Synthesis and Characterization of Diametrically Substituted *p*-Diacetylcalix[4]arene

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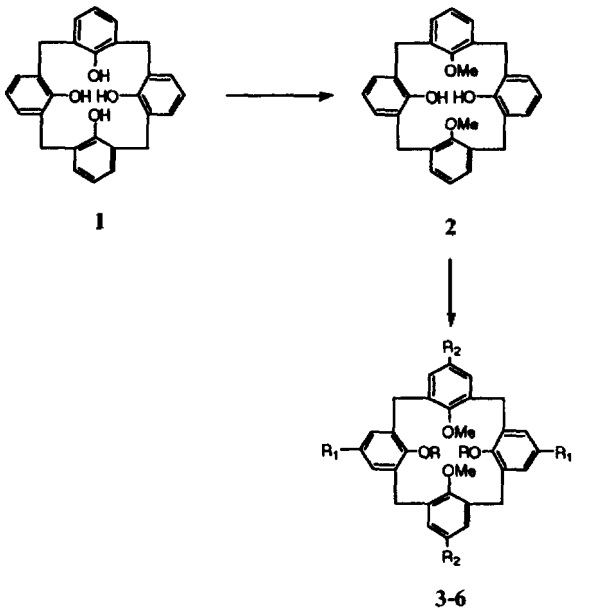
Methods for the selective functionalization of calix[4]arene at the upper rim are described. The diametrically substituted calix[4]arene dimethyl ether **2**, obtained from the treatment of calix[4]arene **1** with methyl iodide in the presence of K_2CO_3, is converted to the two isomeric *p*-diacetylcalix[4]arene dimethyl ether **3** and **6** by direct substitution and by Fries rearrangement of corresponding diacetyloxycalix[4]arene dimethyl ether **5** respectively. Diametrically substituted *p*-diacetylcalix[4]arene **8** was also prepared by Fries rearrangement of calix[4]arene tetraacetate **7** using a limited amount of $AlCl_3$.

Introduction

The functionalization of calixarenes on the phenyl ring (upper rim) has attracted our attention[1] and that of several research groups[2-4] because of the possibility of easily obtaining new host molecules for the complexation of ions and neutral molecules or new type of enzyme mimics[5]. Although several routes have been developed to introduce functional groups into the phenyl rings[1-4], they all lead to tetra substituted calix[4]arenes, having four identical substituents at the para positions. The stepwise routes giving access to differently substituted calix[4]arenes were developed by Gutsche and No[6] and Bohmer *et al*[7]. but the methods are relatively long and tedious, producing low yields. The purpose of the present work is to exploit the possibility of adapting the short synthesis to the preparation of selectively substituted calix[4]arenes containing more than two different functional groups. And this methodology could be utilized for the introduction of chirality to the calix[4]arenes. Therefore we are currently investigating the selective functionalization of calixarenes at the upper rim. In this regard, recently Reinhoudt and coworkers[8] reported that the difference in reactivity of phenyl rings of the diametrically dimethoxylated calix[4]arene can be utilized for the selective functionalization of calixarenes with various functional groups. Here we report the synthesis of selectively 1,3-subsituted *p*-diacetylcalix[4]arene *via* three different methodologies. Parts of this work were reported elsewhere[9,10].



1 2 3-6

	R	R_1	R_2
3:	H	H	$COCH_3$
4:	H	H	$CH(OH)CH_3$
5:	$COCH_3$	H	H
6:	H	$COCH_3$	H

Scheme 1.

Results and Discussions

Due to the carbonyl group can be converted to various functional groups by several ways such as oxidation, reduction, Grignard reaction and Wittig reaction, *p*-acetylcalix[4]arene can serve as admirable precursor for the functional group introduction, therefore few years ago we reported the syntheses of various *p*-acylcalix[4]arene using the Fries rearrangement of calix[4]arene tetraacyl ester[1]. In this report, we prepared selectively 1,3-diacetylated calix[4]arene **3**, **6** and **8** as shown on Scheme 1 and 2. Since it is not possible to discriminate directly between the four para positions of the phenyl rings in calix[4]arene **1**, we have first used a method to introduce selectively at the lower rim. In subsequent reactions this selectivity could be used to differentiate the reactivity of upper rim. The selective partial alkylations of lower rim of calix[4]arene were reported by Gutsche[11], Reinhoudt[12], Shinkai[13] and our laboratory[9,10].

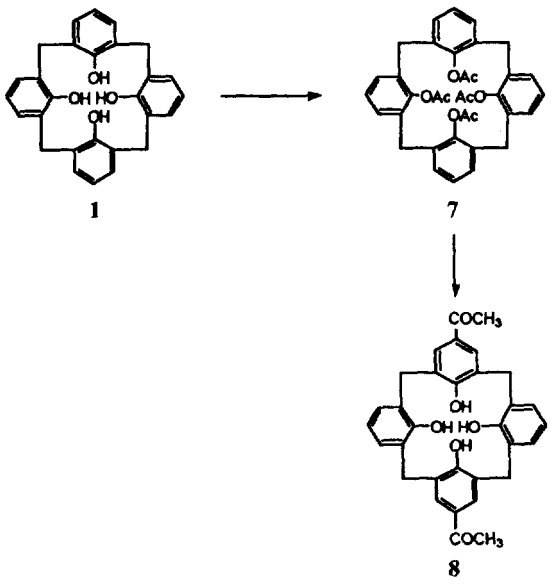
When calix[4]arene **1**, obtained by the $AlCl_3$-catalyzed de-*t*-butylation of *p-tert*-butylcalix[4]arene, was reacted with methyl iodide in the presence of K_2CO_3 in refluxing acetone, the 26,28-dimethoxy calix[4]arene **2** was obtained in 85% yield. This reaction leads to diametrically alkylated calixarene in the cone conformation[8,10,14], as was indicated by ^1H-NMR spectrum, showing a typical AB quartet pattern for the methylene bridge protons ($J = 13$ Hz). When excess K_2CO_3 was used with longer reaction time, mixture of di-, tri- and tetramethoxy calix[4]arene were resulted which was extremely difficult to separate. The reaction mechanism was proposed by Reinhoudt[8] as follows, the first step is the mono

alkylation of calix[4]arene. Under the reaction conditions subsequently a proton is abstracted from the monoalkoxycalix[4]arene giving anion. Since the negative charge at the oxygen atom opposite to the alkoxy group will be stabilized by two hydrogen bonds, thus keeping the calix[4]arene in the cone conformation, the second electrophile will react on this position.

The first approach for the introduction of acetyl groups at upper rim comprises the selective substitution at two anisol phenyl rings using Friedel-Crafts reaction. When a solution of compound **2** in methylene chloride was stirred with acetyl chloride in the presence of $AlCl_3$, compound **3** was produced in 63% yield. The *p*-acetylation was confirmed by IR and ^{1}H-NMR spectra. In the IR spectrum, the OH stretching band remained and the carbonyl band appeared at 1680 cm^{-1}, indicating the aromatic ketone rather than ester. In the ^{1}H-NMR spectrum, the resonance peak from methyl protons adjacent to the carbonyl group was observed at δ 2.53, whereas that of ester usually appears at around δ 1.50. The typical AB quartet pattern of the ^{1}H-NMR resonance peaks of the methylene bridge protons at δ 4.29 and 3.45 (J=13 Hz), indicates that compound **3** exists in the cone conformation. It was reported[1,15] that the treatment of the calix[4]arene **1** with acetyl chloride under Friedel-Crafts conditions resulted in O-acetylation, producing the ester, rather than C-acetylation, and the resulting ester failed to undergo further reaction at the para positions. However, when calix[4]arene tetramethyl ether was treated under the same conditions, C-acetylation at the para positions occurred with concomitant partial demethylation. The other aromatic substitution reactions, such as bromination, nitration and Mannich reaction exclusively took place at the phenol ring rather than the anisol rings of compound **2** as reported by Reinhoudt[8]. The structure of compound **3**, in which two acetyl groups are introduced into anisol rings rather than phenol rings, was supported by the comparison of physical data of this compound with those of isomeric compound **6**, which was prepared by the Fries rearrangement of corresponding diacetoxydimethoxycalix[4]arene **5**.

To acetylate the remaining two hydroxyl groups compound **3** was treated with NaH and acetyl chloride to give the desired product **5** in 93% yield. The conformation of compound **5** was assigned on the base of ^{1}H-NMR and ^{13}C-NMR spectroscopic evidence. Particularly significant is the positions of the methylene in the ^{13}C-NMR spectrum which were appeared at 37.63 and 30.61 ppm, in agreement with the recently introduced single rule for the determination of calix[4]arene conformation[16]. The ^{13}C-NMR spectrum of this compound showed twelve peaks from phenyl carbons, and two peaks each from the carbonyl and methyl adjacent to carbonyl carbons, indicating this compound is in partial cone conformation. Two non-equivalent singlet peaks from the protons of methyl groups adjacent to carbonyl groups were appeared on ^{1}H-NMR spectrum. Compund **5** was also prepared by treatment of compound **3** with acetic anhydride in the presence of conc sulfuric acid catalyst in 92% yield[1].

When a solution of compound **5** and $AlCl_3$ in nitrobenzene was stirred overnight at room temperature, the rearranged product **6** was obtained in 68% yield. The rearrangement was confirmed by spectral comparison. In IR spectrum, the OH stretching band was appeared and the position of carbonyl band was shifted from 1735 cm^{-1} of ester to 1670 cm^{-1} of aromatic ketone. ^{1}H-NMR spectrum also showed the resonance peak of OH protons, and that of methyl protons adjacent to carbonyl was shifted from δ 1.53 of ester to δ 2.50 of ketone. The cone conformation of compound **6** was indicated by a typical AB quartet pattern of the methylene bridge protons. A similar but not identical spectral characteristics and different melting point of compounds **3** and **6** (365 ℃ vs. 354℃) indicate these two are isomers each other rather than identical compound. The introduction of acetyl groups at the diametrical para position of calix[4]arene can be accomplished by the Fries rearrangement of the calix[4]arene tetraacetate **7** as shown on Scheme 2.



1 7 8

Scheme 2.

Treatment of calix[4]arene **1** with acetic anhydride and conc sulfuric acid yielded a tetraacetate **7** whose ^{1}H-NMR spectrum shows four sharp singlets for the methyl protons of acetyl group (δ 2.33, 2.03, 1.77 and 1.53), which indicates the product is the mixture (approximately 3 : 1) of 1,3-alternate and partial cone conformers. Reaction of compound **1** with acetyl chloride and NaH afforded the compound **7** in 84% yield. According to ^{1}H-NMR spectrum, the product was a mixture of 1,3-alternate and partial cone conformer, however, in this preparation partial cconformer was major product. The mixture of conformers were used in Fries rearrangement reaction without further isolation of pure conformer. Gutche[11] reported the synthesis of 1,3-alternate conformer of compound **7** by treatment compound **1** with acetic anhydride and *p*-toluenesulfonic acid.

When calix[4]arene tetraacetate **7** was treated with excess of $AlCl_3$ in nitrobenzene at room temperature, acetyl groups were rearranged to the para positions of calix[4]arene to yield *p*-acetylcalix[4]arene[1]. However, reaction with smaller amount of $AlCl_3$ produced partially rearranged products mixture and extremely difficult to isolate the pure product. When the compound **7** was treated with limited amount (1.5 mole equivalent per carbonyl group) of $AlCl_3$, only two diametrical acetyl groups were rearranged and the remaining two groups were simply cleaved to produce compound **8** in 82% yield. The structure of compound **8** was determined

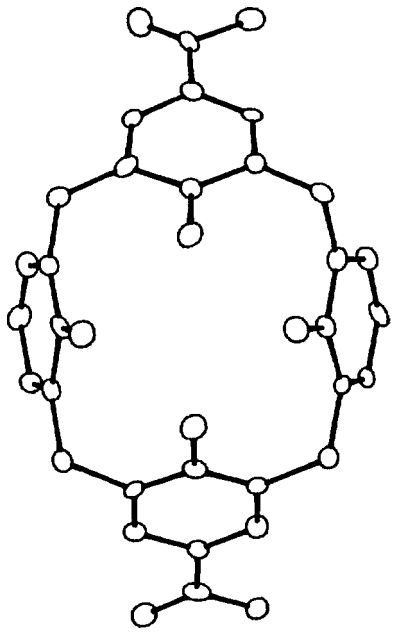


Figure 1. Crystal structure of **8**. Hydrogen atoms are not shown.

by X-ray diffraction method. As shown on Figure 1 calixarene **8** has a distorted cone conformation compared to the ideal 4-fold symmetry found for *p-tert*-butylcalix[4]arene[17].

The angle between the mean plane through the connecting methylene groups and four phenyl rings are 135.2°, 116.3°, 131.7° and 112.4° respectively. The phenyl rings substituted by acetyl group are more distorted than the remaining two phenyl rings without substituent. Compound **8** was also prepared by BBr_3 catalyzed demethylation of compound **3** and **6**. When a solution of compound **3** or **6** in methylene chloride was treated with BBr_3 at room temperature compound **8** was produced in 85% and 88% yield respectively. This also supports the suggested structures of **3** and **6**.

As mentioned earlier this paper, *p*-diacetylcalix[4]arene seems to provide an attractive starting material for the further functionalization of calixarenes. The empty para positions are potential sites for reaction, and the carbonyl functions can be converted to other functions. As a preliminary experiment to explore these possibilities, the reduction was investigated. Treatment of **3** with $NaBH_4$ at room temperature *p*-di(1-hydroxyethyl)calix[4]arene dimethyl ether **4** was afforded in 54% yield. The reduction was confirmed by spectral data. An additional OH band at 3540 cm^{-1} was appeared and carbonyl band was disappeared in IR spectrum. ^{1}H-NMR resonance peak of methyl protons adjacent to carbonyl at δ 2.56 was changed to doublet at δ 1.42, and that of CH proton was appeared. In ^{13}C-NMR spectrum resonance peak of C=O was disappeared and a new resonance peak of CH was appeared at 70.41 ppm.

Experimentals

Melting points of all compounds were taken in sealed and evacuated capillary tubes on a Syblon themolyne apparatus with polarizing microscope and were not corrected. IR spectra were determined on a Shimadzu IR-435 spectrometer. ^{1}H-NMR spectra were recorded on Varian EM-360A (60 MHz) or Varian Gemini 300 (300 MHz) instrument and ^{13}C-NMR spectra on the Varian Gemini 300 (75 MHz) spectrometer. Chemical shifts are reported as δ values in parts per million relative to TMS (δ 0.0) as an internal standard. TLC analyses were carried out on silica gel plates (absorbant thickness 250 μm). Flash chromatography[17] was carried out with E. Merck silica gel (230-400 mesh ASTM). Elution rate were 2 in./min.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene was prepared in 52% yield from *p-tert*-butylphenol and formaldehyde as described elsewhere[19]; mp. 344-346℃ (lit[19] 344-346℃)

25,26,27,28-Tetrahydroxycalix[4]arene 1 was prepared in 74% yield by $AlCl_3$-catalyzed removal of the *tert*-butyl groups from the above compound following the published procedure[1]; mp. 315-317℃ (lit[20] 314-318℃).

25,27-Dihydoxy-26,28-dimethoxycalix[4]arene 1. To a heated suspension of compound **1** (2.00 g, 4.72 mmol) and K_2CO_3 (0.70 g, 5.07 mmol) in 150 m*l* acetone, 6 m*l* of MeI was added dropwise, the resultant mixture was refluxed 6 hr. After evaporation of the solvent, the residue was treated with 50 m*l* of 10% HCl and the resulting solid was collected by filtration, washed with water several times, dried, and boiled with 100 m*l* of acetone. The acetone insoluble solid was recrystallized form *n*-butanol to yield 1.81 g (85%) of white crystalline solid; mp. 301-303℃ (lit[8]>300℃); IR (KBr) 3375 cm^{-1} (OH stretching); ^{1}H-NMR ($CDCl_3$) δ 7.80 (s, 2, OH), 7.02-6.61 (m, 12, ArH), 4.34 (d, 4, J=12 Hz, CH_2), 4.00 (s, 6, OCH_3), 3.30 (d, 4, J=13 Hz, CH_2).

5,17-Diacetyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arrene 3. Compound **2** (0.52 g, 1.15 mmol) was dissolved in 30 m*l* of dichloromethane, chilled in an ice-bath, added dropwise the solution of 0.61 g of $AlCl_3$ and 0.9 m*l* of acetyl chloride in 20 m*l* of dichloromethane. After stirring was extended for 3.5 hr at room temperature, reaction mixture was poured into 100 m*l* of 6 N HCl. Organic layer was separated, washed with water, dried, evaporated the solvent. The residue was recrystallized form chloroform/hexane to yield 0.46 g (63%) of compound **3** as a white crystalline solid; mp. 365-367℃; IR(KBr) 3250 (OH stretching), 1667 cm^{-1} (C=O stretching); ^{1}H-NMR ($CDCl_3$) δ 8.49 (s, 2, OH), 7.78-6.75 (m, 10, ArH), 4.30 (d, 4, J=13 Hz, CH_2), 4.00 (s, 6, OCH_3), 3.50 (d, 4, J=13 Hz, CH_2), 2.56 (s, 6, $COCH_3$); ^{13}C-NMR ($CDCl_3$) 197.58 (C=O), 158.59, 153.64, 132.69, 130.09, 129.85, 129.48, 128.35, 126.07 (Ar), 64.04 (OCH_3), 31.24 (CH_2), 25.36 ($COCH_3$).

5,17-Di (1-hydroxyethyl)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene 4. To a solution of compound **3** (0.50 g, 0.93 mmol) in 50 m*l* of THF, 0.46 g of $NaBH_4$ and 20 m*l* of methanol was added and then stirred for 30 min at room temperature. The reaction was quenched by adding 20 m*l* of 1.5% KOH solution, extracted twice with 50 m*l* portion of chloroform. The organic layer was washed with water, dried and evaporated solvent to produce a waxy residue, which was triturated with hexane. The resultant precipitate was collected and purified with flash chromatography on silica gel (eluent was 2 : 3 mixture of acetone and hexane) to yield 0.27 g (54%) of the desired product as white crystalline solid; mp 350℃ (melt then decompose); IR (KBr) 3540 and 3330 cm^{-1} (OH stretching); ^{1}H-NMR ($CDCl_3$) δ 7.93 (s, 2, ArOH), 7.10-6.78 (m, 10, ArH), 4.78 (q, 2, CH), 4.30 (d,

J=13 Hz, 4, CH_2), 3.98 (s, 6, OCH_3), 3.41 (d, J=13 Hz, 4, CH_2), 1.78 (br.s, 2, OH), 1.42 (d, 6, CH_3); ^{13}C-NMR ($CDCl_3$) 153.81, 153.02, 136.99, 139.49, 129.57, 128.59, 128.48, 126.20, 126.11, 125.82 (Ar), 70.41 (CH), 63.87 (OCH_3), 31.43 (CH_2), 24.97 (CH_3).

25,27-Diacetyloxy-26,28-dimethoxycalix[4]arene 5. To a solution of compound **2** (0.68 g, 1.5 mmol) and 0.25 g of NaH in 70 m*l* THF, a solution of acetyl chloride (1.00 m*l*) in 30 m*l* THF was added dropwise and then the mixture was stirred for 2 hr at room temperature. After solvent was evaporated the resulting residue was treated with 100 m*l* of cold water, extracted twice with 60 m*l* portions of chloroform. Organic layer were combined, washed with water four times, dried and then evaporated solvent. The resultant solid was recrystallized from chloroform/methanol to give 0.75 g (93%) of the desired product as a crystalline solid; mp. 273-275℃; IR (KBr) 1735 cm^{-1} (C=O stretching); ^{1}H-NMR ($CDCl_3$) δ 7.32-6.66 (m, 12, ArH), 4.00-3.18 (m, 8, CH_2), 3.62 (s, 6, OCH_3), 1.82 (s, 3, $COCH_3$), 1.54 (s, 3, $COCH_3$): ^{13}C-NMR ($CDCl_3$) 172.71, 169.27 (C=O), 135.93, 134.50, 133.74, 133.11, 130.48, 130.07, 129.71, 129.34, 128.97, 126.22, 125.60, 123.21 (Ar), 60.59 (OCH_3), 37.63, 30.61 ($ArCH_2Ar$), 21.29, 21.15 ($COCH_3$). This compound was also prepared by treatment of compound **2** with acetic anhydride. A solution of compound **2** (0.90 g, 2.0 mmol) in 30 m*l* of acetic anhydride was added 1 drop of conc sulfuric acid. The mixture was heated under reflux for 1.5 hr, poured into 100 m*l* cold water and then stirred for a while. The resulting precipitate was collected by filtration, washed with water, and dried to give light brown colored solid, which was recrystallized from benzene to yield to yield 0.98 g (92%) of the desired product as a crystalline solid.

5,17-Diacetyl-26,28-dihydroxy-25,27-dimethoxycalix[4]arene 6. A solution of compound **5** (0.56 g, 1.04 mmol) in 60 m*l* nitrobenzene was treated with 2.09 g of $AlCl_3$ and the mixture was stirred for overnight at room temperature. The reaction was quenched by adding water and solvent was removed by steam distillation. The resultant solid was collected, crushed into powder, washed with water, dried and then boiled with 30 m*l* of benzene. The flash chromatographic separation (eluent 2:5 mixture of acetone/hexane) of the benzene insoluble material furnished 0.38 g (68%) or crystalline solid; mp. 354-355℃ (decompose, softening and sublimation at around 340℃); IR (KBr) 3250 cm^{-1} (OH stretching); 1680 (C=O stretching); ^{1}H-NMR ($CDCl_3$) δ 8.53 (s, 2, OH), 7.84, 7.43 and 6.91 (s, 10, ArH), 4.33 (d, 4, J=13 Hz, CH_2), 3.98 (s, 6, OCH_3), 3.49 (d, 4, J=13 Hz, CH_2), 2.50 (s, 6, $COCH_3$).

25,26,27,28-Tetraacetyloxycalix[4]arene 7. was prepared in 75% yield as colorless crystaline solid as described elsewhere[1]. The same compound was also prepared by treatment of compound **1** with acetyl chloride as follows. Compound **1** (0.70 g, 1.65 mmol) was dissolved in 50 m*l* of THF, chilled in an ice-bath, treated with NaH (0.74 g), added dropwise a solution of acetyl chloride (1.4 m*l*) in 20 m*l* of THF and then reaction mixture was refluxed for 1.5 hr. The white solid residue, obtained from the evaporation of THF, was treated with 50 m*l* of water and extracted with 50 m*l* of chloroform. The organic layer was separated, washed with water, dried and the evaporated to dryness. A recrystallization of residue from chloroform and methanol afforded 0.82 g (84%) of compound **7** as white crystalline solid. This was approximately 2:1 mixture of partial cone and 1,3-alternate conformer of product which was used in next reaction without further isolation of pure conformer.

5,17-Diacetyl-25,26,27,28-tetrahydroxycalix[4]arene 8. A mixture of compound **7** (1.00 g, 1.69 mmol) and 1.40 g of $AlCl_3$ (1.5 mole equivalent per carbonyl group) in 100 m*l* nitrobenzene was stirred for overnight at room temperature, and then 100 m*l* water was added to stop the reaction. After nitrobenzene was removed by steam distillation, the residue was collected by filtration, crushed into powder, washed with water several times, and then dried. Light brown colored solid showed major one spots with three other minor spots on TLC. Colorless powder which was obtained by triturating that solid with acetone was recrystallized from chloroform/hexane to give 0.68 g (80%) of crystalline solid; mp. >350℃; IR (KBr) 3450 cm^{-1} (OH stretching), 1670 (C=O stretching); ^{1}H-NMR ($CDCl_3$) δ 10.3 (s, 4, OH), 7.87 (s, 8, ArH), 7.30-6.84 (m, 6, ArH) 4.00 (br.s, 8, CH_2), 2.48 (s, 6, $COCH_3$). This compound was also prepared from compound **3** and **6** *via* BBr_3 demethylation as follows; A solution of 0.67 g (1.25 mmol) of compound **3** or **6** in 60 m*l* of CH_2Cl_2 was treated dropwise with 30 m*l* of BBr_3 in CH_2Cl_2 and the mixture was stirred at room temperature for 18 hr in an atmosphere protected from moisture. The reaction mixture was poured into 100 m*l* of water, stirred for 1 h, and the organic layer was separated, washed with water, dried, evaporated and triturated with acetone to leave 0.54 g (85%) and 0.56 g (88%) of the desired product respectively.

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Notes

Oxidative Decomposition of *Meso*-Azobis-α-phenylethane by Thianthrene Cation Radical

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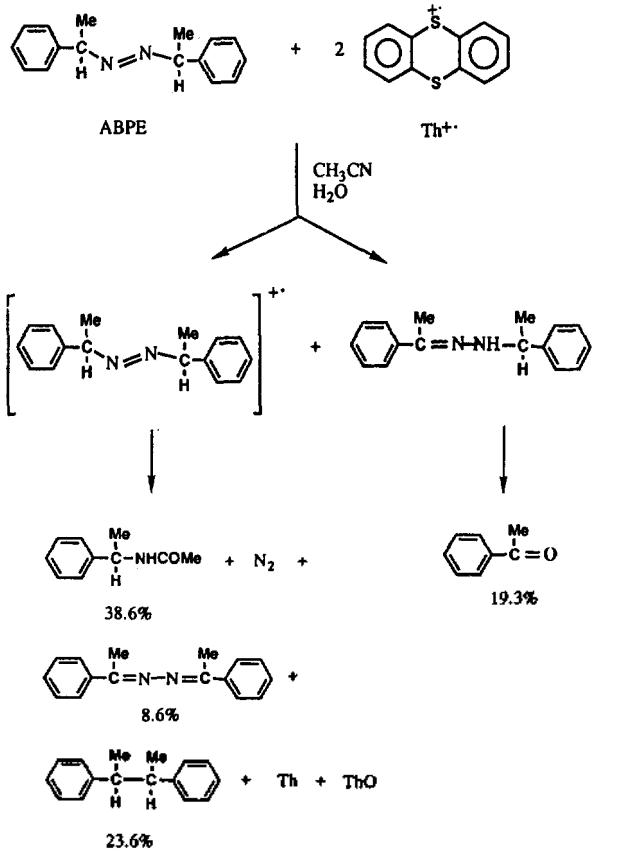
Cation radical-induced, oxidative chemistry of azoalkane has begun to emergy only in the last few years.[1-5] For example, azoalkane such as 1,1'-azoadamantane (AA), which has no α hydrogen, is oxidized by thianthrene cation radical perchlorate in acetonitrile solution, affording primarily nitrogen and cation-derived products.[1] However, 1,4-diphenylazomethane (DPAM) possesing two α hydrogens reacts with cation radicals and undergoes facile oxidative cycloaddition with the nitrile solvent to form 1,2,4-triazole.[2] The results from oxidation of AA and DPAM tell us quite clearly that the type of α-carbon in azoalkanes determines the products of oxidative cleavage. The present investigation arose from questions whether *meso*-azobis-α-phenylethane (ABPE) [1,1'-diphenylazoethane] possesing one α hydrogen is oxidized to its cation radical and decompose to liberate N_2, or tautomerized to its hydrazone and lead to oxidative cycloaddition to the nitrile solvent. The purpose of this study is to know the effects of structure on the oxidation of azoalkane and to validate the reaction mechanism which had been proposed for the oxidation of azoalkane by cation radical.

meso-ABPE undergoes thermolysis into α-phenylethyl radical in solution at reasonable rates at 100-160℃, leading to the 2,3-diphenylbutane (DPB) and rearranges to their hydrazone tautomer more readily than the simple aliphatic azo compounds.[6] In contrast, this azoalkane reacted with thianthrene cation radical ($Th^{+\cdot}$) at room temperature rapidly and evolved nitrogen and rearranged to a tautomer of *meso*-ABPE, acetophenone α-phenylethylhydrazone. While $Th^{+\cdot}$ was reduced quantitatively to thianthrene (Th), products from *meso*-ABPE, a traditional source of free radicals,[7] were N-α-phenylethylacetamide (38.6%), 2,3-diphenylbutane (23.6 %), acetophenone (19.3%) and acetophenone azine (8.6%). The overall view of the behavior of azoalkane in reaction with $Th^{+\cdot}$ can be explained by Scheme 1. Thus, the major initial trappable products of oxidative decomposition were the α-phenylethyl cations, which reacted with the solvent acetonitrile to give a Ritter-type intermediate PhC(Me)HN $=^{+}$CMe. The Ritter-type intermediate reacted with water during workup to give N-α-phenylethylacetamide. One of the possible routes for the formation of the carbocationic product, N-α-phenylethylacetamide is shown in Eq. (1)-(5).

$$Th^{+\cdot} + ABPE \rightleftharpoons Th + ABPE^{+\cdot} \quad (1)$$

$$ABPE^{+\cdot} \longrightarrow PhC(Me)H\cdot + PhC(Me)H^{+} + N_2 \quad (2)$$

$$Th^{+\cdot} + PhC(Me)H\cdot \longrightarrow Th + PhC(Me)H^{+} \quad (3)$$



Scheme 1. Mechanism of product formation from *meso*-ABPE and thianthrene cation radical.

$$PhC(Me)H^{+} + MeCN \longrightarrow PhC(Me)HN = {}^{+}CMe \quad (4)$$

$$PhC(Me)HN = {}^{+}CMe + H_2O \longrightarrow PhC(Me)HNHCOMe + H^{+} \quad (5)$$

All these reactions may involve prior complexation, as was proposed for the cation radical oxidation of anisole.[8]

In contrast to the oxidation of AA, and of DPAM with cation radical, acetophenone and small amounts of azine, PhC (Me)=N-N=(Me)CPh were obtained. The formation of acetophenone can be attributed to the hydrolysis of either the corresponding hydrazone or acetophenone azine. However, when an attempt was made to hydrolyze the authentic azine by 70% perchloric acid in acetonitrile solution, the azine was recovered quantitatively. Hence, the formation of acetophenone from the hydrolysis of the azine can be ruled out. Azoalkanes possesing α-protons can tautomerize easily to the more stable isomeric hydrazones.[9] We are not sure whether the tautomerization occurred in solution prior to the oxidation of *meso*-ABPE or after oxidation, but the cation radical of *meso*-ABPE tautomerized to the cation radical of acetophenone α-phenylethylhydrazone. In this study, 1,2,4-triazole can't be formed from the oxidative cycloaddition of acetophenone α-phenylethylhydrazone cation radical to the solvent MeCN, because ABPE has only one α hydrogen. Acetophenone azine was a product of oxidation of the azo com-

pound. A possible mechanism for the formation of the azine is shown in Eq. (6)-(9).

$$PhC(Me)HN=NH(Me)CPh + Th^{+\cdot} \longrightarrow Th + [PhC(Me)HN=NH(Me)CPh]^{+\cdot} \quad (6)$$

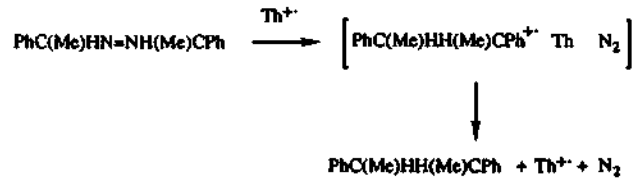
$$PhC(Me)\overset{+}{H}N\text{-}\dot{N}H(Me)CPh \longrightarrow PhC(Me)=N\text{-}\dot{N}H(Me)CPh + H^{+} \quad (7)$$

$$PhC(Me)=N\text{-}\dot{N}H(Me)CPh + Th^{+\cdot} \longrightarrow PhC(Me)=N\text{-}\overset{+}{N}H(Me)CPh + Th \quad (8)$$

$$PhC(Me)=N\text{-}\overset{+}{N}H(Me)CPh \longrightarrow PhC(Me)=N\text{-}N=(Me)CPh + H^{+} \quad (9)$$

The formation of the thianthrene 5-oxide (ThO) can be rationalized by hydrolysis of either some of $Th^{+\cdot}$ by incompletely dried solvent during the course of reaction, or unused $Th^{+\cdot}$ during workup.[10]

No evidence for ethylbenzene was found from the α-phenylethyl radical disproportionation reaction or from hydrogen abstraction from MeCN. When the reaction of $Th^{+\cdot}$ with *meso*-ABPE was carried out in the presence of $BrCCl_3$ in MeCN, as we did earlier with AA, the formation of DBP was not stopped. Therefore, we can conclude that DPB is probably not formed in the oxidative reactions by dimerization of α-phenylethyl radical. Generally, radical is destined to abstract hydrogen atom fro MeCN rather than to dimerize in the absence of a competing reaction.[11] The mechanism for the formation of DPB is rationalized in Scheme 2, which is very similar to that of formation of AdAd by $Th^{+\cdot}$.[11] DPB may have arisen from the DPB cation radical [PhC(Me)HH-(Me)$CPh^{+\cdot}$], formed by a cage recombination between α-phenylethyl cation and α-phenylethyl radical, rather than the coupling between two α-phenylethyl radicals. Conversion of DPB cation radical into DPB would have to occur by electron-transfer reaction from $Th^{+\cdot}$ within solvent cage. In that case, $Th^{+\cdot}$ would have served as a catalyst for the formation of DPB from *meso*-ABPE. It is interesting to compare the yield of AdAd and DPB from oxidative decomposition of corresponding azoalkane $Th^{+\cdot}$. Whereas 2.5% of AdAd was obtained from oxidation of AA, 23.6% of DPB was formed in the oxidative of *meso*-ABPE by $Th^{+\cdot}$. In the oxidation of *meso*-ABPE with $Th^{+\cdot}$, α-phenylethyl radical would not survive so long enough to be reduced to cation as tetriary adamantyl radical. Therefore, relatively lots of α-phenylethyl radical would recombine with α-phenylethyl cation to form a DPB without further oxidation in the solvent cage. *Meso*-ABPE gave 21.8% of *meso* and 1.8% of non-*meso*-DPB, indicating that some changes in orientations (by out-of-plane rotation) of the cations and radicals are occurring in these original cages prior to combination between α-phenylethylcation and



Scheme 2. Possible reaction pathways for the formation of 2,3-diphenylbutane.

α-phenylethyl radical.

In conclusion, the reaction of $Th^{+\cdot}$ with *meso*-ABPE, possesing one α hydrogen, in acetonitrile follows not only the carbocationic route but also unundergoes tautomerization to its hydrazone, and no oxidative cycloaddition was observed.

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The Crystal Structure and Magnetic Properties of Triethylenediaminenickel(II)-Bis(maleonitriledithiolato)nickelate(II); $[Ni(C_2H_8N_2)_3]$-$[Ni(C_4N_2S_2)_2]$

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Bidentate dithiolate ligands form very well square planar complexes with Ni-triad ions of different oxidation states,