

## PROBLEM OF SPIN-CHARGE SCATTERING IN ORGANIC ION-RADICALS\*

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### SUMMARY

*Organic molecules with fragments which have a specific affinity for a charge (negative or positive) and, separately, for an electron can form ion-radicals of the special (distonic) type. Such a type is characterized by a scattering of charge and spin densities between different atoms of an organic skeleton. Reasons and results of this phenomenon constitute the aim of this report.*

### INTRODUCTION

Traditional consideration of ion-radical electron structures and reactivities was restrained with distribution of an unpaired electron through a molecule skeleton. It was deemed that the appearance of a suitable charge naturally involved a population of MO with that electron: a charge was distributed by the same manner as an electron. Ion-radicals of that type are named as "classic"[1]. However ion-radicals with the charge and radical centers localized at different atoms or molecular fragments do exist and possess a specific reaction ability. Such species are named "distonic ion-radicals" [1].

### DISTONIC STABILIZATION OF ANION-RADICALS

A correlation between classic and distonic anion-radicals is defined by a difference of energy store for these forms. For instance, non-empirical calculations [1] predict classic radical-anions  $(\text{CH}_3\text{M})^{\cdot-}$  to be more advantageous thermodynamically than distonic ones  $(\text{H}_2\text{C}^{\cdot-}-\text{MH})$  in the case of metalloorganic compounds of the  $\text{CH}_3\text{M}$  type (where  $\text{M} = \text{Li}, \text{Na}, \text{MgH}$  or  $\text{AlH}_2$ ). But in the  $\text{M} = \text{BeH}$  case both forms appear to be isoenergetic. According to [1], distonic form is stabilized by substituents attracting an unpaired electron to a carboradical center.

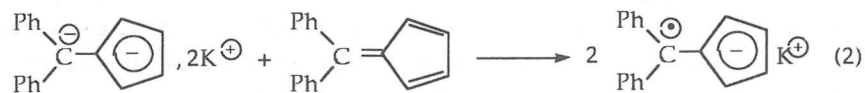
For instance, methoxyacetonitrile forms a carbanion after gas phase deprotonation and, as a result of further fragmentation, such an anion-radical in which the carboradical center is stabilized (scheme 1) [2].

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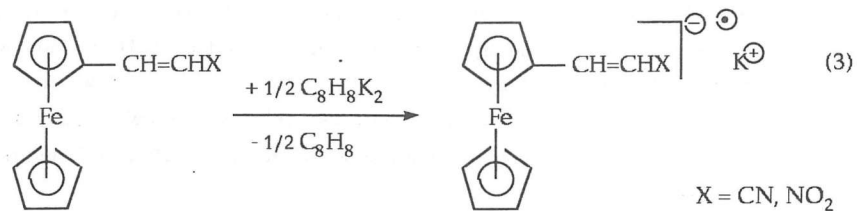
\* Plenary lecture held at the VI Meeting of the Portuguese Electrochemical Society, October, 7 - 10, 1992, Vila Real, Portugal



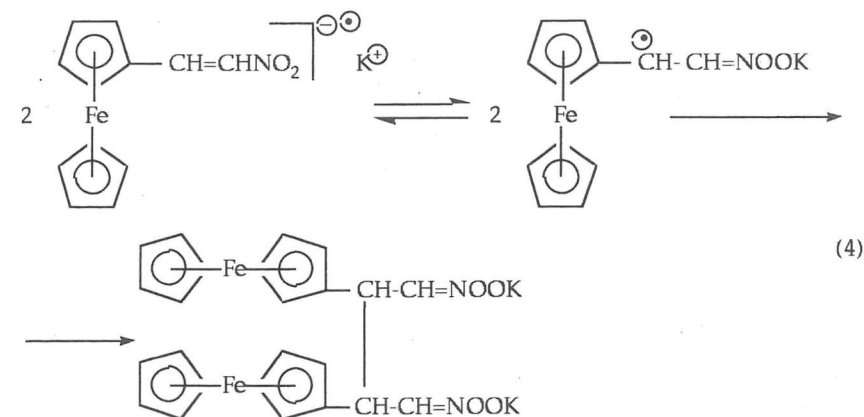
The typical (and performed [3]) example is the 1,1-diphenylfulvene radical-anion. The ethylenic bond of neutral fulvene is placed between biphenylmethane and cyclopentadienyl fragments:  $\text{Ph}_2\text{C}=\text{C}_5\text{H}_4$ . A single electron reduction leads to the anion-radical  $\text{Ph}_2\text{C}^{\ominus}-\text{C}_5\text{H}_4^{\ominus}$ , where an unpaired electron is delocalized over through the phenyl rings (compare with the triphenylmethyl radical  $\text{Ph}_2\text{C}^{\bullet}$ ), and a negative charge is included into the aromatic pentagonal ring (as in the known stable cyclopentadienyl salt  $\text{C}_5\text{H}_5^-\text{K}^+$ ). The distonic anion-radical  $\text{Ph}_2\text{C}^{\ominus}-\text{C}_5\text{H}_4^{\ominus}$  is stable. It doesn't disproportionate, and can be even produced by the inverted reaction of the correspondent dianion with the neutral molecule (scheme 2) [3]. That radical anion is not inclined to dimerization, possibly due to steric shielding of the carboradical center. In the absence of that shielding, dimerization is likely to proceed readily. That dimerization is available to distinguish distonic forms among relative anion-radicals.



For example, in reference [4] reactions of cyclooctatetraendipotassium ( $\text{C}_8\text{H}_8\text{K}_2$ ) with ferrocenyl derivatives  $\text{FcCH}=\text{CHX}$  ( $\text{Fc} = \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ,  $\text{X} = \text{CN}$ ,  $\text{NO}_2$ ) (scheme 3), were compared.

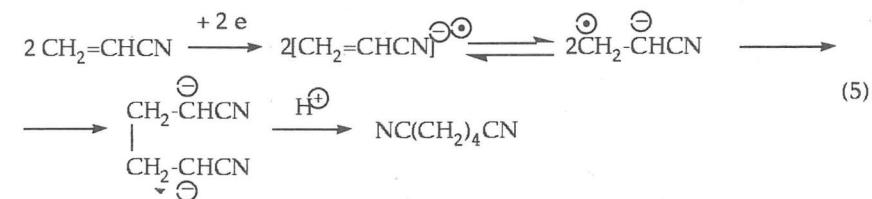


A conversion of a substrate into an anion-radical is an end stage for  $\text{X} = \text{CN}$ . The ESR signal is stable throughout the time. In the case of  $\text{X} = \text{NO}_2$ , the ESR signal can't be fixed, and the anion-radical is converted into a dimer just after its formation (scheme 4).



Experimental conditions are strictly compared, in both cases, and a product was isolated identically by treating a mixture with proton donors.  $\text{FcCH}=\text{CHCN}$  and the dihydrodimer mentioned above were produced.

That difference in behaviour of structurally similar nitro- and cyanoderivatives is a problem under discussion. A reduction of cinnamitrile and relative aromatic nitriles (as well as of acrylonitrile) is known to proceed up to hydrodimers (scheme 5).



But such a dimer is absent among products of one electron liquid phase reduction of a ferrocenic analog of cinnamitrile, as well as after one electron reduction of  $\text{FcCH}=\text{CHCN}$  at a mercury drop or at a stirring mercury cathode [5,6].

The ferrocenyl group is a constant fragment of compared nitro- and nitrile-anion-radicals. So, a shielding effect of the ferrocenyl group is evident not to be a determinant factor (in spite of its bulky size). It could be concluded that a character of influence of the ferrocenyl substituent depends on the group nature in anion-radicals of the  $(\text{FcCH}=\text{CHX})^{\ominus}$  type. In the  $\text{X}=\text{NO}_2$  case, the Fc group can't resist a "sucking out" of unpaired electron by the nitro group, and as a result the distonic radical-anion  $\text{FcC}^{\bullet}\text{H}=\text{CHNO}_2^{\ominus}$  (with spin and charge

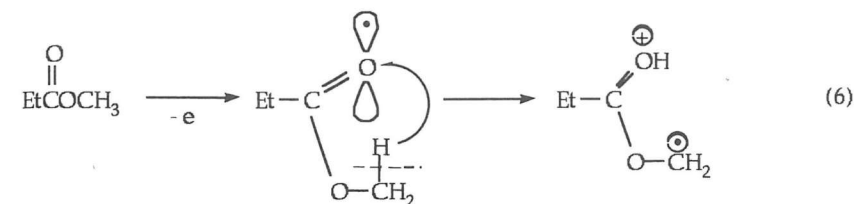
densities separately localized on different centers) is fixed. But in the case of X = CN, Fc group can compete for an unpaired electron. The Fc group ability to participate in unpaired electron delocalization is discussed in reference [7]. A competition of the Fc and CN acceptors leads to strong delocalization of an unpaired electron overthrough a molecule skeleton. The stability of the "classic" anion-radical formed is similar to that of other anion-radicals of  $\pi$  - electron nature, and dimerization does not occur.

#### DISTONIC STABILIZATION OF CATION-RADICALS

Classic cation-radicals in most cases are of little stability. The stability of cation-radicals increases in the case of energetically profitable distonic forms. For instance, methylamine, methanol or methylfluoride in the cation-radical state are to exist as isomers:  $\text{H}_2\text{C}^+\text{NH}_3^+$  (more stable than  $\text{H}_3\text{CNH}_3^+$  for 3 kJ),  $\text{H}_2\text{C}^+\text{OH}_2^+$  (more stable than  $\text{H}_3\text{COH}^+$  for 39 kJ),  $\text{H}_2\text{C}^+\text{FH}^+$  (more stable than  $\text{H}_3\text{CF}^+$  for 22 kJ). This energetic difference (in kJ) is even greater for the corresponding Si-analogues:  $\text{H}_2\text{Si}^+\text{NH}_3^+$  (88),  $\text{H}_2\text{Si}^+\text{OH}_2^+$  (137),  $\text{H}_2\text{Si}^+\text{FH}^+$  (151). Energetic characteristics (mentioned in brackets) were obtained by a non-empirical SCF MO LCAO method, basis 3-21 GF [8].

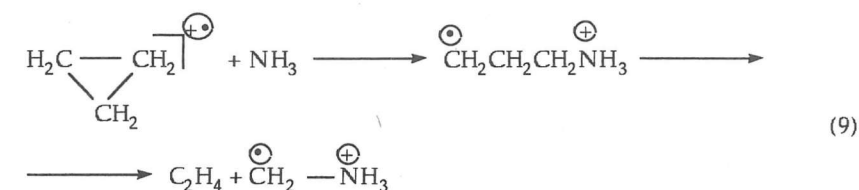
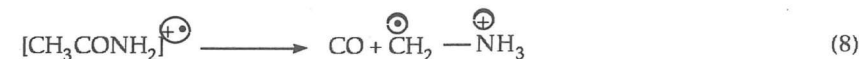
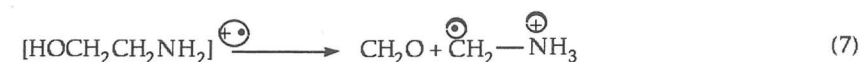
The form of the most stable cation-radical is found to be isomeric with respect of the neutral (parent) molecule. There is an atom of high electronegativity in the compounds compared. While forming the classic cation-radical, one electron is to be eliminated from the non-bonding orbital localized on that atom. On the other hand, that atom could preserve an electron octet if converted into the "onium" state. But in that case an unpaired electron is localized on the neighbour atom (carbon or silicon in the examples mentioned). That localization increases the reaction ability of the radical center but at the same time appears to be advantageous for functional group requirements. So, the total stability of distonic cation-radical becomes higher.

For instance, ethylacetate cation-radical in dilute frozen  $\text{CFCl}_3$  solution (77K) transforms rapidly into the onium form according to scheme 6 [9]. In the case given the onium (distonic) form of the cation-radical can be discovered by the ESR method: this form is more stable than the "carbonyl" form almost by 50 kJ.

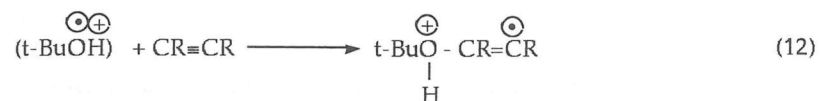
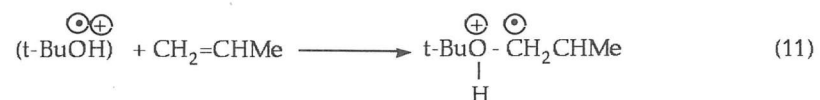
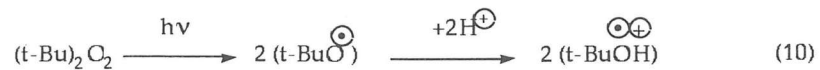


Naturally in the case of other elements the other factors could arise. For example, a tendency to convert into ilydic structures, into the highest oxidation state, promotes a distonic stabilization of radical cations. So, a wide range of cations-radicals  $\text{H}_m\text{X}-\text{ZH}_n^+$  (X = Be, B, C, Si, P, S; Z = N, O, F; m = 1, 2, 3, 3, 2, 1, respectively; n = 2,1,0) was investigated [10] by means of the same method of calculation. The formation of structures  $\text{H}_{m-1}\text{X}^+-\text{Z}^+\text{H}_{n+1}$  was found to be most probable for such systems with X = Si, P or S.

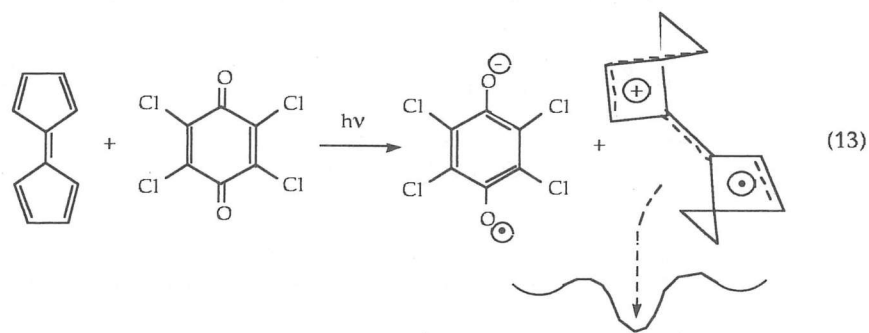
Experimentally, many of these distonic cation-radicals were observed in the mass spectrometer camera only. The most common case is followed by an elimination of small neutral molecules ( $\text{CH}_2\text{O}$ , CO, etc), (schemes 7-9) [11,12].



A generation of distonic cation-radicals through the addition of tert-butoxy radicals (protonated by  $\text{CF}_3\text{COOH}$ ) to multiple bonds is also described (schemes 10-12) [13,14].

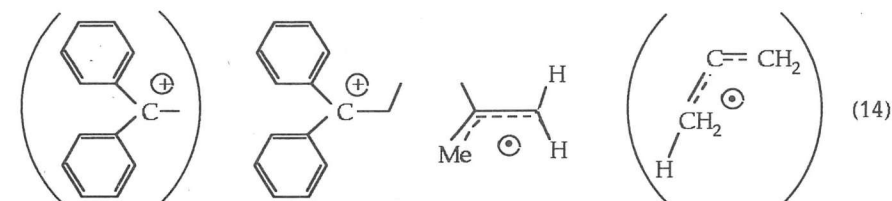


A preservation of the full electron octet around a heteroatom of molecular skeleton is not the only means to realize a distonic stabilization of radical-cations. Cation-radicals of a homoatomic type exist as well. For instance, photolysis of dicyclopentadiene in the presence of chloroanil leads to cation-radical formed by two pentagon rings connected with an ordinary bond (scheme 13).

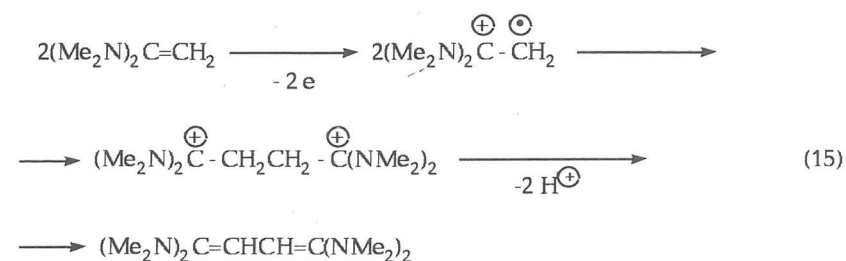


One ring delocalizes a positive charge, but another delocalizes a spin density [15]. This structure corresponds to a high placed non-deep minimum of potential energy surface of dicyclopentadiene [16]. A tendency to separate the charge and radical centers could be explained by an allyl stabilization process, taking place in a pentagonal ring populated with an unpaired electron.

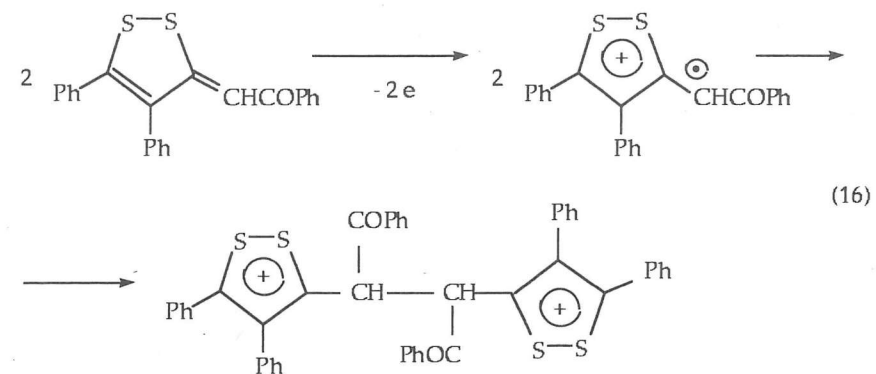
The distonic structure of radical cation of the 1,1-diphenyl-3-methylbuta-1,3-diene is stabilized for two reasons: a positive charge is localized around the tert-carbon atom in the position 1 (as these carbenium ions are stable), but an unpaired electron is distributed over through the methylvinyl group (as conjugation an allyl type fragment is created), as shown in scheme 14 [17].



A positive charge in the 1,1-bis(dimethylamino)ethylene cation-radical is stabilized at that carbon atom which carries two Me<sub>2</sub>N groups. A radical center is localized at the other carbon. As a result of such spin-hole scattering a dimerization occurs. Dication formed yields 1,1,4,4-tetrakis-(dimethylamino)butadiene after two protons abstraction (scheme 15) [18,19].



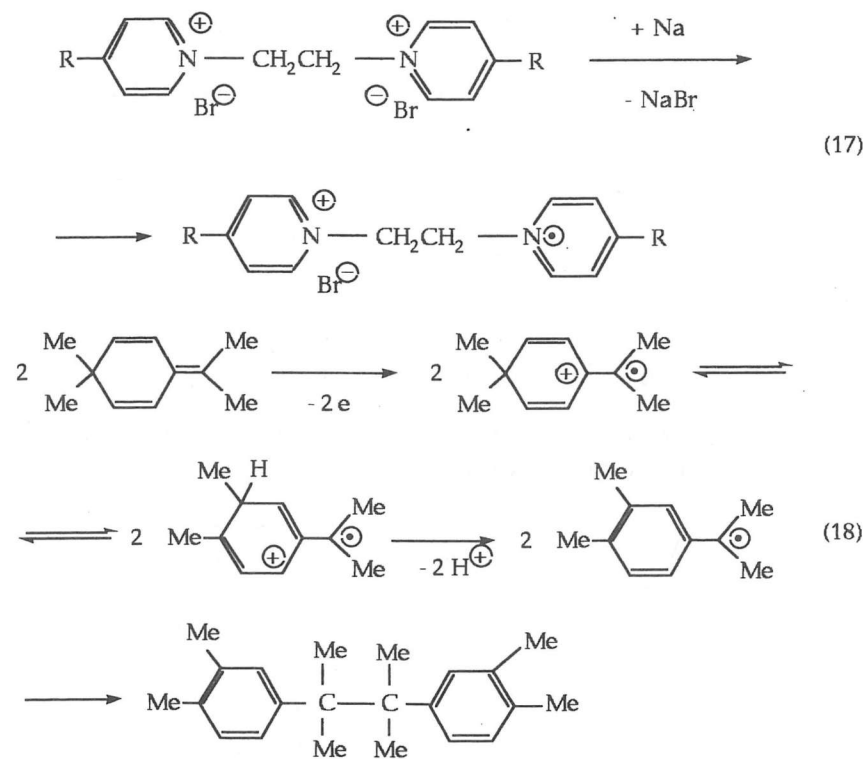
Another clear case of the spin-hole scattering with a following dimerization is depicted by the scheme 16 [20].



The carbonyl group (as the nitrile group mentioned above) assists in a localization of a carboradical center. This is the probable reason why only the 4,4'-diacetoxy derivative is characterized by the localization of a spin in a single ring in the cation-radical depicted in the scheme 17, where R = OCOMe. In the

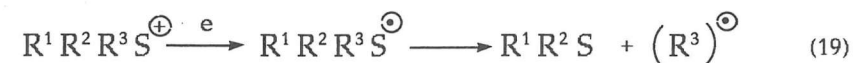
case of  $R = CMe_3$ , ESR spectra visualize the spin delocalization in both pyridine rings (bromide-ion is, accordingly, transferred swiftly also) [21,22].

The methyl group is able to migrate, as in an arenonium ion. This can assist in positive charge-electron scattering and, as assumed in reference [23], explains the transformation of 1-iso-propylidene-4,4'-dimethylcyclohexa-2,5-diene into its criss-cross dimer upon the action of the cation-radical salt of tris(2,4-dibromophenyl)amine as an oxidant (scheme 18). The distonic cation-radical is the key-particle.

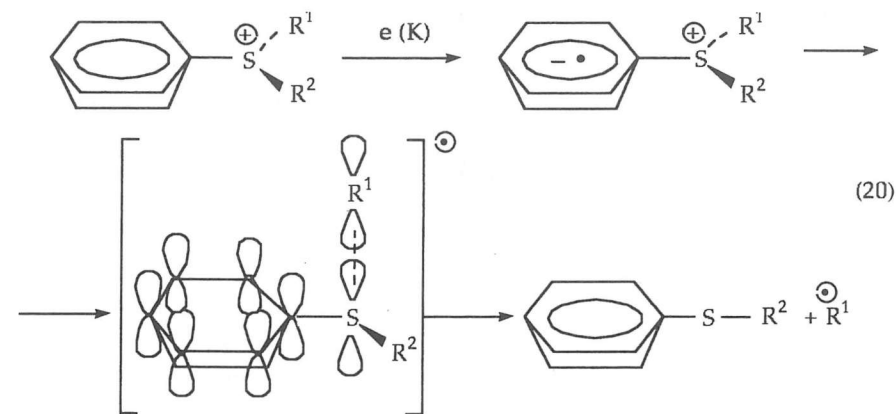


Chemical reduction of sulfonium salts (with potassium in graphite in THF) gives sulfide and radicals; the result, at first sight, is a quite obvious one. However, trialkylsulfonium salts do not react under these conditions; phenyldialkylsulfonium salts expel alkyl groups, and preferably the bulkier ones (scheme 19); that effect is not quite an obvious one. At the opinion of authors [24], in spite of a positive charge at the sulfur atom, an electron is delocalized into the phenyl ring with formation of the novel "π - ligand radical anion"

sulfonium cation" [24]. This phenomenon is illustrated by the scheme 20, and stereochemical aspects of the reaction can be explained. Namely, an electron, passing from potassium metal to phenyldialkylsulfonium salt, touches the lowest unoccupied molecular orbital. The later must not only be vacant but low-energetic also.

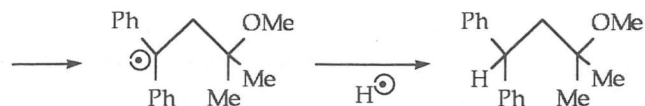
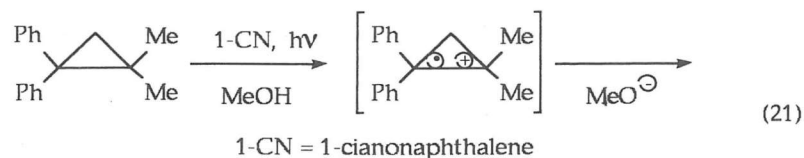


Trialkylsulfonium cations are inert in the potassium reduction, that is, they cannot supply the low-lying vacant orbitals although they have positive charges on sulfur atoms. Phenyldialkylsulfonium cations have low-lying orbitals and these are essentially benzene ring orbitals. The anion-radical of a phenyl-containing sulfonium cation, "π - ligand anion-radical cation", is an unusual distonic particle. Its disintegration is clear from the scheme 20: the transition state for such a cleavage involves overlap of the singly occupied molecular orbital of the aromatic ring with the σ\* orbital of the bond being broken homolytically. Thus the selectivity in the reduction discussed is sterically determined, with the bulkier group being preferentially cleaved. The bond between that group and a sulfur atom becomes longer and so weaker. Moreover, a group of a greater size inevitably enters a plane which is perpendicular to a plane of an aromatic ring. The total picture becomes clear.



Charge-spin scattering can reverse the normal regioselectivity of substitution. This leads to the surprising result that nucleophile substitutions

according to scheme 21 occur at the more hindered center, even when it is tertiary or neopentyl [25].



In this three-electron transition state of the reaction (i.e. in the distonic radical-cation of 1,1-diphenyl-2,2-dimethylcyclopropane), the electronic effects apparently overwhelm the smaller steric effects and the unhindered C3-substitution is not detected [25].

#### CONCLUSION

Research on spin-charge scatterings in organic ion-radicals is being carried out for several recent years, and the stage of a theoretical estimation is the main topic. The most attention is paid to prove their existence and participation in the reaction mechanisms. The next stage is likely to consist in the discovery of distonic ion-radical organic salts stable in common conditions. From this, the application of the salts will be possible for a creation of magnetic, conducting and other materials with practically useful properties. Successes in the reviewed direction can open also a new widening of organic reactivities. Chemists' interest is worth to turn into such a promising field.

#### REFERENCES

1. K. Pius, Ja. Chandrasekhar, *J. Chem. Soc. Perkin Trans. Part II*, 1291 (1988)
2. K. Pius, Ja. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, 41 (1990)
3. Z. V. Todres, V. Ya. Bepalov, *Zhurn. Organ. Khim.*, 8, 19 (1972)
4. Z. V. Todres, T. M. Tsvetkova, *Izv. AN SSSR. Ser. Khim.*, 1553 (1987)
5. Z. V. Todres, T. M. Chernyshova, A. A. Koridze, L. I. Denisovich, D. N. Kursanov, *Doklady AN SSSR*, 254, 902 (1980)
6. L. I. Denisovich, A. A. Koridze, *Izv. AN SSSR. Ser. Khim.*, 276 (1981)
7. Z. V. Todres, A. I. Safronov, D. S. Ermelov, R. M. Minyaev, *J. Organometal. Chem.*, 441, 479 (1992)

8. K. Pius, Ja. Chandrasekhar, *Intern. J. Mass Spectrom. and Ion Process.*, 87, R15 (1989)
9. Ch. J. Rhodes, *J. Chem. Soc., Chem. Commun.*, 1477 (1988)
10. K. Pius, Ja. Chandrasekhar, *Curr. Sci. (India)*, 56, 857 (1987)
11. Th. M. Sack, R. L. Cerny, M. L. Gross, *J. Amer. Chem. Soc.*, 107, 4562 (1985)
12. Th. Drewello, N. Heinrich, W. P. M. Maas, N. M. M. Nibbering, Th. Weiske, H. Schwarz, *J. Amer. Chem. Soc.*, 109, 4810 (1987)
13. P. G. Cookson, A. G. Divies, B. R. Roberts, M. W. Tse, *J. Chem. Soc., Chem. Commun.*, 937 (1976)
14. A. J. Bloodworth, A. G. Divies, R. S. Hay-Motherwell, *J. Chem. Soc., Chem. Commun.*, 862 (1988)
15. H. D. Roth, M. L. M. Shilling, Ch. J. Abelt, *Tetrahedron*, 42, 6157 (1986)
16. H. D. Roth, *Accounts Chem. Res.* 20, 343 (1987)
17. Ts. Miyashi, Ya. Takahashi, K. Yokogawa, T. Mukai, *J. Chem. Soc., Chem. Commun.*, 175 (1987)
18. J. M. Fritsh, H. Wiengarten, *J. Amer. Chem. Soc.*, 90, 793 (1968)
19. J. M. Fritsh, H. Wiengarten, J. D. Wilson, *J. Amer. Chem. Soc.*, 92, 4038 (1970)
20. C. T. Pedersen, V. D. Pedersen, O. Hammerich, *Acta Chem. Scand.*, B30, 478 (1976)
21. Y. Ikegami, T. Muramatsu, K. Hanaya, S. Onodera, N. Nakayama, E. M. Kosower, *J. Amer. Chem. Soc.*, 109, 2876 (1987)
22. Y. Ikegami, T. Muramatsu, K. Hanaya, *J. Amer. Chem. Soc.*, 111, 5782 (1989)
23. S. F. Nelsen, M. F. Feasley, *J. Org. Chem.*, 54, 2667 (1989)
24. P. Beek, Th. A. Sullivan, *J. Amer. Chem. Soc.*, 104, 4450 (1982)
25. J. P. Dinnocenzo, D. R. Lieberman, T. R. Simpson, *J. Amer. Chem. Soc.*, 115, 366 (1993)