

Hard-soft acid-base (HSAB) principle and difference in *d*-orbital configurations of metals explain the regioselectivity of nucleophilic attack to a carbinol in Friedel-Crafts reaction catalyzed by Lewis and protonic acids

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The alkylations of aromatic compounds in presence of protonic acids yield two alkylated products arising from attack of a nucleophile (hard or soft) at two different carbocation (hard or soft) centers of a single compound. Hybrid density functional theory at B3LYP/6-31G* and B3LYP/6-31G levels and semiempirical calculations are employed to explain the observed trends in Friedel-Crafts reaction. Local HSAB principle based on local softness values explains the observed experimental reactivities.

Keywords: Nucleophile, Friedel-Crafts reaction, HSAB principle, tight-ion pair

IPC: Int.Cl.⁷ C 07 C

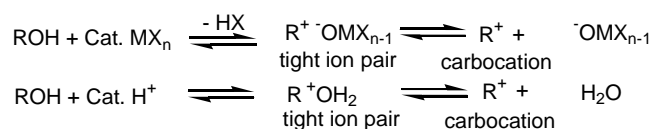
The alkylation of aromatic rings, commonly known as Friedel-Crafts (FC) alkylation, is a powerful tool for new carbon-carbon bond formation¹. It is a reaction between an aromatic ring and substrates such as alkyl halides, olefins, alcohols and many other types of reagents in the presence of Lewis acids or protonic acids¹. Regardless of which reagent is used, a catalyst is always required². Acidic metal halides, of which AlCl₃ and AlBr₃ are the most frequently used, comprise a large number of Lewis acid catalysts for Friedel-Crafts reactions³. Other frequently used active metal halide catalysts include: ZnCl₂, BF₃, BCl₃, BBr₃, GaCl₃, GaBr₃, TiCl₄, ZrCl₄, SnCl₄, SbCl₅, BiCl₃ and FeCl₃. Such Lewis acids possess an electron-deficient central atom, capable of accepting electrons from basic substances.

A Lewis acid catalyst can interact with reagents containing a functional group having a donor atom with non-bonded pairs of electrons. Depending on the substrates, the reaction gives rise to a positively polarized complex (tight-ion pair) or carbocationic species, which then reacts with the π -donor substrate (aromatic, alkenic or alkynic hydrocarbons). Reactions that are catalysed by metal halides are also catalysed by protonic acids⁴. The most commonly used Brönsted acids are conc. H₂SO₄, H₃PO₄ or PPA and HF. When a suitable Lewis acid halide and

protonic acid are combined, conjugate Friedel-Crafts acids are formed, which are, indeed, superacids with a wide range of activity. Anhydrous HF-BF₃ and HCl-AlCl₃ are widely used examples of such acids⁴.

The alkylations of arenes with alcohols are of considerable interest and constitute a significant part in the field of Friedel-Crafts alkylations. The relative ease of alkylation with alcohols follows the order: benzyl, allyl > tertiary > secondary > primary > methyl. This is in accord with the knowledge that carbocations rearrange in the direction of primary < secondary < tertiary < benzyl, allyl. In each case either a carbocation or a tight-ion pair is formed from the attacking reagent and the catalyst (**Scheme I**)⁵.

In this study, density functional theory (DFT) based reactivity descriptors have been used to understand site- and regio-selective reactions⁷⁻⁹. Several studies have been reported the applicability of local hard-soft acid-base (HSAB) principle in examining the site selectivity in a molecule⁹⁻¹³. According to Li-Evans HSAB rule⁹,



Scheme I

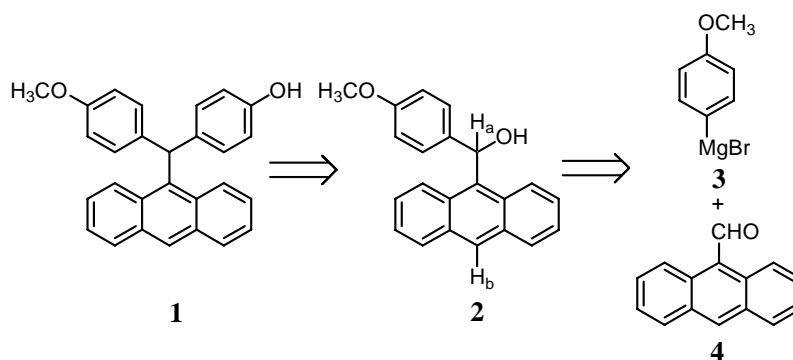
soft-soft interactions prefer the sites of maximal Fukui functions whereas the minimal Fukui function sites are preferred for hard-hard interactions. Local softness values were calculated in this study in order to understand the experimentally observed reactivities.

Results and Discussion

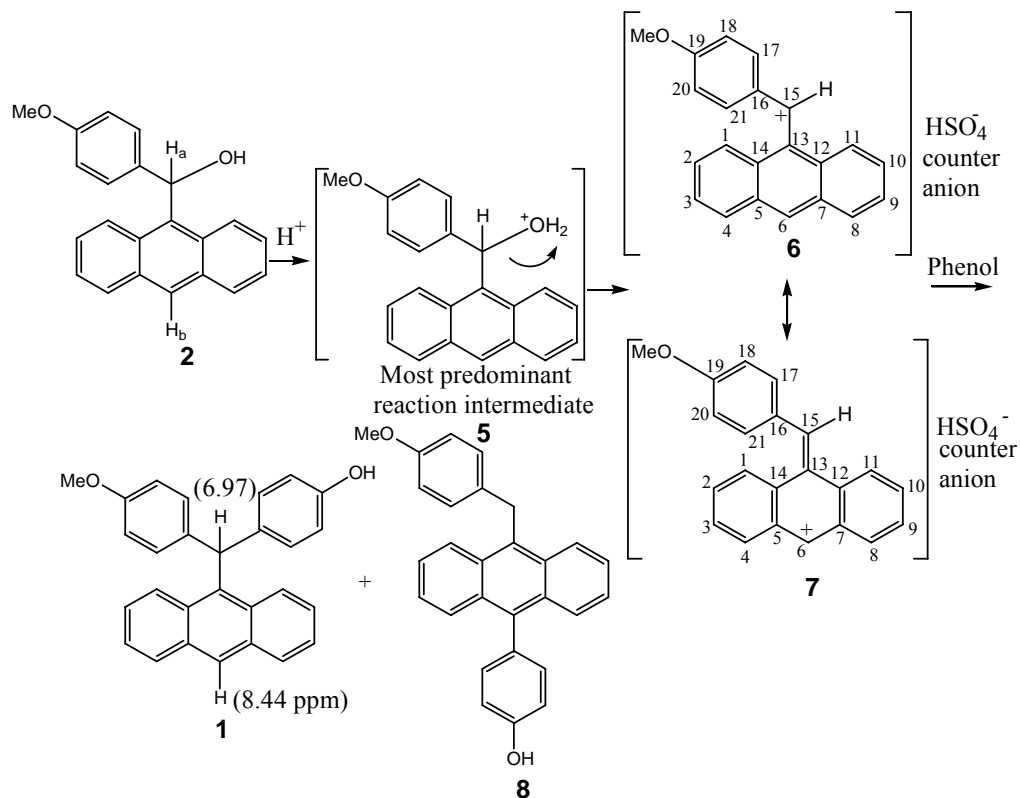
In our ongoing program towards synthesizing diaryloxy methano anthracenes as TRAMs (triaryl methanes), we have identified **1** as a target molecule. Retrosynthetic analysis of **1** leads to compound **2** as the precursor which can be obtained from the nucleophilic addition of Grignard reagent 4-methoxyphenylmagnesium bromide **3** onto anthracene-9-carbaldehyde **4** (**Scheme II**). As discussed in

Scheme II, the reaction between Grignard reagent **3** and **4** in dry THF furnished the carbinol **2** in 70% isolated yield. IR frequency at 3431 cm^{-1} indicates the presence of hydroxyl group in **2**. The characteristic singlets at δ 7.34 and 8.46 ppm in its ^1H NMR spectra were assigned for benzylic methine proton (H_a) and aromatic proton (H_b), respectively. ^{13}C NMR and mass spectral data (molecular ion peak at 314 amu) further confirmed the structural identity of **2**.

Having obtained the precursor **2** in appreciable quantity, Friedel-Crafts alkylation with phenol in presence of Conc. H_2SO_4 as a catalytic protonic acid in dry benzene was attempted. To our surprise, we isolated compound **8** as the major product along with compound **1** (90:10), (**Scheme III**). Compound **1** was



Scheme II



Scheme III

characterized from its singlet aromatic proton (δ 8.44 ppm) and singlet methine proton (δ 6.97 ppm) resonances, respectively. Whereas in ^1H NMR spectra of **8**, both the singlets were absent and a new singlet appeared at δ 4.85 ppm due to methylene protons. The structural identity of **8** was further confirmed by its ^{13}C NMR and mass spectrum fragmentation analysis. Treatment of carbinol **2** with conc. H_2SO_4 in dry benzene gives reactive intermediate **5** which after elimination of water gives two resonating structures **6** and **7**, respectively. Thereafter, compounds **1** and **8** are formed by the nucleophilic attack of phenol to carbocation centers C15 and C6 that are shown in resonating structures **6** and **7**, respectively. Due to +R effect of *para*-methoxy group on benzene ring, the availability of net +ve charge on C15 atom in **6** will be less than that of C6 atom in **7**. Thus, in resonance forms between **6** and **7**, the proportion of **7** will be more than **6** in the mixture. Hence, nucleophilic attack of phenol occurs through *para*-carbon atom of benzene ring onto the electrophilic C6 atom in **7** giving rise to **8** as major product and **1** as minor one. We have not observed any O-alkylated product due to better nucleophilicity of carbon atom than oxygen atom of phenol ring. The reaction does not proceed through tight-ion pair complex like **9**, **Scheme IV**. There will be less probability of resonance carbocationic forms like **6** and **7** in complex **9**. If the reaction proceeded through tight-ion pair complex like **9**, then nucleophilic attack of phenol on **9** should have given **1** as a major product. But that does not happen, **Scheme III** (comp. **8** as major product). Similar results were also obtained when the reaction was

conducted in HCl, PPA or H_3PO_4 as protonic acid (**Table I**).

In order to obtain the desired compound **1** as a major one, FC alkylations of **2** were attempted in the presence of Lewis acids as catalysts, (plausible reaction mechanism is shown in **Schemes V** and **VI**). In this study, AlCl_3 , ZnCl_2 , FeCl_3 and TiCl_4 were chosen as Lewis acid catalysts. All reactions were

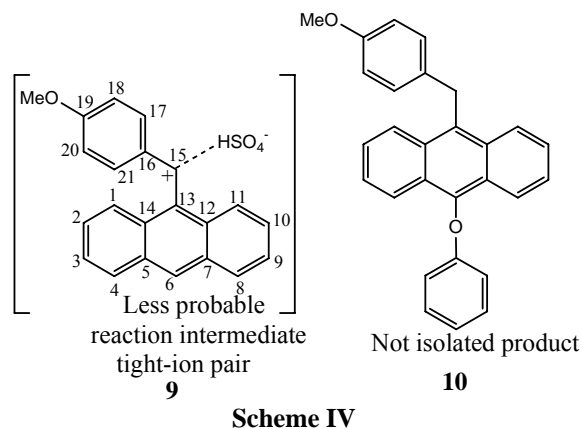
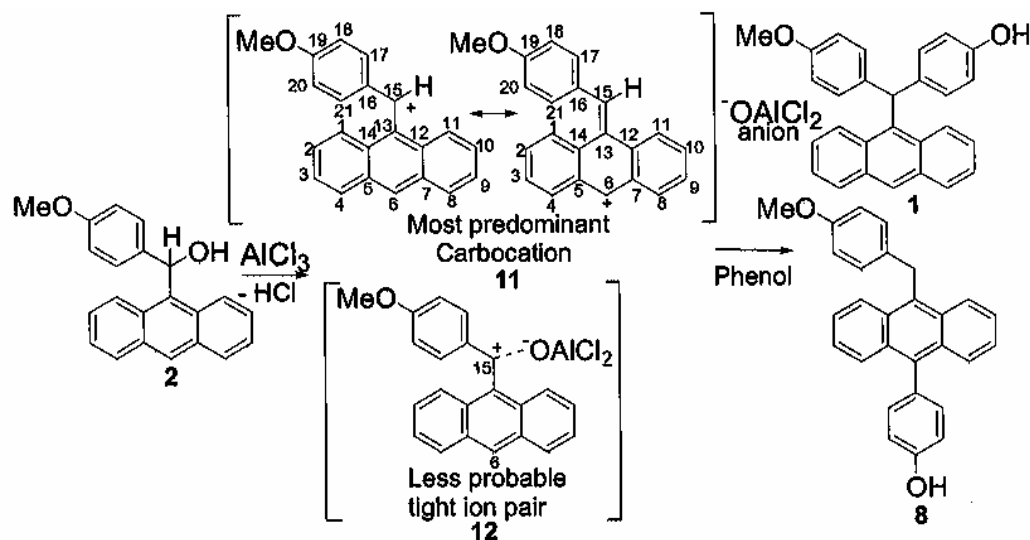
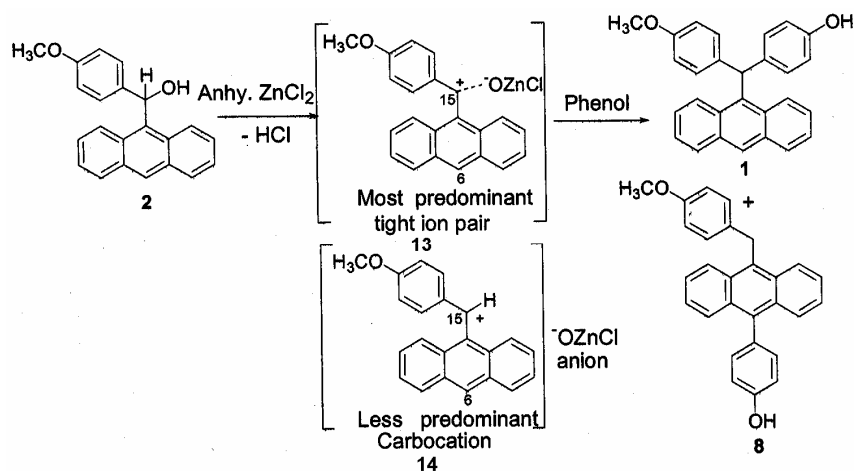


Table I — Alkylation of phenol with carbinol in presence of protonic acids

Protonic Acids	Temp. °C	Time (hr) ^a	Alkylated product (1 : 8)	Yield (%)
Conc. H_2SO_4	80	1	10:90	95
HCl	80	1	12:88	98
PPA	80	1	15:85	95

^aAll reactions were performed through microwave irradiation in dry benzene and were complete within 1 min. Yields were comparable as in **Table I**.





Scheme VI

Table II — Alkylation of phenol with carbinol in presence of Lewis acids

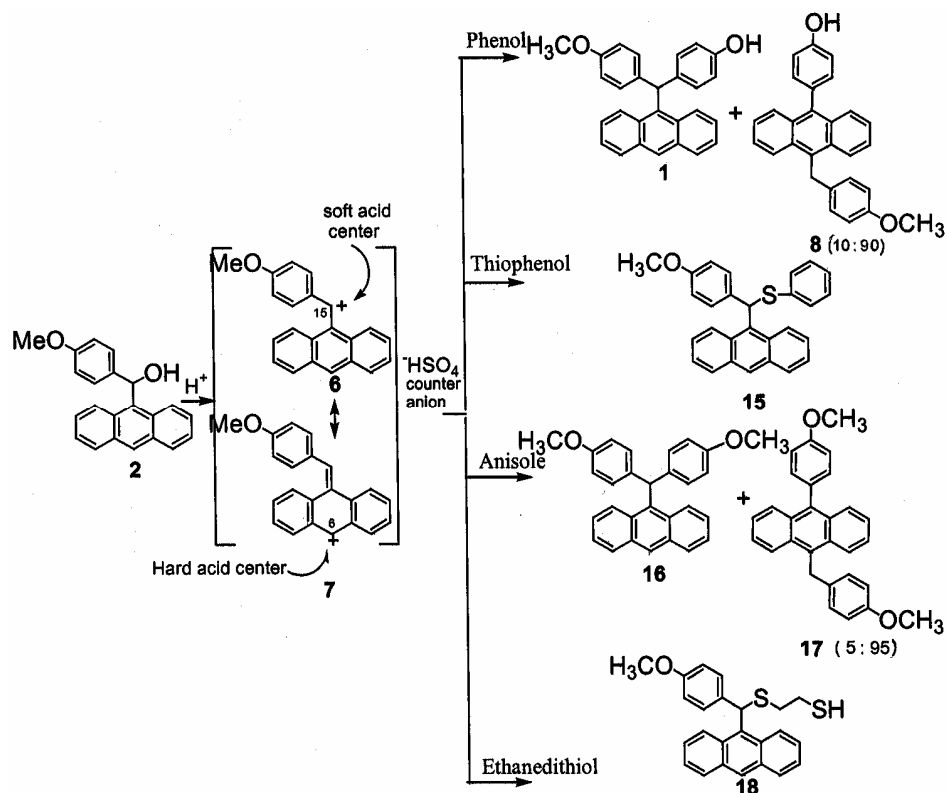
Lewis Acids	Temp. °C	Time (hr)	Alkylated product (1 : 8)	Yield (%)
AlCl ₃	0-5	1	35: 65	40
TiCl ₄	0-5	1	40: 60	45
FeCl ₃	0-5	1	55: 45	45
ZnCl ₂	0-5	1	70: 30	45

carried out in dry benzene as a solvent. Reaction conditions, product ratios and percentage yields are given in **Table II**.

The formation of compound **1** could be explained on the basis of the fact that FC alkylation proceeded via tight-ion pair intermediate. The electronic configuration of outer shell of Al, Ti, Fe and Zn is as follows. Al ($3d^0 3s^2 3p^1$), Ti ($3d^2 4s^2$), Fe ($3d^6 4s^2$) and Zn ($3d^{10} 4s^2$). After the reaction between ROH and MX_n ($M = Al, Ti, Fe, Zn, X = Cl$), ($n=0-4$), the complex $ROMX_{n-1}$ exists as a tight-ion pair⁵ R^+OMX_{n-1} like **13** as shown in **Scheme VI** or dissociates into carbocation R^+ like **11** in **Scheme V**. Existence of tight-ion pair⁵ like R^+OMX_{n-1} will increase when the electron charge density on oxygen atom increases and thereafter give a stable tight-ion pair complex. For example, the complex R^+OAlCl_2 behaves in this fashion. Al having a vacant $3d$ orbital ($3d^0 3s^2 3p^1$) would like to pull the electron cloud around oxygen towards it and that results in more cationic charge on carbon atom as shown in structure **11** in **Scheme V**. Once the carbocation **11** exits, it is expected to be in equilibrium with its resonance forms like **6** and **7** with $^-OAlCl_2$ as counter anion instead of⁻

HSO_4 . Due to +R effect of *p*-methoxy group, the availability of +ve charge on C15 atom in **11** will be less than that of C6 atom in **11**. Then the attack of phenol will be more on electrophilic C6 atom in **11** giving rise to compound **8** as a major product and **1** as a minor one. On the other hand, Zn having filled $3d$ orbital ($3d^{10} 4s^2$) tends to have less tendency to pull the electron cloud as compared to that of Al and therefore the electron charge density around oxygen atom is higher which results in the existence of tight ion pair intermediate **13**. Once the intermediate **13** is formed, the rearrangement of positive charge to atom C6 i.e. the resonance species **14** is reduced and thus the attack of phenol will have no other option but to attack C15 atom in **13** giving **1** as the major product. The tight-ion pair **12** and **13** are expected to be in equilibrium with their carbocationic intermediate, **11** and **14**, respectively. Although the reaction will preferably go through carbocationic intermediates **11** or tight-ion pair intermediate **13**, some portion of **12** and **14** will always be there in the mixture and the attack of phenol on **12** and **14** will give minor product. We also noticed that when other transition metal Lewis acids like $TiCl_4$ or $FeCl_3$ were used as catalysts for FC alkylation of **2**, the difference in ratio of **1** and **8** were comparable. This may be attributed to partially filled *d* orbital of Ti ($3d^2 4s^2$) and Fe ($3d^6 4s^2$) where half life of intermediates like **11** and **12** or **13** and **14** with their corresponding anions would be more or less the same (**Table II**).

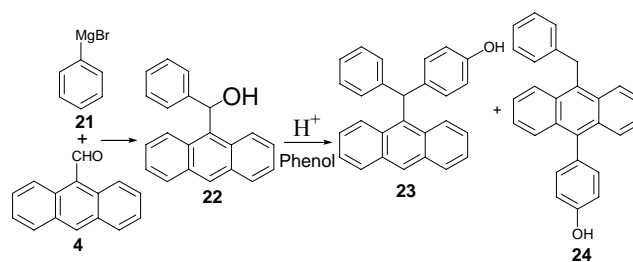
We then turned our attention towards studying the attack of nucleophiles thiophenol, anisole, ethanedithiol, aniline and *N*-ethylaniline with carbinol **2** in the presence of Conc. H_2SO_4 . We have interpreted the



Scheme VII

outcome of FC reactions on the basis of hard and soft acid base principle (HSAB).¹⁴ The theory is quite useful and is used for different purposes. The facility with which an acid-base reaction takes place depends on the strengths of the acid and base. According to the principle, hard acids prefer to bond to hard bases and soft acids prefer to bond to soft bases. Carbocation center C15 of **6** is a soft acid center due to +R effect of *p*-methoxy group on benzene ring and carbocation center C6 in **7** is hard acid center due to absence of any +R effect of nearby group.

The reaction of the carbinol **2** with the nucleophiles thiophenol, anisole and ethanedithiol gave FC alkylated products **15**, **17** and **18** as major products respectively (Scheme VII). We have applied HSAB principle to explain the ratio of the products. The *para* carbon atom of phenol being a hard nucleophile center will prefer to bond to hard acid center C6 giving rise to **8** as the major product. On the other hand, the sulfur atom of thiophenol, being a soft base center will prefer to bond to soft acid center C15 and thus gave **15** as the major product. Sulphur of ethanedithiol being also a soft base center will bond to soft acid center C15 and gave **18** as major product. As a nucleophile, anisole behaves like phenol. There is no possibility of *O*-alkylated product in case of



Scheme VIII

anisole and *para* carbon atom of anisole being a hard nucleophile prefers to bond to hard acid center C6 and gave compound **17** as major product. To some extent, there will be nucleophilic attack of anisole on soft acid center C15, giving rise to **16** as minor product.

We also have prepared carbinol **20** from the treatment of Grignard reagent **19** on anthracene-9-carbaldehyde **4**. Reaction of carbinol **20** with phenol in presence of conc. H₂SO₄ and benzene furnished two FC alkylated products **21** and **22** (4.5 : 5.5) in good yield (80%), Scheme VIII. Thus, in absence of *para*-methoxy group, **21** and **22** were obtained in more or less equal amounts (4.5 : 5.5).

Computational results

Theoretical calculations were carried out to obtain a better understanding of the reactivity of the

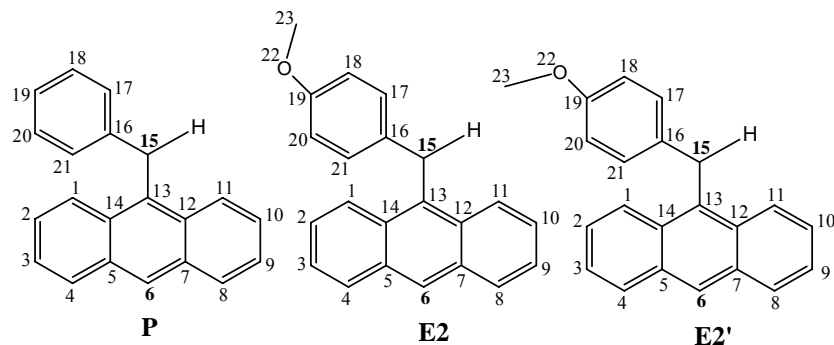
reactants, which possess more than one reactive site. Local softness values were calculated for all the atomic sites in order to identify the preferable reactive sites of the reactants that are involved in the reactions considered. The parent carbocation (**P**) is also considered to examine the effect of OMe group in the reactivity of these reactions. **Scheme VII** depicts the parent cation and two conformers (**E2'** and **E2'**) of electrophile. The structures of the nucleophiles are shown in **Scheme VIII**. Atomic charges, local softness values only for the potential sites along with HOMO and LUMO energies and global softness values obtained at B3LYP/6-31G* level are given in **Table III** and **IV** for electrophiles and nucleophiles respectively. The local softness s_k^+ and s_k^- are the pertinent quantities for electrophiles and nucleophiles, respectively, to predict the reactivity. Expectedly, the more preferable reactive sites C6 and C15 have s_k^+ values higher than s_k^- indicating the electrophilic nature of **P**, **E2** and **E2'** (**Table III**, **Scheme IX**). Similarly, s_k^- values are higher than s_k^+ values for nucleophiles (**Table IV**). **Table III** shows that in case of **E2** and **E2'**, atom C15 possesses higher s_k^+ value compared to site C6 indicating that the former atom is the soft center and the latter is the hard center. But in case of parent system (**P**), the difference in s_k^+ values between these two centers is only 0.007 thus unambiguous categorization of the nature of the reactive center either as soft or hard is difficult. The above computational analysis quantifies the influence of OMe substitution on altering the hard/soft nature of the reactive centers. The atomic charges on C6 and C15 are almost the same in case of **P** whereas C15 has higher negative charge compared to C6 in **E2** and **E2'**, this can be attributed to the effect of OMe substitution.

According to local hard-soft acid-base (HSAB) principle, soft-soft interactions are preferred in the

site of the maximum Fukui function whereas the sites of minimum Fukui function are favoured for hard-hard interactions. Structure **E2** is about 0.4 kcal/mol more stable than that of **E2'** at B3LYP/6-31G* level. Hence, the softness values corresponding to **E2** are taken for explaining the reactivity between **E2** and nucleophiles. Local softness values predicted the reactivity of C4 atoms (hard center) of phenol and anisole towards the C6 atom (hard center) of **E2**. The hard-hard interactions in these cases are in agreement with the experimental observations. Sulfur atoms of thiophenol and ethanedithiol are predicted to be the soft centers (s_k^- values are 1.628 and 1.503 a.u respectively), thus bond formation with C15 (soft center) of **E2** is much favoured. Local-local softness matching approach explains the observed products in all the reactions.

Total and relative energies of the products for all the reactions are given in **Table V**. The relative energies obtained at AM1 and B3LYP levels are very similar. In both the levels, the product formed by the attack of nucleophile to the hard acid center C6 of **E2** is predicted to be more stable than the other product in which nucleophile is attached to soft acid center.

It is interesting to study how the conformations alter atomic charges, hardness and softness values at the two reactive centers (C6 and C15) in case of **E2** and parent carbocation (**P**). Attempts to locate different conformers for **P** and **E2** were futile and yielded only the lowest energy conformer reported in this study. Hence, the conformations with specific value for the dihedral angle $\Phi_{16-15-13-14}$ were generated using relaxed potential energy surface scan at B3LYP/6-31G level. The atomic charges, hardness and softness values at two reactive centers along with the total and relative energies for the conformations with specified dihedral angle are provided in **Tables VI** and **VII** for systems **E2** and **P**, respectively. **Tables VI** and **VII** indicate that the



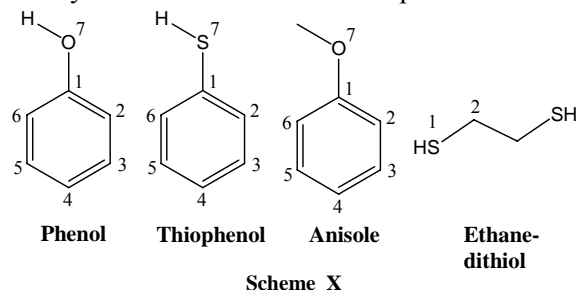
Scheme IX

atomic charges at C15 are more negative than those at C6 for both **E2** and **P**. In almost all the conformations, s_k^+ values are higher than s_k^- . The reasons for obtaining the negative local softness values have been explained by Roy *et al.*¹⁶

Table VI and **Figure 1a** indicate that few of the conformations have very high softness values e.g. the conformations with dihedral angle 82.5 and 102.5 degrees and in many cases, the reactive site C15 is the soft center. This situation is similar to the parent system (**P**) (**Table VII** and **Figure 1b**). It is to be noted that the reactivity at atom C6 is not significantly changed when we change the conformations in both **E2** and **P**. The present study indicates that conformations may trigger the reactivity crossovers in cases of reactant possessing different reactive sites. In cases of both **E2** and **P**, the charges at C15 are more negative than those at C6.

Conclusion

The present study reports the Friedel-Crafts alkylation reactions by the nucleophilic attack to the carbinol **2** which possesses two reactive sites. We report for the first time that the stability of tight-ion pair⁵ increases in the FC alkylation with the use of Lewis acids having metal with filled *d*-orbital. It is noteworthy that the ratio of FC alkylated products can be varied using different Lewis acids with different *d*-shell configurations and different protonic acids. We have interpreted the outcome and ratio of Friedel-Crafts products on the basis of hard-soft acid-base principle (HSAB). Hard nucleophiles (phenol and anisole) prefer to bond to hard acid center whereas soft nucleophiles (thiophenol and ethanedithiol) prefer to bond to soft acid center (**Scheme X**). B3LYP/6-31G* method was employed to calculate density functional theory based reactivity descriptors, local softness values, to examine the experimental observations of the reactions. Local HSAB principle based on local softness values explains the experimental reactivity of the reactions. The computational investi-



gations indicate that OMe group controls the nature of hard and soft reactive sites. The present study also indicates that the conformations may trigger the reactivity crossovers in the reactant having more than one reactive center. Further experimental and mechanistic studies of the FC reaction in different solvents (polar, nonpolar and aprotic) under different conditions are currently underway.

Experimental Section

General procedure

All the reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% CeSO₄ in 2N H₂SO₄) sprayed plates in hot plate or in oven at about 100°C. Silica gel 60-120 mesh was used for column chromatography. Melting point was recorded on an electrically heated apparatus and was uncorrected. IR spectra were recorded on Perkin-Elmer 881 or FT IR 820/PC instrument and values are expressed in cm⁻¹. Electron impact mass spectra were recorded on JEOL (Japan) /D-300 instrument and FAM mass spectra were recorded on JEOL SX 102/DA-6000 mass using Argon /Xenon (6 KV, 10 MA) as the FAB gas. ¹H and ¹³C NMR spectra were recorded on Bruker Advance DPX 200 MHz using TMS as internal reference. Chemical shift value is expressed in δ ppm. Specific rotation was determined with Rudolph Autopol IIIrd polarimeter at 28°C. Elementary analysis was carried out on Carlo ERBA-1108 analyzer. Commercially available grades of organic solvents of adequate purity are used in many reactions. Acetone was refluxed with KMnO₄ for 4 hr, after that it was distilled and stored in a bottle containing dried K₂CO₃. Benzene was refluxed with freshly cut and dried sodium metal pieces pressed in 3Å sieves for 4-6 hr. It was distilled and stored in a dry bottle. Tetrahydrofuran first dried initially over calcium sulphate and then refluxed over lithium aluminium hydride. Peroxide was removed by passage through a column of aluminum and distilled and stored over molecular sieves 3Å.

Anthracene-9-calbaldehyde 4. A mixture of anthracene (5 gm, 28.09 mmoles), N-methylformanilide (7.59 g., 56.18 mmoles), POCl₃ (5 mL, 80.0 mmoles) was taken in *o*-dichlorobenzene (15 mL) and was refluxed at 100°C for 1 hr. Colour of the reaction mixture changed to deep red and it was cooled to room temperature. Sodium acetate (31 gm) in water (60 mL) was added and stirring was continued for

Table III — Atomic charges and local softness values for the reactive centers obtained at B3LYP/6-31G* level for parent carbocation (**P**), conformers of electrophiles **E2** and **E2'**. HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) and global softness (S) values are also given. All values are in atomic units (see **Scheme VII** for atom numbering and nomenclature.)

Electrophile	E_{HOMO}	E_{LUMO}	Global softness (S)	Reactive atoms	Atomic charge	Local softness	
						s_k^+	s_k^-
P	-0.341	-0.256	11.784	C6	-0.230	0.376	0.176
				C15	-0.233	0.369	0.101
E2	-0.320	-0.243	12.512	C6	-0.244	0.760	0.431
				C15	-0.256	0.842	0.097
E2'	-0.323	-0.244	12.553	C6	-0.244	0.760	0.435
				C15	-0.254	0.867	0.073

Table IV — Atomic charges and local softness values for the reactive centers obtained at B3LYP/6-31G* level for nucleophiles along with HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) and global softness (S) values. All values are in atomic units (see **Scheme VIII** for structures and atom numbering.)

Nucleophile	E_{HOMO}	E_{LUMO}	Global softness (S)	Reactive atoms	Atomic charge	Local softness	
						s_k^-	s_k^+
Phenol	-0.219	0.001	4.541	C4	-0.135	0.366	-0.067
				O7	-0.643	0.636	0.188
Thiophenol	-0.218	-0.005	4.690	C4	-0.136	0.277	-0.070
				S7	-0.028	1.628	0.632
Anisole	-0.215	0.004	4.563	C4	-0.134	0.327	-0.060
				O7	-0.507	0.564	0.093
Ethanedithiol	-0.240	0.002	4.144	S1	-0.077	1.503	1.170

Table V — Total energies (in hartrees) and relative energies (in kcal/mol) at AM1 and B3LYP/6-31G**/AM1 levels for the products of the nucleophilic attack on two different reactive sites of **E2**^a

Nucleophile	Prod.	AM1		B3LYP/6-31G**/AM1	
		E	ΔE	E	ΔE
Phenol	1	0.06584	7.4	-1230.65655	7.3
	8	0.05409	0.0	-1230.66823	0.0
Thiophenol	15	0.15297	4.8	-1553.61609	5.4
	15'	0.14538	0.0	-1553.62473	0.0
Anisole	16	0.07593	7.4	-1269.96127	7.5
	17	0.06418	0.0	-1269.97319	0.0
Ethane-dithiol	18	0.10440	5.1	-1799.37113	2.6
	18'	0.09635	0.0	-1799.37532	0.0

(a) Structures of **15'** are shown in ref. 15.

2 hr. It was extracted with chloroform (150 mL) and dried over Na_2SO_4 . It was recrystallized from methanol (4.7 g, 81%).

Anthracen-9-yl-(4-methoxy-phenyl)-methanol 2. To a solution of 4-bromoanisole (16.15 g, 0.086 mole) in dry THF (20 mL) was added activated magnesium (2.06 g, 0.086 moles) and was stirred at room temperature under dry nitrogen for 2 hr. To Grignard

reagent thus formed was added anthracene-9-carbaldehyde **4** (5.94 g, 0.028 mole) in THF (25 mL) and stirring was continued for another 3-4 hr. The reaction mixture was quenched by gradual addition of saturated NH_4Cl (~10 mL) and THF was removed *in vacuo*. The mixture was extracted thrice with ethyl acetate, washed with brine and dried over sodium sulphate. It was concentrated and charged over silica gel. Elution with 10% ethylacetate in hexane furnished the title compound **2** (6.0 gm, 66%). m.p. 82°C ; IR (KBr): 3510, 2362, 1604, 1507, 1242, 1169, 732 cm^{-1} ; ^1H NMR: δ 8.46 (s, 1H), 8.36 (d, 2H, $J = 9\text{ Hz}$), 8.03 (d, 1H, $J = 7.8\text{ Hz}$), 8.01 (d, 1H, $J = 9\text{ Hz}$), 7.47-7.34 (m, 5H), 7.27 (d, 1H, $J = 9\text{ Hz}$), 6.79 (d, 2H, $J = 10\text{ Hz}$), 3.74 (s, 3H), 2.64 (d, 1H, $J = 5.4\text{ Hz}$); MS: 314 (M^+), MS (EI): m/z 314 (M^+).

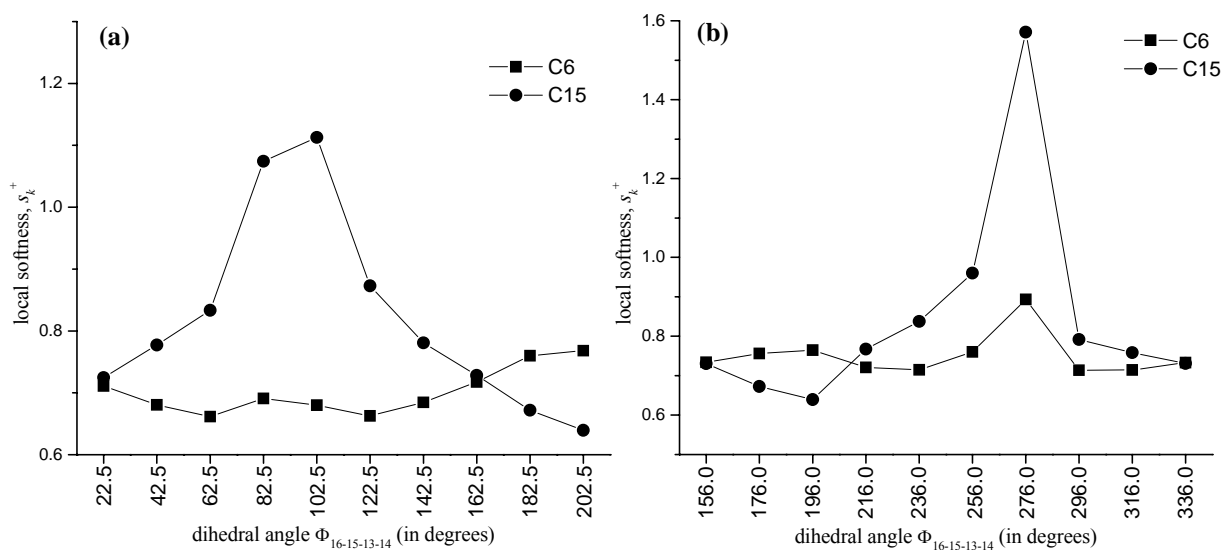
4-[Anthracen-9-yl-(4-methoxyphenyl)methyl]-phenol 1,4-[10-4-(methoxybenzyl)anthracen-9-yl]-phenol 8. To a solution of carbinol **2** (500 mg, 1.59 mmoles) taken in dry benzene (10 mL) and pentane (15 mL) at room temperature was gradually added phenol (0.196 mL, 2.37 mmoles) and the reaction mixture was stirred at 0°C for 30 min. AlCl_3 (212 mg, 1.58 mmoles) was added followed by SnCl_4 (468 mg, 1.79 mmoles) and stirring was continued for another

Table VI — Total energy, rel. energy, atomic charge, local softness values for **E2** obtained at B3LYP/6-31G for conformations with dihedral angle $\Phi_{16-15-13-14}$.

Sl. No.	Dihedral angle $\Phi_{16-15-13-14}$ (degrees)	Total Energy E (hartrees)	Relative energy ΔE (kcal/mol)	Atomic charge		Local softness (a.u)			
				C6	C15	s_k^+		s_k^-	
1	22.5	-923.35486	0.0	-0.174	-0.199	0.711	0.724	0.431	0.107
2	42.5	-923.35479	0.0	-0.178	-0.198	0.681	0.777	0.467	0.077
3	62.5	-923.35003	3.0	-0.184	-0.194	0.661	0.833	0.534	0.053
4	82.5	-923.34080	8.8	-0.188	-0.199	0.691	1.074	0.684	-0.054
5	102.5	-923.34134	8.5	-0.183	-0.219	0.680	1.113	0.673	-0.010
6	122.5	-923.35034	2.8	-0.179	-0.212	0.663	0.873	0.534	0.081
7	142.5	-923.35497	-0.1	-0.176	-0.204	0.684	0.781	0.463	0.087
8	162.5	-923.35426	0.4	-0.171	-0.197	0.717	0.728	0.425	0.110
9	182.5	-923.34940	3.4	-0.162	-0.194	0.760	0.672	0.426	0.107
10	202.5	-923.34084	8.8	-0.161	-0.195	0.768	0.639	0.427	0.136

Table VII — Total energy (hartrees), relative energy (kcal/mol), atomic charge and local softness values (a.u) for parent carbocation **P** obtained at B3LYP/6-31G level for the conformations with specific dihedral angle $\Phi_{16-15-13-14}$.

Sl. No.	Dihedral angle $\Phi_{16-15-13-14}$ (degrees)	E (hartrees)	ΔE (kcal/mol)	Atomic charge		Local softness			
				C6	C15	s_k^+		s_k^-	
1	156.0	-808.86163	0.0	-0.165	-0.188	0.734	0.731	0.397	0.255
2	176.0	-808.85930	1.5	-0.157	-0.184	0.756	0.673	0.378	0.247
3	196.0	-808.85262	5.7	-0.155	-0.189	0.765	0.640	0.372	0.262
4	216.0	-808.86088	0.5	-0.169	-0.194	0.721	0.767	0.421	0.253
5	236.0	-808.85533	4.0	-0.172	-0.202	0.715	0.838	0.489	0.243
6	256.0	-808.84482	10.5	-0.174	-0.210	0.760	0.960	0.575	0.275
7	276.0	-808.83130	19.0	-0.181	-0.207	0.893	1.571	0.943	0.381
8	296.0	-808.85384	4.9	-0.179	-0.185	0.714	0.792	0.452	0.260
9	316.0	-808.86014	0.9	-0.172	-0.189	0.714	0.759	0.430	0.235
10	336.0	-808.86163	0.0	-0.165	-0.188	0.733	0.731	0.398	0.255

**Figure 1** — Variation of local softness, s_k^+ values at centers C6 and C15 of (a) **E2** and (b) **P** by changing $\Phi_{16-15-13-14}$ for 180° rotation from optimized geometry.

1 hr. Water was slowly added and the reaction mixture was extracted with ethylacetate. The organic layer was washed with water, brine and dried over anhydrous Na₂SO₄. It was concentrated to give an oily residue which was charged over silica gel. Elution with 15% ethyl acetate in hexane furnished **1** (158 mg) and **8** (368 mg, combined yield 85%). **1**: m.p. 78°C; IR (KBr): 3431, 1605, 1507, 1443, 1245, 1172, 1028 cm⁻¹; ¹H NMR: δ 8.44 (s, 1H), 8.14 (d, 2H, *J* = 9 Hz), 8.00 (d, 2H, *J* = 8.5 Hz), 7.45-7.20 (m, 4H), 7.14-6.90 (m, 4H), 6.97 (s, 1H), 6.77 (d, 2H, *J* = 8 Hz), 6.69 (d, 2H, *J* = 8 Hz), 3.75 (s, 3H); MS: 390 (M⁺); **8**: ¹H NMR: δ 9.04 (s, 1H), 8.15 (d, 2H, *J* = 8.7 Hz), 7.72 (d, 2H, *J* = 8.7 Hz), 7.3 (t, 2H, *J* = 6.9 Hz), 7.22 (d, 2H, *J* = 8.1 Hz), 7.16 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 8.4 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 6.64 (d, 2H, *J* = 8.4 Hz), 4.85 (s, 2H), 3.58 (s, 3H); ¹³C NMR: δ 157.2, 156.2, 136.6, 132.4, 131.8, 131.3, 130.0, 129.5, 129.1, 128.5, 127.4, 125.0, 124.2, 124.1, 115.0, 113.3, 54.6, 32.2; MS: 390 (M⁺); Anal. Calcd: C, 86.13; H, 5.68. Found: C, 87.41; H, 5.71%.

Alternative procedure for 8. To a solution of carbinol **2**, 3.0 g, 9.55 mmole) and phenol (3.15 mL, 38.22 mmole) in dry benzene (40 mL) catalytic amount of conc. H₂SO₄ was added and the reaction mixture was refluxed at 80°C for 1 hr. It was cooled to room temperature, treated with saturated NaHCO₃ and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na₂SO₄. Column chromatography over silica gel and elution with 15% ethyl acetate in hexane furnished the desired compound **8** (2.6 g, 69%), m.p. 194 °C; IR (KBr): 2362, 1606, 1242, 1168, 737 cm⁻¹; MS: 390 (M⁺).

9-[(4-Methoxyphenyl)phenylsulfanylmethyl]anthracene 15. To a solution of carbinol **2** (100 mg, 0.318 mmole) and thiophenol (140 mg, 1.274 mmole) in dry benzene (10 mL) catalytic amount of conc. H₂SO₄ was added and the reaction mixture was refluxed at 80°C for 1 hr. It was cooled to room temperature, treated with saturated NaHCO₃ and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na₂SO₄. Column chromatography over silica gel and elution with 15% ethyl acetate in hexane furnished the desired compound **15** (29 mg, 22%). IR (KBr): 3014, 1673, 1602, 1509, 1218, 1031, 760 cm⁻¹; ¹H NMR: δ 8.43 (s, 1H), 8.1 (d, 2H, *J* = 9 Hz), 8.00 (d, 2H, *J* = 9 Hz), 7.41 (d, 2H, *J* = 8 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 7.33 (m, 3H), 7.22 (d, 2H, *J*

= 8.0 Hz), 6.94 (s, 1H), 6.77 (d, 2H, *J* = 8 Hz), 3.74 (s, 3H). ¹³C NMR: δ 158.8, 138.6, 134.5, 134.4, 132.3, 130.5, 130.0, 129.7, 129.4, 128.4, 128.0, 127.6, 126.9, 126.2, 125.3, 114.2, 55.6, 51.5; MS: 297 (M⁺-SC₆H₅); Anal. Calcd: C, 82.72; H, 5.45. Found: C, 82.27; H, 6.00%

9-[Bis-(4-methoxyphenyl)methyl]anthracene 16 and 9-[4-methoxybenzyl]-10-(4-methoxyphenyl)-anthracene 17. To a solution of carbinol **2** (100 mg, 0.318 mmole) and anisole (57 mg, 0.478 mmole) in dry benzene (10 mL) catalytic amount of conc. H₂SO₄ was added and the reaction mixture was refluxed at 80°C for 1 hr. It was cooled to room temperature, treated with saturated NaHCO₃ and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na₂SO₄. Column chromatography over silica gel and elution with 15% ethyl acetate in hexane furnished the desired compound **16** (7 mg) and **17** (28 mg), total (35 mg, 27%). **17**: IR (KBr): 3470, 2929, 1508, 1240, 1174, 1033, 734 cm⁻¹; ¹H NMR: δ 8.16 (d, 2H, *J* = 8.7 Hz), 7.64 (d, 2H, *J* = 8.7 Hz), 7.3 (t, 2H, *J* = 6.9 Hz), 7.22 (d, 2H, *J* = 8.1 Hz), 7.16 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 8.4 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 6.64 (d, 2H, *J* = 8.4 Hz), 4.89 (s, 2H), 3.83 (s, 3H), 3.61 (s, 3H); ¹³C NMR: δ 159.4, 158.3, 137.1, 136.2, 132.4, 131.8, 131.3, 130.0, 129.5, 129.1, 128.5, 127.4, 125.0, 124.2, 124.1, 114.3, 114.1, 55.8, 55.6, 33.3; MS: 404 (M⁺), Anal. Calcd: C, 86.11; H 5.98. Found: C, 86.90; H, 6.01%.

2-[Anthracen-9-yl-(4-methoxyphenyl)methylsulfanyl]-ethanethiol 18. To a solution of carbinol **2** (100 mg, 0.318 mmole) and ethanethiol (45 mg, 0.478 mmole) in dry benzene (10 mL) catalytic amount of conc. H₂SO₄ was added and the reaction mixture was refluxed at 80°C for 1 hr. It was cooled to room temperature, treated with saturated NaHCO₃ and extracted with ethylacetate. The organic layer was washed with water and dried over anhydrous Na₂SO₄. Column chromatography over silica gel and elution with 15% ethyl acetate in hexane furnished the desired compound **18** (25 mg, 20%). **18**: IR (KBr): 3456, 2926, 1650, 1601, 1505, 1247, 1169, 729 cm⁻¹; ¹H NMR: δ 8.35 (s, 1H), 8.16 (d, 2H, *J* = 8.8 Hz), 7.92 (d, 2H, *J* = 8.0 Hz), 7.3-7.1 (m, 6H), 6.70 (s, 1H), 6.38 (d, 2H, *J* = 8.6 Hz), 3.63 (s, 3H), 2.66 (t, 2H, *J* = 6 Hz), 2.45 (t, 2H, *J* = 6 Hz); ¹³C NMR: δ 158.7, 133.9, 133.8, 132.2, 130.3, 129.8, 129.2, 128.6, 125.3, 114.2, 55.6, 47.3, 38.0, 30.1, 25.3; MS: 297 (M⁺-SC₂H₅).

Computational details

Structures of electrophiles **P**, **E2** and **E2'** and nucleophiles were optimized and characterized at B3LYP/6-31G* level. Frequency calculations indicate that all the structures are minima. These optimized geometries were taken for single point calculations at the same level with N_0+1 and N_0-1 electrons to calculate local softness values. Structures of two possible products in each reaction were optimized at AM1¹⁷ level and the single point calculations were performed at B3LYP/6-31G* level on the AM1 optimized geometries. Relaxed potential energy surface scan has been performed using modredundant option implemented in Gaussian package for **P** and **E2**. The atomic charges and local softness values at each dihedral angle $\Phi_{16-15-13-14}$, with a 20 degree increment. The partially optimized structure at every step was taken for single point calculations with N_0 , N_0+1 and N_0-1 electron systems to calculate the local softness values. All the calculations were carried out using Gaussian 98 program package¹⁸.

Local softness values were calculated in the present study using the following equations:

$$s_k^+ = [\rho_k(N_0 + 1) - \rho_k(N_0)]S \quad \dots (1)$$

(for electrophiles)

$$s_k^- = [\rho_k(N_0) - \rho_k(N_0 - 1)]S \quad \dots (2)$$

(for nucleophiles)

where $\rho_k(N_0)$, $\rho_k(N_0-1)$ and $\rho_k(N_0+1)$ are the electronic population on the atom k for the N_0 , N_0-1 and N_0+1 electron system respectively, these values were calculated using the Mulliken population analysis.

Within Koopman's approximation,

$$\text{Global softness, } S = \frac{1}{E_{LUMO} - E_{HOMO}}$$

Fukui function and local softness values are closely related.

$$s_k^+ = f_k^+ S \quad \dots (3)$$

$$s_k^- = f_k^- S \quad \dots (4)$$

Thus, local softness values were taken for discussion in this paper.

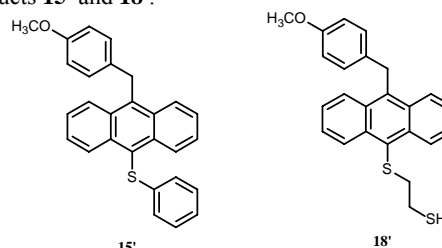
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