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DISCUSSIONS

On the General Relations Holding in Dimerization of Radicals

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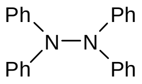
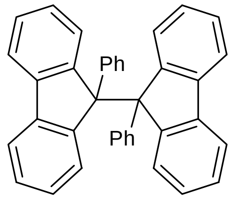
Abstract—Analysis of the conditions of dimerization of stable radicals leads to a hypothesis according to which symmetric and asymmetric dimers are formed, respectively, under kinetic and thermodynamic control of the process.

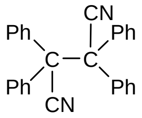
Up to mid 1960s, triphenylmethyl radical dimer was believed to have the structure of hexaphenylethane on the assumption that the most reactive center in a radical is an atom possessing the greatest unpaired electron density. Therefore, dimerization of radicals should give rise to symmetric structures. These views were supported by formation of symmetric dimers from diphenylaminyl radical (**I**) [1], 9-phenylfluorenyl radical (**II**) [2], and some other C-centered radicals like **III** and **IV** [3–8].



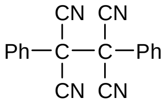
I



II

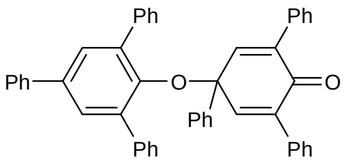


III

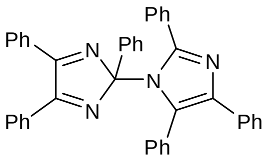


IV

On the other hand, it is known that some radicals, e.g., triphenylimidazolyl, are capable of producing both symmetric and asymmetric dimers [9, 10]. In 1968, Lankamp *et al.* [11] discovered the cyclohexadiene structure of the triphenylmethyl radical dimer. Since that time, the formation of asymmetric dimers was interpreted in terms of steric hindrances created by substituents at the reaction center [12, 13]. However, a more probable is a hypothesis implying donor–acceptor character of dimerization of stable radicals as the main factor responsible for formation of asymmetric dimers [14]. Radicals having a fairly complex structure and characterized by partial charge separation give rise to interaction between donor center of one radical and acceptor center of the other. This may be illustrated by dimers formed from 2,4,6-triphenylphenoxyl (**V**) and 2,4,5-triphenylimidazolyl (**VI**) as examples.



V



VI

It is reasonable to presume that factors responsible for formation of symmetric and asymmetric dimers should be general for all kinds of radicals and that these factors could be identified by analyzing the behavior of radicals capable of forming dimers of both types. An example is triphenylimidazolyl radical. Oxidation of 2,4,5-triphenylimidazole in aqueous alcohol with potassium hexacyanoferrate(II) in alkaline medium yields poorly soluble symmetric dimer **VII** which precipitates from the solution. On dissolution in benzene or other nonpolar organic solvents, dimer **VII** dissociates into radicals which then combine to give asymmetric dimer **VI** [9, 15] (Scheme 1). It should be noted that equilibrium exists only between radicals and

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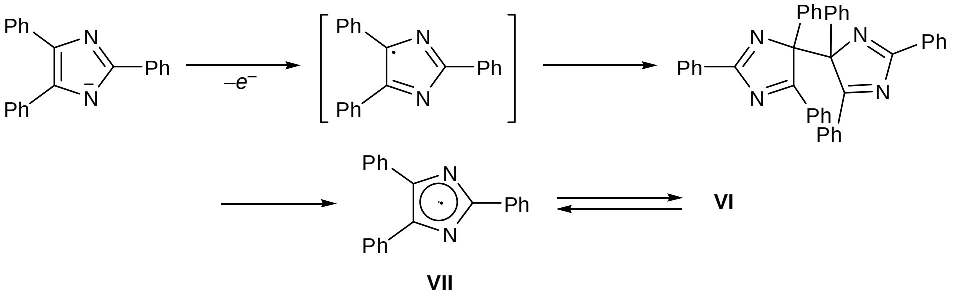
Scheme 1.



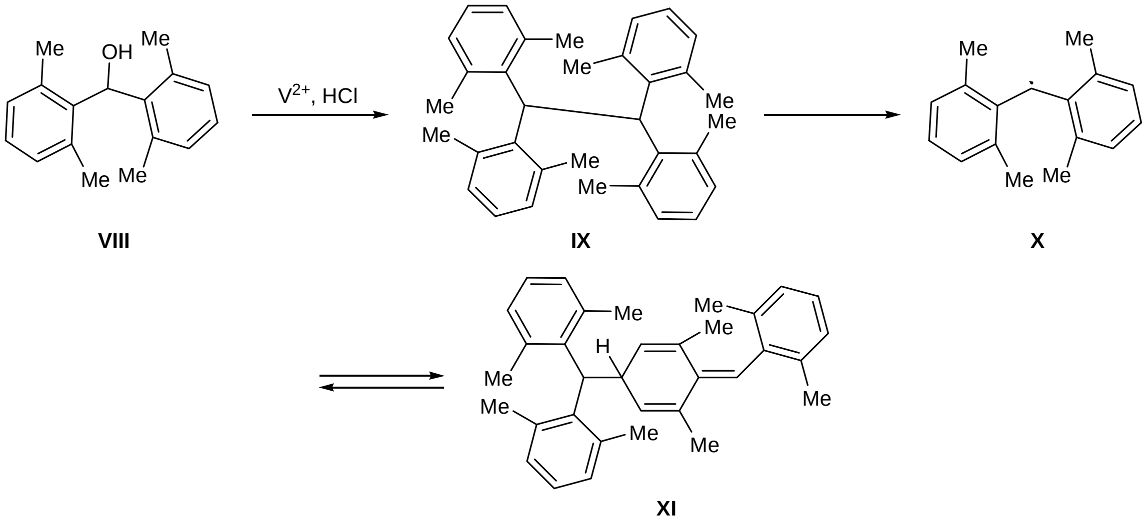
asymmetric dimer **VI**, whereas dissociation of symmetric dimer **VII** is irreversible.

Analogous reactions were observed for other radicals. For example, reduction of diarylcarbinol **VIII** with vanadium(II) chloride in a mixture of acetone with hydrochloric acid at room temperature affords symmetric dimer **IX** having an ethane structure [11]. Heating of the latter in an organic solvent leads to dissociation into radicals **X** whose combination yields asymmetric dimer **XI** having a methylenecyclohexadiene structure [11] (Scheme 2). On the other hand, the corresponding diarylmethyl halide reacts with silver in an organic solvent to give only asymmetric dimer **XI** [11]. It should be noted that in the above cases symmetric dimers are formed from triphenylimidazolyl and bis(2,6-dimethylphenyl)methyl radicals when the latter are generated by oxidation or reduction of ions in strongly polar media which are incapable of solvating the resulting radicals. When the same radicals are generated in nonpolar solvents, both triphenylimidazolyl and di(2,6-dimethylphenyl)methyl give rise to only asymmetric dimers [11].

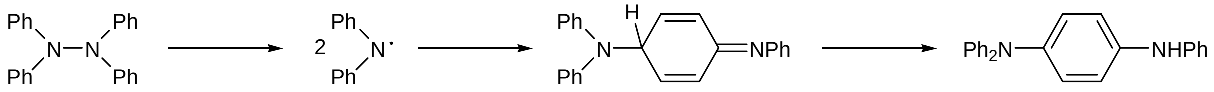
The above stated suggests that there are two paths of radical dimerization, depending on the conditions of their generation. If radicals are generated from ions in strongly polar media, the dimerization process is kinetically controlled, and it requires a fairly low activation energy. This is typical of reactions involving atoms with the highest spin density, which leads to formation of symmetric dimers. In weakly polar and nonpolar solvents, which are capable of effectively solvating radical species, the dimerization process is characterized by greater energy of activation (7.4 kcal/mol for triphenylimidazolyl [16]), and it results in formation of thermodynamically more stable asymmetric dimer.

If this relation is general, the formation of symmetric dimer under conditions of kinetic control, and of asymmetric dimer, under thermodynamic control, should be observed for other radicals. Here, it may be expected that short-lived radical species would give rise to only symmetric dimers via combination at atoms possessing the greatest spin density. However, one should keep in mind that the lifetime of a radical

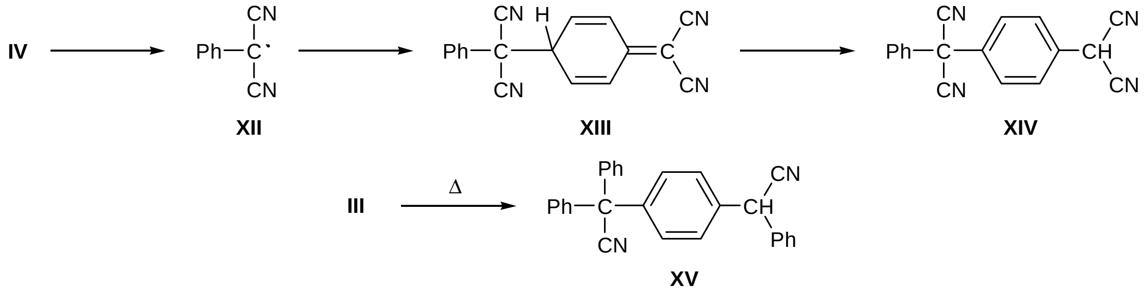
Scheme 2.



Scheme 3.



Scheme 4.



species is determined by a number of factors. One of these may be poor solubility of a radical in the solvent in which it was generated (e.g., by oxidation or reduction of the corresponding ions). The other factor is low stability of a radical due to low degree of delocalization of unpaired electron or/and insufficient steric shielding of the radical center. For example, donor–acceptor dimerization of diphenylaminyl leads to formation of *o*- and *p*-semidines and polymers derived therefrom [16, 17] (Scheme 3).

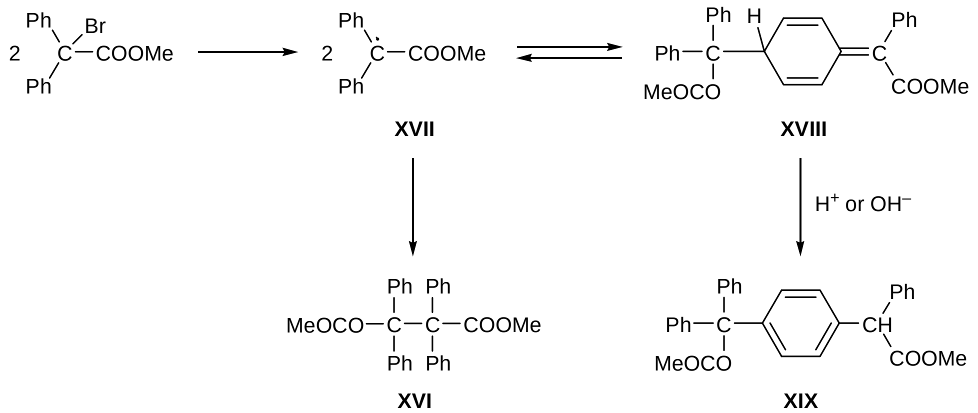
An analogous pattern was observed for some other radicals [6]. 1,1,2,2-Tetracyano-1,2-diphenylethane (**IV**) dissociates into radicals **XII** on heating in benzene, and the subsequent combination of **XII** yields dimer **XIII** having a quinoid structure. Compound **XIII** was not isolated in the pure state, and only isomerization product **XIV** was obtained [6] (Scheme 4). Likewise, tetraphenylsuccinodinitrile (**III)** was converted into asymmetric dimer **XV** [18].

Radical **XVII** generated from methyl bromo(diphenyl)acetate is likely to be more stable. An attempt to synthesize dimethyl tetraphenylsuccinate (**XVI**) resulted in formation of only asymmetric dimer **XVIII** which dissociated into radicals **XVII** at room temperature (Scheme 5). Dimer **XVIII** was isolated as a crystalline substance which was transformed into compound **XIX** on heating. The process occurred under conditions of both acid and base catalysis [19]. Compound **XVI** was reported in [8] (it was synthesized by a different procedure).

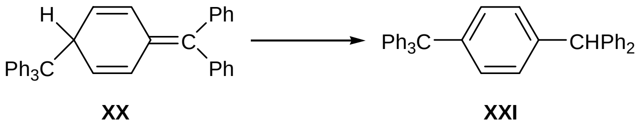
The isomerization into more stable product is also typical of triphenylmethyl dimer **XX** having a methylenequinoid structure [11]. As with **XVIII**, the rearrangement leading to so-called Ulmann–Borsum hydrocarbon **XXI** is accelerated in the presence of both acids [20] and bases [21] (Scheme 6).

Presumably, hexaphenylethane was obtained by Conant [22] via reduction of triphenylmethanol with vanadium(II) chloride in strongly acidic medium. The product obtained under these conditions is yellow, and it gives a strong ESR signal (in the solid state) and behaves similarly to symmetric triphenylimidazolyl

Scheme 5.



Scheme 6.



dimer. The central carbon atom in triphenylmethyl is shielded by phenyl rings which hamper radical combination; therefore, a considerable part of the generated radicals precipitates from the solution as a solid substance. Naturally, dissolution of this product gives an intense yellow color of the solution, which gradually disappears due to formation of asymmetric dimer.

Thus the above data indicate the existence of general relations holding in dimerization of radical species, which allow prediction of the dimer structure, depending on the conditions of radical generation.

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