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SYNTHESIS OF SOME SUBSTITUTED NAPHTHALENES VIA BENZYNE AND THEIR ^{13}C-NMR AND ^{1}H-NMR STUDIES

E. Mallakpour

Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, Islamic Republic of Iran

Abstract

Aprotic diazotization of anthranilic acid with isoamylnitrite or amylnitrite gave benzenediazonium-2- carboxylate. Subsequent thermal decomposition of this diazonium salt (*in situ*) in 1, 2-dichloroethane as a solvent at 85°C and in the presence of 2, 5-diethyl-3, 4-diphenylcyclopentadienone as a trapping agent gave 1,4-diethyl-2, 3-diphenylnaphthalene in high yield, after loss of carbon monoxide. Also, thermal decomposition of this diazonium salt (*in situ*) was carried out in 1,1,2-trichloroethane as a solvent at 108°C in the presence of 2,5-dimethyl-3,4-diphenylcyclopentadienone (monomer) and after loss of carbon monoxide, 1,4-dimethyl- 2,3-diphenylnaphthalene was obtained in excellent yield. These naphthalene derivatives were studied by IR, ^{1}H-NMR, ^{13}C-NMR mass spectra and elemental analysis.

Introduction

Benzyne (3) as a reactive intermediate can be generated by a wide variety of methods. It has been obtained from dihalobenzene [1,2], anthranilic acid [3,4], diphenyliodonium-2-carboxylate [5,6], O-aminophenylboronic acid [7], 2-azobenzoic acids [6,8-10], 2-carboxyl benzene diazonium chloride [11], 1,2,3-benzole -1,1-dioxide [12], N-aminobenzotriazoles [13], and so on.

One of the best methods of forming benzyne is through the aprotic diazotization of anthranilic acid (1) and the subsequent thermal decomposition of diazonium salt (2). This technique to generate benzyne avoids the isolation and handling of the hazardous and explosive benzenediazonium-2-carboxylate (2) and serves as a convenient preparative source for benzyne.

The purpose of this work was to generate benzyne from a convenient source and trap it with 2,5-diethyl-3,4-diphenylcyclopentadienone and 2,5-dimethyl-3,4-diphenylcyclopentadienone (monomer) via [4+2] Diels-Alder cycloaddition reaction and ^{13}C-NMR, ^{1}H-NMR analysis of the resulting adducts.

Keywords: Diazotization; Benzyne; Cyclopetadienone derivatives

Results and Discussion

Although cyclopentadienone derivatives are very effective dienes for trapping benzyne, precursor and reaction conditions for the generation of this intermediate in high yields are very important. Cadogan and coworkers [14] have reported that N-nitrosoacetanilide and hence benzenediazonium acetate decomposes in benzene solution to give benzyne intermediate. The [4+2]cycloadduct (5) after loss of carbon monoxide and a long work up was isolated in 60% yield.

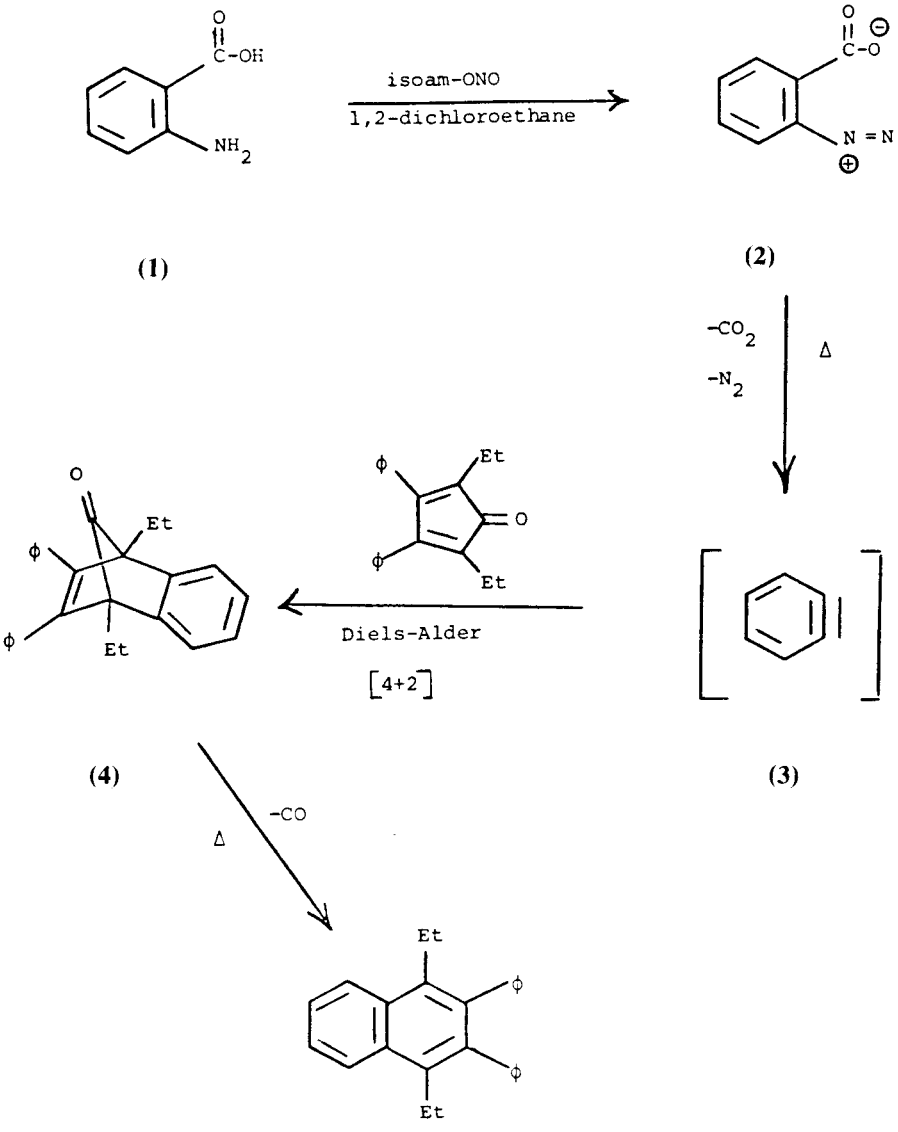
In this investigation, anthranilic acid (1) was used as a benzyne precursor. Thus, anthranilic acid was diazotized in 1,2-dichloroethane solution at 85°C under aprotic conditions with isoamylnitrite or amylnitrite to yield benzenediazonium-2-carboxylate (2). This explosive dia-

zonium salt (2) was not isolated. Thermal decomposition of this diazonium salt gave the benzyne intermediate, nitrogen and carbon dioxide. This intermediate was trapped with 2,5-diethyl-3,4-diphenylcyclopentadienone via [4+2] Diels-Alder cycloaddition reaction. This adduct (4) is not stable at the reaction temperature, it lost carbon monoxide and gave 1,4-diethyl-2,3-diphenylnaphthalene (5) in more than 88% yield (Scheme I). The compound (5) was isolated with a convenient and simple work up.

The compound (5) was recrystallized from hot methanol instead of acetic acid [14]. ^{1}H-NMR spectrum of compound (5) has already been reported [14], but it was reported that all the aromatic ring protons appeared between 7.0-8.2 ppm as multiple peaks. In a closer look, however, it is clear that naphthalene's protons are quite different from phenyl's protons.

The ^{1}H-NMR spectrum of compound (5) showed peaks at 8.20 ppm (distorted double of double) and 7.58 ppm (distorted doublet of doublet) were assigned to the four protons of the naphthalene ring (Figure 1). The protons on position 5 and 8 of the naphthalene ring (H_A and H_A') are chemical shift equivalent to each other and the protons on position 6 and 7 of the naphthalene ring (Hx and Hx') are chemical shift equivalent to each other. J_{AX} and $J_{A'X'}$ are the same and are equal to 6.72 Hz. $J_{A'X}$ and $J_{AX'}$, are also the same but smaller and are equal to 3.36 Hz. Since H_A and H_A'

Scheme I



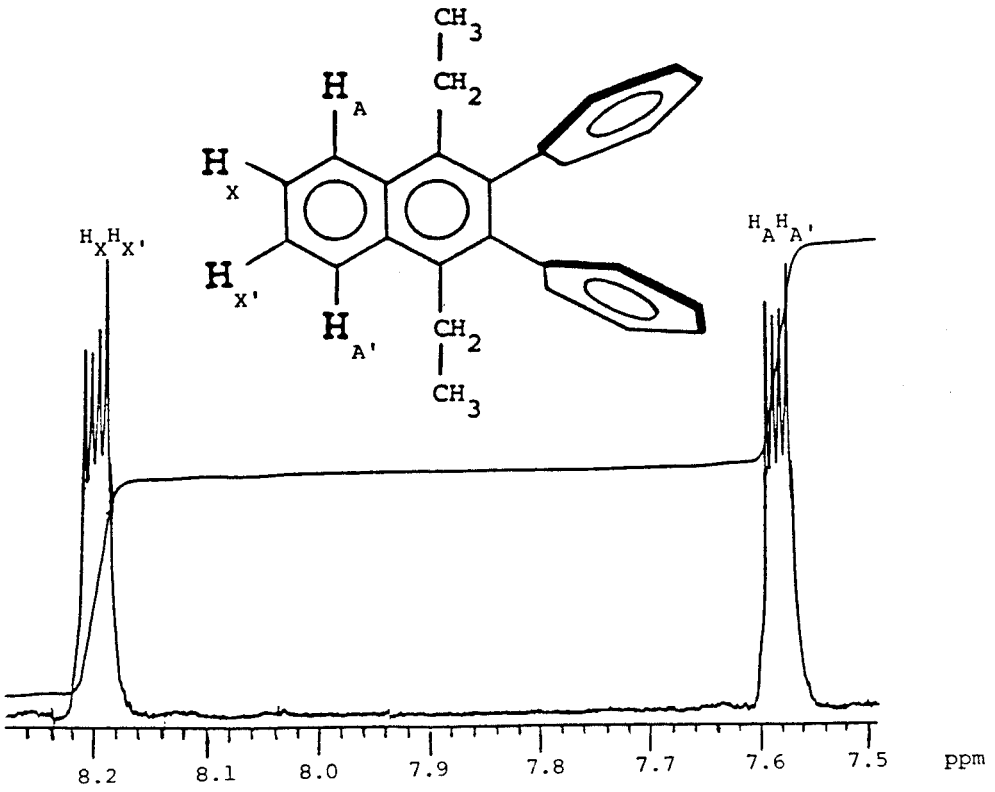


Figure 1. Expanded regions of the 500 MHz ^{1}H-NMR spectrum of 1,2-diethyl-2,3-diphenylnaphthalene

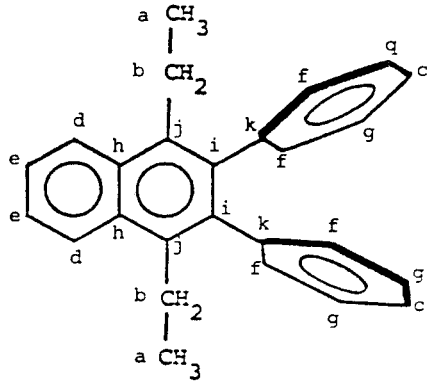
couple differently to another specific proton, they are not magnetically equivalent. Thus, it resembles an AA'XX' pattern of two distorted doublet of doublet.

The compound (5) has 26 carbon atoms in its skeleton. Since this compound has a plane of symmetry, therefore its ^{13}C-NMR signal reduces to fewer peaks. Thus 11 signals were observed on ^{13}C-NMR spectrum which are completely assigned to the corresponding carbon atoms (Table I).

Nakayama and coworkers [15] have generated benzyne by thermal decomposition of 2-carboxybenzenediazonium chloride in the presence of propylene oxide. This reactive intermediate was trapped with 2,5-dimethyl-3,4-diphenylthiophene-1, 1-dioxide. The Diels-Alder cycloadduct lost sulfur dioxide and 1,4-dimethyl-2,3-diphenylnaphthalene (9) was obtained in 25% yield.

2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone exists as a dissociative dimer (6). In the solid state it is completely dimer and appears as a white crystalline solid. But in solution it slowly dissociates to monomer as a red solution (Scheme II). The degree of dissociation was measured by ^{1}H-NMR studies in C_6D_6 solution at various temperatures [16]. The extent of dissociation is about 5% at 80°C, 10% at 100°C and 70% at 120°C.

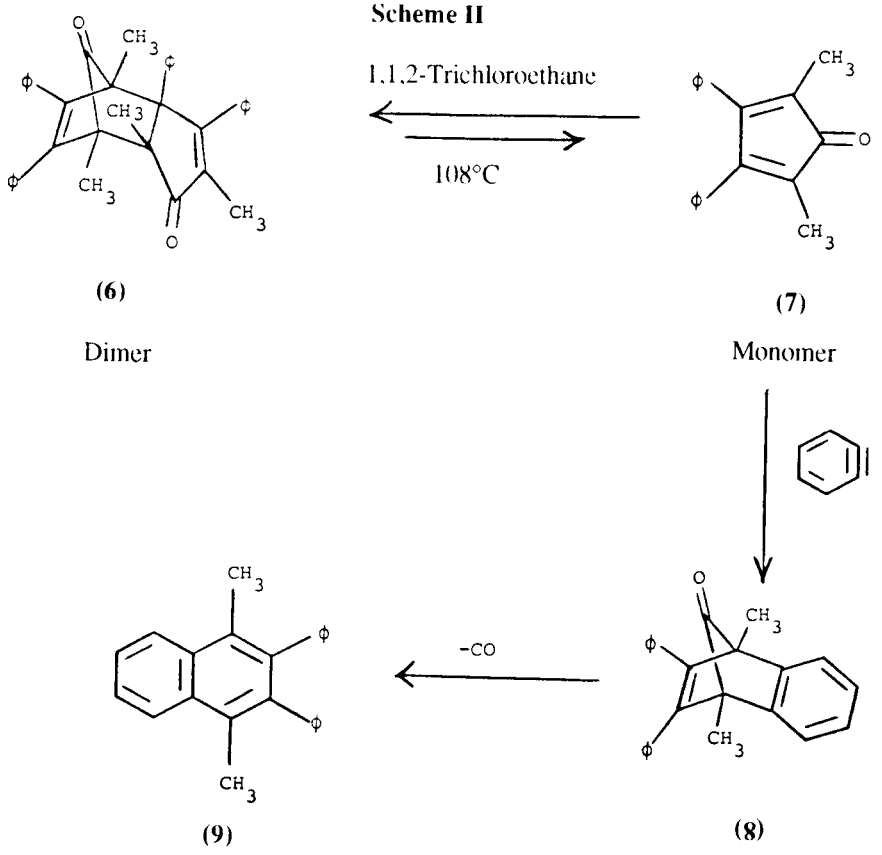
Table I. ^{13}C-NMR (125 MHz) Data of Compound (5)



(5)

type of carbon	δ ppm	type of carbon	δ ppm
a	15.65	g	130.10
b	23.24	h	131.20
c	125.21	i	136.69
d	125.57	j	139.09
e	125.81	k	141.47
f	127.12		

Scheme II



(6) Dimer

(7) Monomer

(8)

(9)

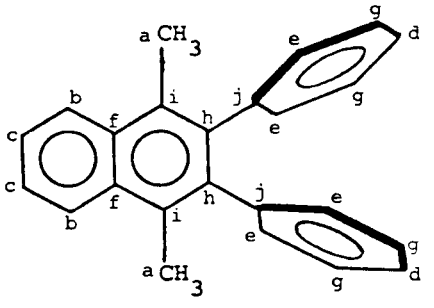
From the above information we became interested in examining the reactivity of this dissociating dimer with benzyne (3).

Thus, 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dione (6) as its dimer was heated in 1,1,2-trichloroethane solution at 108°C. A red solution was obtained. Benzyne as a reactive intermediate was generated in this solution from aprotic diazotization of anthranilic acid with amylnitrite and subsequent thermal decomposition of the diazonium salt. This reactive intermediate was trapped with monomeric 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dione (7) via [4+2] Diels-Alder cycloaddition reaction. Upon heating, this adduct (8) spontaneously lost CO and aromatic compound 1,4-dimethyl-2,3-diphenylnaphthalene (9) was obtained in high yield (Scheme II).

The ^{1}H-NMR (500 MHz) spectrum of compound (9) showed peaks at 7.54 ppm (distorted doublet of doublet) and at 8.10 ppm (distorted doublet of doublet) were assigned to the four protons of the naphthalene ring. These protons resemble an AA'XX' pattern. The other peaks are in agreement with the assigned structure (9).

The ^{13}C-NMR (125 MHz) spectrum of compound (9) showed 10 peaks due to plane of symmetry. These data are summarized in Table II.

Table II. ^{13}C-NMR (125 MHz) Data for compound (9)



(9)

type of carbon	δ ppm	type of carbon	δ ppm
a	16.84	f	129.39
b	125.00	g	130.39
c	125.74	h	132.01
d	125.82	i	139.39
e	127.22	j	141.71

Experimental Section

All chemicals were used as received; 3-pentanone was purchased from Aldrich Chemical Co., 4-heptanone was obtained from Fluka Chemical Co. All melting points were taken with a Gallenhamp melting point apparatus and are uncorrected.

Infrared spectra were recorded on a Shimadzu 435 Infrared Spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) and carbon-^{13}NMR(125 MHz) spectra were obtained on a Varian XL-500 spectrometer. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, I.R. Iran.

Synthesis of 2,5-diethyl-3,4-diphenylcyclopenta-2,4-dienone

This cyclopentadienone derivative was prepared by base-catalyzed condensation reaction of benzil with 4-heptanone and subsequent dehydration by acid-catalyzed reaction. The yield for the first step was 80% and for the second step 99%. This cyclopentadienone derivative is a red crystalline solid, m.p. 97-99°C (Lit 103°C [17]).

Synthesis of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone as its dimer

The dissociating dimer was prepared by acid-catalyzed dehydration of the base-catalyzed condensation product of benzil and 3-pentanone and was recrystallized from acetone-water, m.p. 180-182°C (Lit 181-182°C [18]). The yield of the first step was 83% and of the second step 92%.

Reaction of benzyne with 2,5-diethyl-3,4-diphenylcyclopenta-2,4-dienone

Into a 100ml three-necked, round-bottomed flask were placed 1.29 g(4.486×10^{-3} mol) of 2,5-diethyl-3,4-diphenylcyclopenta-2,4-dienone, 20 ml of 1,2-dichloroethane and a magnetic stirring bar. The flask was fitted with a water cooled condenser and two constant-pressure dropping funnels. A solution of 0.615 g(4.486×10^{-3} mol) of anthranilic acid in 25 ml of 1,2-dichloroethane was placed in one of the dropping funnels. The other funnel was charged with a solution of 1.2 ml (8.560×10^{-3} mol) of amylnitrate in 25 ml of 1,2-dichloroethane.

The flask was heated by a heating mantle and the stirrer was started. Solutions from the dropping funnels were added dropwise simultaneously to the refluxing mixture over a period of 30 mins. Refluxing was continued for 2 hours. The red solution turned to a pale orange color. The solvent was removed by simple distillation under mild reduced pressure. The residue was triturated with 20 ml of 95% ethanol. The white solid formed, filtered, and dried to give 1.32 g(88%). Recrystallization from hot methanol gave white crystals m.p. 137-138°C (lit [14] 141-142°C).

IR(KBr): 3080(w), 3000(w), 2990(m), 2900(m), 2880(m), 1600(w), 1570(w), 1485(m), 1462(sh), 1440(m), 1405(w), 1380(m,br), 1320(w), 1060(m), 1030(m), 1008(m), 980(m), 920(m), 760(s), 740(s), 700(s), 640(w), 600(w) cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$, int.ref.$CDCl_3$): δ 1.16 (t, 6H, J=8.0 Hz), 2.84 (q, 4H, J=8.0 Hz), 7.00-7.20 (m,10H), 7.58 (dd, 2H, $J_{AX}=J_{A'X'}$ = 6.72 Hz), 8.20 (dd, 2H, $J_{A'X}=J_{AX'}$ = 3.36Hz).

Mass spectrum calcd m/e for $C_{26}H_{24}$ 336.48, obsd. 336.48. Anal. Calcd $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.60; H, 7.30.

Reaction of benzyne with monomeric 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone

2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (as its dimer) (0.260 g, 1.0×10^{-3} mol based on monomeric form), 30 ml of 1,1,2-trichloroethane and a magnetic stirring bar were placed in a 100 ml three-necked round-bottomed flask. The flask was equipped with two constant-pressure dropping funnels and a water cooled condenser. Then it was heated by a heating mantle under reflux for 30 mins. and a red solution was obtained.

A solution of 0.137 g(1.0×10^{-3} mol) of anthranilic acid in 10 ml of 1,1,2-trichloroethane was placed in one of the dropping funnels. The other funnel was charged with a solution of 0.50 ml (3.7×10^{-3} mol) of isoamylnitrite in 10 ml of 1,1,2-trichloroethane.

Solutions from the dropping funnels were added dropwise simultaneously to the refluxing mixture over a period of 60 mins. The red solution turned to a pale yellow color. Refluxing was continued for 5 hours. The solvent was removed under reduced pressure. The residue was triturated with 25 ml of ethanol. The off white solid formed, filtered, and dried to give 0.29 g(93.5%). Recrystallization from methanol gave white needle crystals m.p. 141-142°C (Lit [15] 146-148°C).

IR (KBr): 3050(m), 3020(m), 2900(m), 2850(w), 1600(m), 1570(m), 1495(m), 1440(s), 1380(s), 1065(m), 1030(m), 960(m), 745(s), 690(s) cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$, int.ref.$CDCl_3$): δ 2.39 (s, 6H), 6.91–7.09 (m, 10H), 7.55(dd, 2H,$J_{AX}=J_{A'X'}$ = 6.72 Hz), 8.10 (dd, 2H, $J_{A'X}=J_{AX'}$ = 3.36 Hz).

Anal. Calcd for $C_{24}H_{20}$: C, 93.40; H, 6.60, Found: c, 93.20; H, 6.80.

Conclusion

From this investigation, it is clear that the benzyne intermediate can be generated quantitatively from the aprotic diazotization of anthranilic acid. This reactive intermediate can be readily trapped with 2,5-diethyl-3,4-diphenylcyclopenta-2,4-dienone and cycloadduct, 1,4-diethyl-2,3-diphenylnaphthalene is obtained in high yield.

This intermediate obtained from the above technique reacts with more than 90% of the monomeric 2,5-diemthyl-3,4-diphenylcyclopenta-2,4-dienone. This result indicates that 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone as its dimer could be dissociated to its monomer in extent of more that 90%.

Cycloadducts obtained from this investigation will serve as model compounds for the reaction of bis-benzyne with the above cyclopentadienone derivatives. Work in this area in our laboratory is under investigation.

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