BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 181—185 (1969)

Studies of Acenaphthene Derivatives. XVI.[1] The Wittig Reaction with Acenaphthenequinone[*1]

Otohiko TSUGE, Masashi TASHIRO and Ichiro SHINKAI

Research Institute of Industrial Science, Kyushu University, Hakozaki, Fukuoka

(Received April 25, 1968)

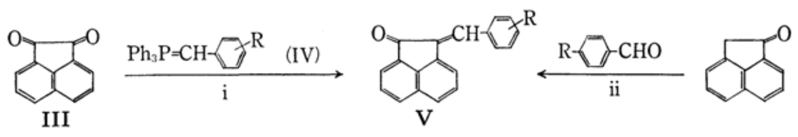
The reactions of acenaphthenequinone (III) with several Wittig reagents have been studied. When III was reacted with equimolar amounts of benzylidenetriphenylphosphoranes (IV) at room temperature, the corresponding benzylideneacenaphthenones (V) were obtained in fairly good yields, but the reactions of benzil and phenanthrenequinone with IV did not take place under similar conditions. The reaction of III with two equivalents of IV under severe conditions afforded only V, and no dibenzylidene compounds were obtained. The reaction of III with resonance-stabilized phosphoranes, such as acetonylidene-, phenacylidene- and *p*-chlorophenacylidenephosphoranes, afforded the expected α,β-unsaturated ketones. In the reaction with ethoxycarbonylmethylenephosphorane, two stereo-isomeric ethoxycarbonylmethyleneacenaphthenones, which were also obtained from the reaction with diethyl ethoxycarbonylmethylphosphonate, were formed. The structures of the isomers were confirmed on the basis of NMR, UV, and mass spectral studies. Methylenephosphorane reacted with III to give methyleneacenaphthenone in a poor yield. On the contrary, the reaction with ethylidenephosphorane gave bis-2,2′-methyleneacenaphthenone, which was also formed by the reaction of acenaphthenone with glyoxal, in a good yield.

It has been shown that the 1,2-bismethylene derivative was obtained in an 85% yield by the Wittig reaction of benzocyclobutenedione with two equivalents of ethoxycarbonylmethylenetriphenylphosphorane at room temperature.[2] On the other hand, Parrick[3] has reported that some α-diketones, such as benzil (I) and phenanthrenequinone (II), will not react with two equivalents of a phosphorane. In both cases, the corresponding monobenzylidene compounds were obtained in low yields from the reaction with benzylidenetriphenylphosphorane at only one carbonyl group.

In earlier papers[4–7] in this series we have found that acenaphthenequinone (III) behaved differently from I and II in some reactions, and it was deduced that one carbonyl group in III is more reactive than that in I or II.

We have little information about the Wittig reaction with III. Accordingly, it will be interesting to investigate whether or not III will be able to react with two equivalents of a phosphorane, and to compare the reactivities of I, II, and III against the phosphorane.

When III was treated with benzylidenetriphenylphosphoranes (IV) in ethanol at room temperature, the corresponding benzylideneacenaphthenones (V) were obtained in fairly good yields. Under similar conditions, however, the reactions of I and II with IV did not take place. Even when two equivalents of IV were used under severe reaction conditions,



III

V

a: R = H, b: R = *p*-CH_3, c: R = *p*-OCH_3 d: R = *p*-Cl,
e: R = *p*-NO_2, f: R = 3,4-Cl_2

---

[1] Part XV: O. Tsuge and M. Tashiro, *Reports of the Research Institute of Industrial Science, Kyushu University*, No. 46, 19 (1967).

[*1] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

[2] M. P. Cava and R. J. Pohl, *J. Am. Chem. Soc.*, **82**, 5242 (1960).

[3] J. Parrick, *Can. J. Chem.*, **42**, 190 (1964).

[4] O. Tsuge and M. Tashiro, This Bulletin, **36**, 970 (1963).

[5] O. Tsuge and M. Tashiro, *ibid.*, **38**, 399 (1965).

[6] O. Tsuge and M. Tashiro, *ibid.*, **39**, 2477 (1966).

[7] O. Tsuge, M. Tashiro and H. Yamashita, *Reports of the Research Institute of Industrial Science, Kyushu University*, No. 46, 11 (1967).

TABLE 1. BENZYLIDENEACENAPHTHENONES (V)

V		Yield, %		Mp,°C (From solvent)	Appearance	IR (C=O) cm^{-1}	Microanalyses, %					
							Found			Calcd		
	R	i	ii				C	H	N	C	H	N
a	H	90	84	120 (MeOH)	yellow needles	1700	89.33	4.80	—	89.04	4.72	—
b	*p*-Me	58	68	116 (EtOH)	yellow needles	1705	88.84	5.13	—	88.86	5.22	—
c	*p*-OMe	61	48	114 (EtOH)	yellow needles	1710	83.91	4.89	—	83.90	4.93	—
d	*p*-Cl	91	92	175 (benzene)	pale yellow needles	1710	78.74	3.85	—	78.62	3.79	—
e	*p*-NO_2	81	90	239 (acetone)	brilliant yellow needles	1710	75.89	3.68	4.35	75.74	3.68	4.65
f	3,4-Cl_2	82	—	142 (EtOH)	yellow needles	1700	70.38	3.12	—	70.15	3.08	—

a) UV λ_{max}^{EtOH} mμ (ε): Va 233.6 (49000), 313 (27000); Vd 232.5 (49000), 324 (22000).

b) NMR in $CDCl_3$ (τ): 6.8 (singlet, $OC\underline{H}_3$), 2.5 (multiplet, 10H aromatic protons), 2.2 (singlet, $=C\underline{H}-$).

c) Reported mp 113°C (J. W. Ager, F. A. Fastwood and R. Robinson, *Tetrahedron, Suppl.* **7**, 277 (1966)).

TABLE 2. CARBONYLMETHYLENE ACENAPHTHENONES (VII)

VII		Reaction time (min)	Yield (%)	Mp, °C (solvent)	Appearance	IR, cm^{-1}	Microanalyses, %			
							Found		Calcd	
	R						C	H	C	H
a	Me	30	45	117—119 (CH*)	yellow needles	1710, 1675 (C=O) 1620 (C=C)	81.41	4.30	81.06	4.54
b	Ph	30	91	109—110 (EtOH)	yellow needles	1710, 1650 (C=O) 1620 (C=C)	84.43	4.20	84.49	4.25
c	*p*-ClC_6H_4	60	49	186—187 (EtOH)	yellow needles	1710, 1650 (C=O) 1620 (C=C)	75.43	3.31	75.47	3.46
d	OEt	120	48	102 (MeOH)	yellow needles	1720, 1700 (C=O) 1640 (C=C)	76.52	4.57	76.18	4.80
d′	OEt		8	97 (MeOH)	white prisms	1720, 1700 (C=O) 1640 (C=C)	76.45	4.43	76.18	4.80

* CH: cyclohexane

IV reacted with only one carbonyl group in III to form V, and no 1,2-dibenzylideneacenaphthenes were obtained.

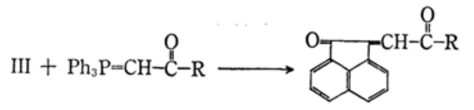
The yields in the reaction of III with equimolar amounts of IV at room temperature for 15 min (method i), and the physical properties and elemental analyses of V are summarized in Table 1.

The compounds V were proved, by admixed melting points and by a study of their infrared spectra as well as by elemental analyses, to be identical with the authentic samples prepared by the reaction of acenaphthenone with the respective benzaldehydes in the presence of sodium hydroxide (method ii). The yields in the method ii are also shown in Table 1.

In general, it is accepted that the reactivity of the phosphorane IV decreases with an increase in the electron-withdrawing power of the substituent. The data in Table 1 show that the phosphoranes with electron-withdrawing substituents, such as the *p*-chloro (IVd), *p*-nitro (IVe), and 3,4-dichloro compounds (IVf), are more reactive than *p*-methyl- (IVb) and *p*-methoxybenzylidene-phosphorane (IVc).

On the basis of the above observations and other data,[4–7] it may be expected that one carbonyl group in III will be able to react with a resonance-stabilized phosphorane.

The reaction of III with acetonylidene- (VIa), phenacylidene- (VIb), *p*-chlorophenacylidene- (VIc), and ethoxycarbonylmethylenetriphenyl-



VI VII

a: R = CH_3, b: R = C_6H_5, c: R = *p*-ClC_6H_4,
d: R = OC_2H_5

phosphorane (VId) at room temperature in ethanol gave the corresponding α,β-unsaturated ketones (VII).

The yields, physical properties, and results of the elemental analyses of VII are listed in Table 2.

In the reaction of III with VId, two compounds, VIId and VIId′, were obtained. The reaction of III with diethyl ethoxycarbonylmethylphosphonate in dioxane in the presence of sodium hydride also gave VIId and VIId′ in 60 and 4% yields respectively.

On the basis of the NMR, mass spectra, and elemental analyses, it is deduced that compounds VIId and VIId′ are cis-trans isomers of ethoxycarbonylmethyleneacenaphthenone. The NMR spectra of VIId and VIId′ are illustrated in Fig. 1.

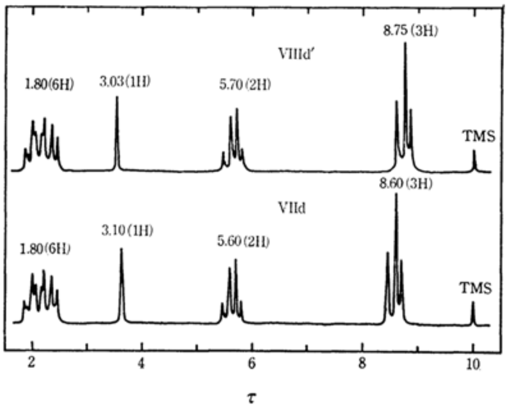
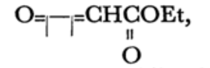
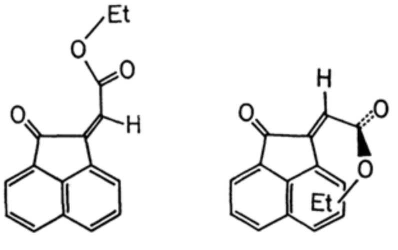


Fig. 1. NMR spectra of VIId and VIId′ in $CDCl_3$.

The vinyl-proton signal of VIId and the methylene-protons signal of VIId′ appeared at a field higher than those of VIId′ and VIId respectively. The differences can be understood in terms of the deshielding effect of the carbonyl group in the ethoxycarbonyl moiety and in terms of the shielding effect of the acenaphthene ring in the respective case.

The ultraviolet spectrum of VIId exhibited an absorption compatible with conjugation, but that of VIId′ indicated the presumable absence of conjugation. In addition, the fragmentation of VIId on electron impact was almost the same as that of VIId′. The mass spectrum of VIId is shown in Fig. 2.

The above observations can be explained by the structures for VIId and VIId′ which are shown in Fig. 3. The moiety,  $\mathrm{O{=}\underset{|}{}\!-\!\underset{|}{}{=}CH\underset{\underset{O}{\|}}{C}OEt}$, in VIId is in a coplanar conformation, while that in VIId′ is not.



VIId VIId′

Fig. 3

The reaction of III with alkylidenetriphenylphosphoranes (VIII) was also investigated.

When III was allowed to react with methylenephosphorane (VIIIa) at room temperature, the expected methyleneacenaphthenone (IX) was obtained in a poor yield, accompanied by a larger amount of resinous material.

The reaction with ethylidenephosphorane (VIIIb) gave yellow needles (X), whose infrared spectrum was similar to that of 2,2′-diacenaphthylidene-

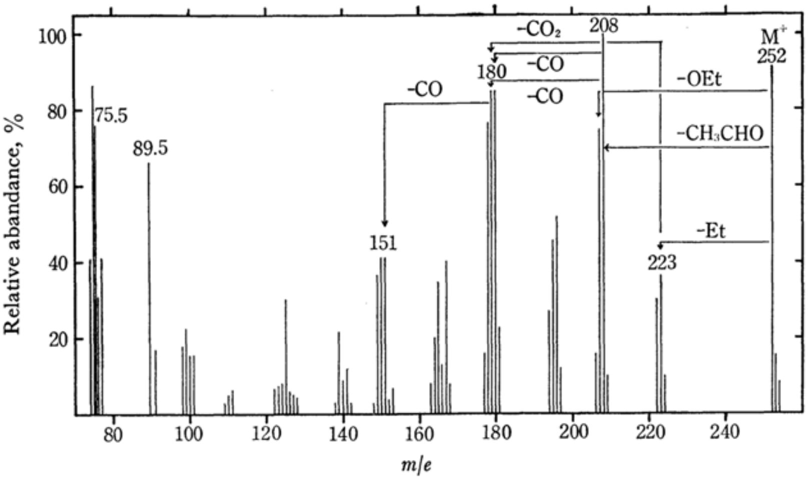
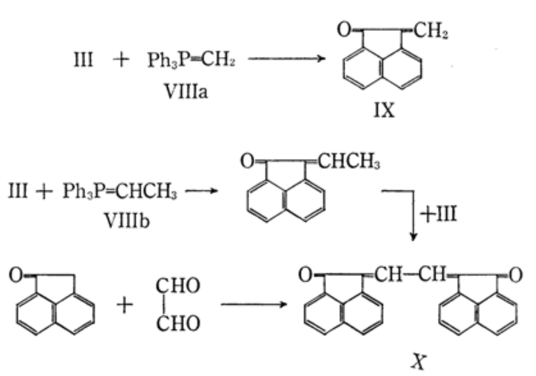


Fig. 2. Mass spectrum of VIId.

1,1′-dione,[8] in an 86% yield. The compound X was proved, by an admixed-melting-point determination and by a study of its infrared spectrum as well as by elemental analysis, to be identical with bis-2,2′-methyleneacenaphthenone prepared by the reaction of acenaphthenone with glyoxal in the presence of sodium hydroxide.

It may be considered that the compound X is formed by the condensation of the expected ethylideneacenaphthenone with a second quinone molecule.



On the other hand, the reaction with propylidenephosphorane (VIIIc) gave a resinous material exclusively under various conditions.

Experimental

All the melting points are uncorrected. The infrared spectra were measured in KBr disks, and the NMR spectra were determined at 60 Mc with a Japan Electron Optics JNM-3H-60 NMR spectrometer, using TMS as the internal reference. The mass spectra were obtained on a Hitachi RMU-6D instrument using a heated inlet, an ionization energy of 70 eV, an inlet temperature of 200—250°C, and a source temperature of 250°C. The elemental analyses were done by Mr. Eiji Shiozaki in our laboratory.

General Method for the Reaction of Acenaphthenequinone (III) with the Benzylidenetriphenylphosphorane (IV). A solution of 0.005 mol of the benzyltriphenylphosphonium bromide in 25 m*l* of absolute ethanol was treated with 5.5 m*l* of a 0.001 M solution of sodium ethoxide in ethanol with continuous stirring under an atmosphere of nitrogen; the orange color of the phosphorane (IV) appeared immediately.

After the solution had been stirred for 10 min, 0.9 g (0.005 mol) of III[9] was added, and then the mixture was stirred at room temperature for 15 min. During this time the mixture turned into a clear solution, except in the reactions with IVd and IVe. The reaction mixture was quenched with 20—30 m*l* of water and then heated on a steam-bath, affording yellow crystals. The crystals were collected by filtration; recrystallization gave the benzylideneacenaphthenone (V).

The yields, physical properties, and results of the elemental analyses of V are listed in Table 1.

General Method for the Reaction of Acenaphthenone with the Benzaldehyde. To a solution of 1.68 g (0.01 mol) of acenaphthenone[10] and 0.012 mol of the benzaldehyde, in 25 m*l* of ethanol, 3 m*l* of a 1 N aqueous solution of sodium hydroxide was added, drop by drop, at room temperature. The mixture was stirred at room temperature for 20 min and then refluxed for another 5 min.

After 5 m*l* of 1 N hydrochloric acid had been added to the reaction mixture, yellow crystals were collected, washed with water, and dried. Recrystallization gave V; the yields are shown in Table 1.

The Reaction with Ethoxycarbonylmethylenetriphenylphosphorane (VId). To a solution of the phosphorane (VId) in 30 m*l* of ethanol which had been prepared by the treatment of ethoxycarbonylmethyltriphenylphosphonium bromide (2.1 g) with sodium ethoxide, 0.9 g of III was added. After the mixture had been stirred at room temperature for 2 hr, filtration gave 0.6 g of a mixture of yellow and white crystals. Fractional recrystallizations from ethanol gave 0.48 g of yellow needles (VIId), mp 102°C, and 0.1 g of white prisms (VIId′), mp 97°C.

VIId: IR (KBr) 1720 (sh, C=O), 1700 cm^{-1} (vs, C=O); UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (logε) 225 (4.73), 232 (4.83), 274 (4.22), 312.8 (4.0).

VIId′: IR (KBr) 1720 (vs, C=O), 1700 cm^{-1} (sh, C=O); UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (logε) 220 (4.46), 260 (3.90).

Similar reactions with other phosphoranes (VIa–VIc) gave the expected α,β-unsaturated ketones (VIIa–VIIc). The yields, physical properties, and results of the elemental analyses of VII are summarized in Table 2.

The Reaction with the Ethoxycarbonylmethylphosphonate Anion. To a suspension of 0.9 g of III and 1.1 g of diethyl ethoxycarbonylmethylphosphonate in 15 m*l* of dioxane, 60 mg of sodium hydride in 50% mineral oil was added, drop by drop, with stirring at room temperature. The mixture was stirred at room temperature for 20 min and then heated at 60—70°C for 5 min. During this time the reaction mixture turned from violet to yellow.

After the reaction mixture had been quenched with 10 m*l* of water, the crystals were collected by filtration. The crystals were then extracted with petroleum benzine (bp 45—60°C), leaving 0.02 g of a solid. After the extract had been concentrated *in vacuo*, the fractional recrystallization of the residue from methanol gave 1.5 g of yellow needles, mp 102°C, and 0.1 g of white prisms, mp 97°C. These compounds were, respectively, identical with the two ethoxycarbonylmethyleneacenaphthenones, VIId and VIId′, which were obtained from the reaction of III with VId.

The Reaction with Methylenetriphenylphosphorane (VIIIa). Into a suspension of 0.9 g of methyltriphenylphosphonium bromide and 0.46 g of III in 20 m*l* of dioxane, 60 mg of sodium hydride in 50% mineral oil was added, drop by drop, with stirring. The reaction mixture was stirred at room temperature

---

[8] O. Tsuge and M. Tashiro, *Reports of the Research Institute of Industrial Science, Kyushu University*, No. 36, 1 (1963).

[9] C. F. H. Allen and J. A. VanAllan, "Organic Syntheses," Coll. Vol. III. p. 1 (1955).

[10] L. F. Fieser and J. Cason, *J. Am. Chem. Soc.*, **62**, 432 (1942).

for 10 hr and then heated at 55—60°C for 1 hr.

The reaction mixture was then quenched with 10 m*l* of water, and the resultant mixture was extracted with 30 m*l* of ether. The extract was washed with 10 m*l* of 50% aqueous ethanol and dried over sodium sulfate. The ether solution was chromatographed on alumina, affording a large amount of resinous materials and 23 mg (5%) of methyleneacenaphthenone (IX) as yellow needles, mp 148°C (decomp.).

Found: C, 86.43; H, 4.35%. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.48%. IR (KBr): 1720 cm^{-1} (C=O).

The reaction with VIIIa, which had been prepared from the phosphonium bromide and sodium ethoxide in ethanol, at room temperature for 30 min gave IX in a 10% yield.

The Reaction with Ethylidenetriphenylphosphorane (VIIIb). To a solution of the phosphorane VIIIb in 30 m*l* of absolute ethanol, which had been prepared from 2.6 g of ethyltriphenylphosphonium bromide and sodium ethoxide, 1.8 g of III was added. After the reaction mixture had then been stirred at room temperature for 10 hr, filtration gave crystals; these crystals were then washed with ethanol and dried, giving 0.48 g (86%) of orange yellow crystals, mp 240—244°C. Recrystallization from dimethylformamide afforded bis-2,2′-methyleneacenaphthenone (X) as orange yellow needles, mp 245°C.

Found: C, 87.41; H, 3.92%. Calcd for $C_{26}H_{14}O_2$: C, 87.10; H, 3.91%. IR (KBr): 1700 cm^{-1} (C=O).

The Reaction of Acenaphthenone with Glyoxal. To a solution of 0.16 g of acenaphthenone and 0.06 g of glyoxal in 10 m*l* of ethanol, 0.5 m*l* of 1 N sodium hydroxide was added, drop by drop, at room temperature; crystals appeared immediately. Filtration gave 0.17 g (96%) of orange yellow crystals which, on recrystallization from dimethylformamide, gave X, mp 245°C. This compound was identical with the product obtained from the reaction of III with VIIIb.