

SYNTHESIS OF SEVERAL SIMPLE PHENAFULVENES AND SOME ADDITION REACTIONS OF  
PHENAFULVENE DERIVATIVES

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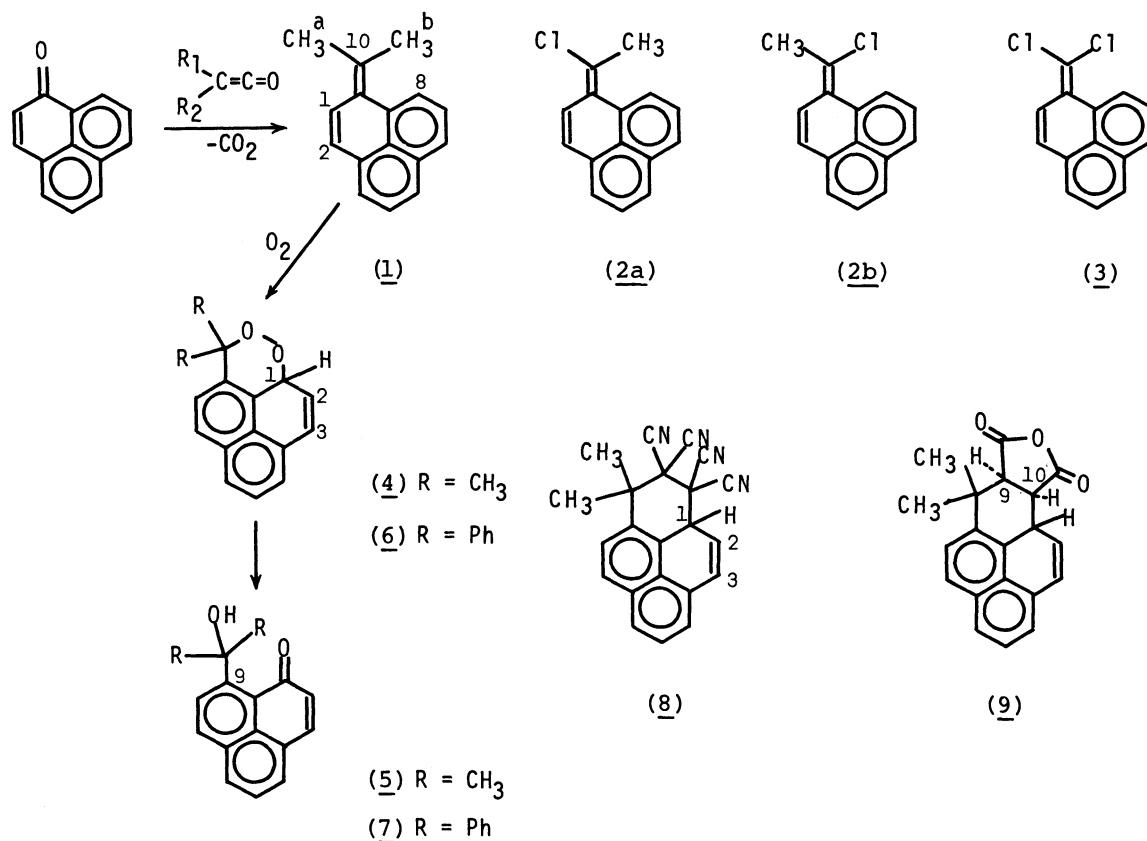
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Phenafulvenes substituted at 10-positions with methyl and/or chloro groups have been synthesized in good yields by the reaction of phenalenone with methyl and/or chloro ketenes. Oxygenations of 10,10-dimethyl- and 10,10-diphenylphenafulvenes afforded epidioxides and cleavage of the oxides gave 8-substituted phenalenones. Diels-Alder reactions of 10,10-dimethylphenafulvene yielded the corresponding adducts at C-8 and C-10 positions.

Recently, phenafulvene itself has been produced as unstable intermediate in transition metal promoted reaction of naphtho[1,8]tricyclo[4.1.0.0<sup>2,7</sup>]heptene.<sup>2)</sup> However, no simple phenafulvenes having alkyl or halogen at 10-position were known although various phenafulvenes substituted at 10-position with several groups capable of strong resonance interaction such as cyano, alkoxy carbonyl, phenyl or substituted phenyl have been obtained as stable compounds.<sup>3,4)</sup>

We have studied the syntheses of fulvenes or fulvalenes by the reaction of ketenes with unsaturated cyclic carbonyl compounds,<sup>5)</sup> and we wish to report the cycloaddition of phenalenone to methyl and/or chloro ketenes with the formation of phenafulvenes with methyl and/or chloro groups at the exocyclic positions, and some reactions of 10,10-disubstituted phenafulvenes with oxygen or dienophiles.

The reaction of phenalenone in anhydrous CCl<sub>4</sub> or benzene with dimethyl-, chloromethyl- and dichloro ketenes formed *in situ* by the reaction of the corresponding acid chlorides and triethylamine afforded the 10,10-dimethyl- (1), 10-chloro-10-methyl- (2) and 10,10-dichlorophenafulvenes (3), respectively, in more than 80% yield.<sup>6)</sup>



Physical data of the products are as follows.

(1); pale yellow oil, uv  $\lambda_{\text{max}}^{\text{CCl}_4}$  nm (log  $\epsilon$ ) 377 (3.98) and 397 (3.94), nmr ( $\text{CCl}_4$ )  $\delta$  1.94 (s,  $\text{CH}_3^a$ ), 2.07 (s,  $\text{CH}_3^b$ ), 6.49 (d,  $J = 10.0$  Hz, H-1 or H-2), 6.87 (d,  $J = 10.0$  Hz, H-2 or H-1), and 7.0-7.5 (m, 6H).

(2); pale yellow oil, uv  $\lambda_{\text{max}}^{\text{CCl}_4}$  nm (log  $\epsilon$ ) 360<sup>sh</sup>(4.07), 379 (4.30), and 399 (4.31), nmr ( $\text{CCl}_4$ )  $\delta$  2.43 [s,  $\text{CH}_3$  (2b)], 2.57 [s,  $\text{CH}_3$  (2a)], 6.63 (m), 7.02-7.95 (m), and 8.74 [d,  $J = 7.0$  Hz, H-8 (2b)].

(3); yellow crystals, mp 68.5-69.5°C, MW 246 (mass spect.), uv  $\lambda_{\text{max}}^{\text{CCl}_4}$  nm (log  $\epsilon$ ) 368<sup>sh</sup>(3.85), 386 (4.07), and 407 (4.06), nmr ( $\text{CCl}_4$ )  $\delta$  6.62 (d,  $J = 8.0$  Hz, H-1), 6.94-7.60 (m, 6H), and 8.60 (d,  $J = 7.0$  Hz, H-8).

The analyses of the nmr of 2 indicate that the compound is a mixture of two stereoisomers, (2a) and (2b), in the ratio of 18 : 7 depending on the direction of methyl and chloro groups: there are two methyl signals at  $\delta$  2.43 and 2.57 ppm with the ratio of 7 : 18, and small doublet at  $\delta$  8.74 which is attributable to H-8 of 2b and is corresponding to one proton compared to the methyl signal at  $\delta$  2.43.

These phenafulvenes can be isolated in almost pure state by chromatographic purification, but are unstable against heating and oxygen. The compounds (2) and (3) are gradually polymerized at room temperature to give black resins.

When the compound (1) is allowed to stand even in refrigerator, it gradually changed, and unstable yellow crystals (4), mp 82-83°C, were obtained. The compound (4) was found to be an addition product of oxygen with 1 from the mass spectrum,  $M^+$  288 (17.8%), and elemental analyses, in addition to the fact that 4 was also easily obtained in a good yield by photosensitized oxygenation of 1 in the presence of rose bengal. The structure of 4 was found to be 1,4-epidioxide as shown in scheme from the following nmr spectrum in  $CDCl_3$ ;  $\delta$  1.56 (s,  $CH_3$ ), 1.64 (s,  $CH_3$ ), 5.97 (d,d,  $J = 10.0, 3.0$  Hz, H-2), 6.30 (m, H-1), 6.56 (d,d,  $J = 10.0, 3.0$  Hz, H-3), and 6.9-7.6 (m, 5H).

When the compound (4) was treated with alumina, silica gel or bases, 9- $\alpha$ -hydroxyisopropylphenalenone (5), mp 126-127°C, was obtained quantitatively; ir (KBr) 3190 and 1630  $cm^{-1}$ , uv  $\lambda_{max}^{EtOH}$  nm ( $\log \epsilon$ ) 256<sup>sh</sup>(4.23), 260 (4.35), 324 (3.66), 367 (4.05), and 396<sup>sh</sup>(3.87), nmr ( $CDCl_3$ )  $\delta$  1.78 (s,  $2 \cdot CH_3$ ), 6.81 (d,  $J = 10.0$  Hz, H-2), 7.5-8.2 (m, 6H), and 8.07 (OH).

The reaction mode, (4 + 2)cycloaddition, of the phenafulvene with oxygen, is similar to the case of trapping experiment of phenafulvene itself by the reaction with dimethyl acetylenedicarboxylate to give dimethyl pyrene-1,2-dicarboxylate,<sup>2)</sup> and the process of oxygenation and cleavage of the epidioxide is considered to be useful method for the synthesis of 8-substituted phenalenones.

Attempted oxygenation of 2 and 3 afforded only resinous products. However, stirring a chloroform solution of 10,10-diphenylphenafulvene<sup>4)</sup> with alumina for a long period or photosensitized oxygenation afforded a mixture of epidioxide (6), mp 213-214°C, and 9-( $\alpha$ -hydroxybenzhydryl)phenalenone (7), mp 164-165°C, the latter one was also obtained from 6 by treatment with bases.

Diels-Alder reaction of 10,10-dimethylphenafulvene (1) with tetracyanoethylene at room temperature and maleic anhydride in boiling benzene yielded the corresponding adducts (8), mp 147-148°C (62.5%), and (9), mp 190-191°C (61.3%), respectively. The structures of the adducts were assumed as shown in the scheme from the following spectroscopic data. (8); ir (KBr) 2250  $cm^{-1}$ , nmr ( $CDCl_3$ )  $\delta$  1.93 (s,  $2 \cdot CH_3$ ), 4.99 (bs, H-1), 6.13 (d,d,  $J = 10.0, 3.0$  Hz, H-2), 6.92 (d,d,  $J = 10.0, 3.0$  Hz, H-3), and 7.1-7.8 (m, 5H). (9); ir (KBr) 1830, 1780  $cm^{-1}$ , nmr ( $DMSO-d_6$ )  $\delta$  1.30 (s,  $CH_3$ ),

1.82 (s, CH<sub>3</sub>), 3.64 (d, J = 9.0 Hz, H-9), 4.22 (t, J = 9.0 Hz, H-10), 4.67 (m, H-1), 6.37 (d,d, J = 10.0, 3.0 Hz, H-2), 6.80 (d,d, J = 10.0, 2.5 Hz, H-3), and 7.1-7.8 (m, 5H).

The facile Diels-Alder reaction of 1 as a 4 $\pi$ -component provides the further evidence for the existence of phenfulvene itself in transition metal promoted reaction of naphtho[1,8]tricyclo[4.1.0.0<sup>2,7</sup>]hepten.<sup>2)</sup>

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- 6) All new compounds gave satisfactory elemental analyses in accord with the assigned structures.

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