purified by recrystallization from water. 1-Acenaphthenone (**1a**),[15] 3-methyl-1-acenaphthenone (**1b**),[16] 5-methyl-1-acenaphthenone (**1c**),[16] 3-ethyl-1-acenaphthenone (**1d**),[17] 5-bromo-1-acenaphthenone (**1h**),[18] 6-bromo-1-acenaphthenone (**1i**),[18] and 5-nitro-1-acenaphthenone (**1j**)[19] were prepared as described in the literature. 6-Ethyl-1-acenaphthenone (**1e**) and 6-chloro-1-acenaphthenone (**1g**) were prepared from the corresponding 5-substituted acenaphthenes by a similar method to the preparation of **1i**.[18]

1e: 35% yield; mp 67—68 °C. (petroleum ether); IR (KBr) 1710 (C=O), 1603, 1495, 835, 765, and 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.37 (t, 3H, *J*=7.6 Hz), 3.11 (q, 2H, *J*=7.6 Hz), 3.69 (s, 2H), and 7.3—7.9 (m, 5H); MS *m/z* 196 (M^+). **1g**: 32% yield; mp 142—143 °C (EtOH); IR (KBr) 1725 (C=O), 1485, 840, 763, and 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.72 (s, 2H), and 7.2—8.3 (m, 5H); MS *m/z* 202 (M^+) and 204 (M^++2). 5-Chloro-1-acenaphthenone (**1f**) was prepared from **1a** and NCS in DMF at room temperature for 2 d. **1f**: 47% yield; mp 173—174 °C (EtOH); IR (KBr) 1705 (C=O), 1390, 825, and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3,77 (s, 2H), and 7.3—8.4 (m, 5H), MS *m/z* 202 (M^+) and 204 (M^++2). 5-Cyano-1-acenaphthenone (**1k**) and 6-cyano-1-acenaphthenone (**1l**) were prepared via the corresponding cyano-1-acenaphthenols which were obtained by Rosenmund-von Braun synthesis.[20] **1k**: 30% yield (based on 5-bromo-1-acenaphthenol); mp 263—265 °C (EtOH), IR (KBr) 2210 (CN), 1718 (C=O), 1495, 1385, 820, and 770 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=3.98 (s, 2H), and 7.7—8.4 (m, 5H); MS *m/z* 193 (M^+). **1l**: 37% yield (based on 6-bromo-1-acenaphthenol); mp 157—158 °C (EtOH); IR (KBr) 2210 (CN), 1720 (C=O), 850, 785, and 660 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=3.93 (s, 2H), and 7.6—8.7(m, 5H); MS *m/z* 193 (M^+).

General Procedure. A mixture of 1-acenaphthenone (**1**) (5 mmol), NBS (5 mmol) and anhydrous DMSO (5 ml) was stirred at room temperature under nitrogen atmosphere. The progress of the reaction was monitored by TLC on silica gel using dichloromethane as eluent. After disappearance of **1**, 100 ml of water was added to the resultant mixture, and the precipitates were collected by filtration and then washed with water. The product was recrystallized from dichloromethane.

Spectral data of acenaphthenequinones are as follows.

3-Methylacenaphthenequinone (2b). IR (KBr) 1720 and 1738 cm^{-1}, (C=O); ^{1}H NMR ($CDCl_3$) δ=2.73 (s, 3H), and 6.8—8.0 (m, 5H); MS *m/z* 196 (M^+).

5-Methylacenaphthenequinone (2c). IR (KBr) 1720 and 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.83 (s, 3H), and 7.3—8.4 (m, 5H); MS *m/z* 196 (M^+).

3-Ethylacenaphthenequinone (2d). IR (KBr) 1720 and 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.37 (t, 3H, *J*=8 Hz), 3.33 (q, 2H, *J*=8 Hz), and 7.6—8.3 (m, 5H); MS *m/z* 210 (M^+).

5-Ethylacenaphthenequinone (2e). IR (KBr) 1720 and 1737 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.37 (t, 3H, *J*=8 Hz), 3.07 (q, 2H, *J*=8 Hz), and 7.4—8.2 (m, 5H); MS *m/z* 210 (M^+).

5-Cyanoacenaphthenequinone (2k). IR (KBr) 1730, 1745 (C=O), and 2250 cm^{-1} (CN); ^{1}H NMR (DMSO-d_6–$CDCl_3$) δ=8.0—8.7 (m, 5H); MS *m/z* 207 (M^+).

This work was supported by the Nitto Kohgyoh Foundation for the promotion of science, which is gratefully acknowledged.

References

1) Tai-Shan Fang and L. A. Singer, *J. Am. Chem. Soc.*, **100**, 6276 (1978); Ja-Young Koo and G. B. Schuster, *J. Org. Chem.*, **44**, 847 (1979).

2) H. Takeshita, A. Mori, M. Funakura, and H. Mametsuka, *Bull. Chem. Soc. Jpn.*, **50**, 315 (1977).

3) H. W. Whitlock Jr., *J. Org. Chem.*, **29**, 3129 (1964); A. Minsky and M. Rabinovitz, *Synthesis*, **1983**, 497.

4) Recent examples: S. Mataka, K. Takahashi, T. Imura, and M. Tashiro, *J. Heterocyclic Chem.*, **19**, 1481 (1982); J. A.-Builla, G. G. Trigo, J. Ezquerra, and M. E. Fombella, *ibid.*, **22**, 681 (1985); J. J. Hlavka, P. Bitha, Y. Lin, and T. Strohmeyer, *ibid.*, **22**, 1317, (1985).

5) C. F. H. Allen and J. A. VanAllan, *Org. Synth.*, Coll.

Vol., III, 1 (1955).
6) R. Lesser and G. Gad, *Ber.*, **60**, 243 (1927); J. Cason, A. Weiss, and S. A. Monti, *J. Org. Chem.*, **33**, 3404 (1968).
7) G. Tsuchihashi and K. Ogura, *Bull. Chem. Soc. Jpn.*, **44**, 1726 (1971).
8) H. E. Nursten, and A. T. Peters, *J. Chem. Soc.*, **1950**, 2389.
9) S. K. Guha, *Chem. Ber.*, **95**, 1569 (1962).
10) F. Dewhurst and P. K. J. Shah, *J. Chem. Soc. (C)*, **1970**, 1737.
11) F. M. Rowe and J. S. H. Davies, *J. Chem. Soc.*, **117**, 1344 (1920).
12) S. Hauptmann, M. Scholz, I. Stopp, and U. Stopp, *Z. Chem.*, **7**, 351 (1967).
13) E. Schipper, M. Cinnamon, L. Rascher, Y. H. Chiang, and W. Oroshnik, *Tetrahedron Lett.*, **1968**, 6201; N. Furukawa, T. Akasaka, T. Aida, and S. Oae, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 372.
14) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957); N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).
15) L. F. Fieser and J. Cason, *J. Am. Chem. Soc.*, **62**, 432 (1940).
16) I. D. Entwistle and R. A. W. Johnstone, *J. Chem. Soc. (C)*, **1968**, 1818; G. Lock, and R. Schneider, *Chem. Ber.*, **91**, 1770 (1958).
17) W. E. Bachmann and J. C. Sheehan, *J. Am. Chem. Soc.*, **63**, 2598 (1941).
18) G. Kalopissis, *J. Recherches Centre Natl. Recherche Sci., Labs. Bellevue (Paris)*, **22**, 1 (1953).
19) Y. V. Samusenko, V. I. Magda, A. P. Karishin, G. F. Dzhurka, and N. F. Grineva, *Zh. Khim.*, **1979**, 1971.
20) L. Friedmann and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).