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QUANTUM-CHEMICAL TREATMENT OF RECYCLIZATION REACTIONS.

9.* PHOTOISOMERIZATION OF FIVE-MEMBERED HETEROCYCLES

Yu. B. Vysotskii and L. N. Sivyakova

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The photoisomerization of a number of five-membered heterocycles has been considered in the framework of the coupled variant of perturbation theory for a one-electron transition density matrix in the π -electronic approximation of the MO-LCAO-SCF method.

A method for describing photochemical reactions of the X type in Dougherty's terminology [3], one of whose main steps is photoelectrocyclic contraction or ring formation, we developed in [2]. In such reactions the energy of the light is utilized only for bringing the reactant into an excited state and is not converted into the thermal energy needed for overcoming the activation barrier, spent on light-induced electron transfer, etc. In this case, the reactivity is determined mainly by the changes in the electronic structure of the molecule upon excitation and is, therefore, more easily subjected to quantum-chemical treatment.

Without dwelling in detail on the problem of using the index approach for the description of the reactivity of molecules in electronically excited states (see, for example, [4, 5]), as well as on the alternative method of correlation diagrams (see [3, 6-8], etc.) in the case of electrocyclic reactions, we note only that expressions for the reactivity indices of such reactions, which were obtained on the basis of the coupled variant of perturbation theory for a transition density matrix in the PPP method [9], were presented in [2]. Here the perturbation may be characterized as intramolecular coupling (see [3]), and the perturbation matrix is represented by the following matrix elements:

$$(H_{ik})_{rs} = (\delta_{ir}\delta_{ks} + \delta_{is}\delta_{hr})\Delta\beta_{ik}. \quad (1)$$

Then from the expression for the change in the π -electronic energy of the ground state in first-order perturbation theory with respect to $\Delta\beta_{ik}$

$$\delta E_{ik}^{\pi} = 2P_{ik}\Delta\beta_{ik} \quad (2)$$

it follows that in the ground state the bond orders between the not directly bonded atoms P_{ik} can serve as the reactivity indices in intramolecular recyclization and cyclization reactions.

*For report 8 see [1].

When a molecule undergoes a transition to an excited state, the change in the π -electronic excitation energy in first-order perturbation theory with respect to $\Delta\beta_{ik}$ may be written for the singlet states in the form [9] (Eq. 15.88)

$$\delta E_{ih}^s = 2 \text{Tr} \{ H_{ih} YD^2 + G(Y_{ih}) YD^2 + [D, G(D)]_+ Y Y_{ih} \} = 2 K_{ih}^s \Delta \beta_{ih}, \quad (3)$$

and for triplet transitions calculated in the Tamm-Dankov approximation, in a similar manner we obtain

$$\delta E_{ih}^T = \text{Tr} \{ 2 H_{ih} YD^2 + 2 G(Y_{ih}) YD^2 + [D, G(D)]_+ Y Y_{ih} + [G(DY), D]_- Y_{ih} \} = 2 K_{ih}^T \Delta \beta_{ih}, \quad (4)$$

where D is the unperturbed transition density matrix corresponding to the excited state under consideration, Y_{ik} is the matrix of bond-bond mutual polarizabilities, which reflects the change in the electronic structure in the ground state under the action of perturbation (1), and supermatrix G describes the interelectronic interaction.

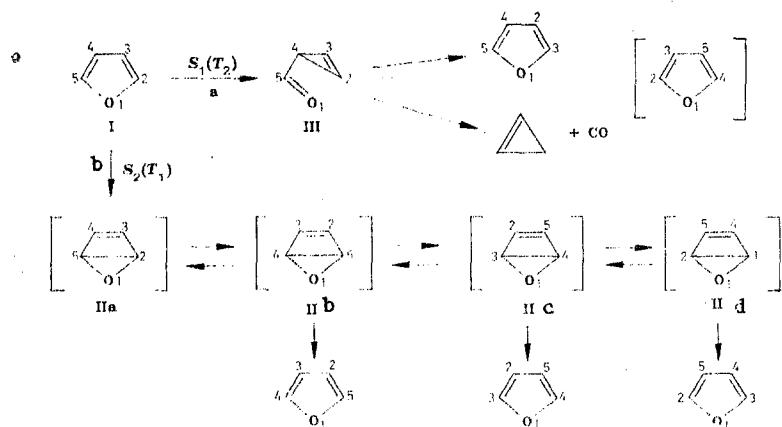
In [2] it was shown in the example of the photochemical ring-contraction reaction of furan that the main contribution to the indices K_{ik} is made by the changes in the long-range bond orders ΔP^*_{ik} upon excitation of the molecule. The latter were used for the treatment of photochemical, particularly, di- π -methane, rearrangements [10, 11]. The arguments in support of the use of ΔP^*_{ik} are based on the correspondence between these quantities (see [11]) and the location of the excitation energy in a molecule, its redistribution during a reaction, and its conversion into the vibrational energy of the ground state. The bond orders in electronically excited states, which are generally calculated according to the Hückel method, served as photoelectrocyclization indices in [12, 13]. Several quantities which are directly or indirectly related to them were used in [13-15]. The use of the sum of the free valences of the positions at which cyclization occurs, Mulliken populations, including transition populations, or localization energies (of course, in a given excited state) as reactivity indices is less substantiated and gives a poorer description than do ΔP^*_{ik} (see, for example, [16, 17]).

In the present work we examined the relationship between the indices K_{ik} and the occurrence of the photoisomerization of several five-membered heterocycles in the PPP approximation.

1. Table 1 presents the indices for the four lowest singlet and triplet states of furan, pyrrole, and thiophene. From the data presented it follows that the transition of a molecule to the excited states is generally accompanied by weakening of the bonds between the directly bonded atoms and strengthening of some of the bonds between the not chemically bonded atoms. In the cases in which this strengthening (increase in the coefficients K_{ik}) is so great that the sum of the indices P_{ik} and K_{ik} becomes positive (see [2]), photoelectrocyclic contraction of the heterocycle, which is the first step in its further conversions, should occur at positions i and k.

For example, from the data in Table 1 (see also [2]) it follows that the photorecyclization of the furan molecule in the S_1 and T_2 states should take place with the formation of acylcyclopropene intermediate III, and in states S_2 and T_1 it should involve the formation of intermediate IIa followed by its isomerization to IIb, etc.

Scheme 1



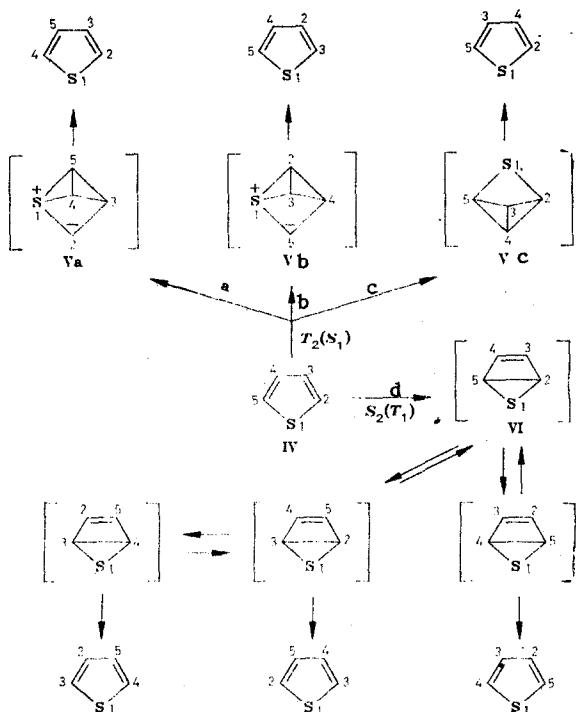
The occurrence of a reaction along path a, especially in the T_2 state, has been thoroughly studied [6, 18-22]. Sensitization by mercury [$Hg(^3P_1)$] gives a steady yield of CO and C_3H_4 , which is large in comparison to the direct irradiation of furan. The latter finding is consistent with the fact that $K_{2,4}S < K_{2,4}T$. There are still no experimental data on the photoisomerization of furan in the S_2 and T_1 states (path b).

2. An analysis of the values of K_{ik} for the pyrrole molecule (Table 1) reveals that in the S_1 state, in contrast to the case of furan, isomerization should not occur owing to the fact that $|K_{2,4}S| < |P_{2,4}|$ and $|K_{2,5}S| < |P_{2,5}|$. In the second triplet state $|K_{2,4}T| > |P_{2,4}|$; however, the 2-3 (4-5) bonds are weaker than the 1-2 (1-5) bonds (see Table 1). This circumstance should result in the photolytic cleavage of these bonds with the evolution of acetylene as the reaction product. In fact, when unsubstituted pyrrole was irradiated in the gaseous phase (S_1), decomposition products, in particular, acetylene, were discovered [23].

It should, however, be stressed, that the presence of strong electron-donor or acceptor substituents in a molecule can cause changes in the relationship between the P_{ik} and the K_{ik} and, as a consequence, the corresponding photoisomerization [19, 22, 24]. In this case, the direct participation of the atoms of functional groups, for example, of the nitro group [25], in the isomerization process is possible. A radical mechanism with subsequent recombination of the radicals has likewise not been ruled out [26].

According to the data from the calculation, the photoisomerization of pyrrole in the second singlet and first triplet states should be similar to that of furan (path b).

Scheme 2



3. As follows from the data in Table 1, the photoisomerization of the thiophene molecule (IV) in the T_2 state should involve the formation of 1-3 and 2-4 (or 1-4 and 3-5) bonds (paths a and b in Scheme 2), i.e., the intermediate formation of a Weinberg zwitterionic tricyclic intermediate [27]. A similar picture is also observed in the S_1 state. A structure of type V implies the active participation of the d orbitals of the sulfur atom [18, 19, 22], and, in fact, without consideration of the d orbitals the positive long-range orders of the 1-3 (1-4) bonds do not appear.

We note that, in contrast to the case of furan, cyclopropene was not discovered either upon the direct irradiation (S_1 state) or upon the sensitization (T_2) of thiophene vapor [28].

Finally, as follows from Table 1, in the case of the S_2 and T_1 states, recyclization should involve the intermediate formation of a structure of type VI along path d in Scheme 2.

TABLE 1. Reactivity Indices in Photoisomerization Reactions of Five-Membered Heterocycles

Compound	State	$K^*_{1,2}$	$K_{2,3}$	$K_{3,4}$	$K_{1,3}$	$K_{2,4}$	$K_{2,5}$
Furan	S_0	0.442	0.763	0.536	-0.205	-0.105	-0.459
	S_1	-0.075	-0.386	-0.270	0.117	0.131	0.254
	S_2	-0.205	-0.205	0.070	0.058	0.032	0.864
	T_1	-0.187	-0.370	0.189	0.088	0.033	0.747
	T_2	-0.021	-0.474	-0.666	0.078	0.170	0.161
Pyrrole	S_0	0.501	0.740	0.609	-0.227	-0.128	-0.424
	S_1	-0.101	-0.354	-0.284	0.165	0.101	0.262
	S_2	-0.223	-0.314	0.091	0.071	0.036	0.849
	T_1	-0.196	-0.356	0.107	0.090	0.024	0.757
	T_2	0.001	-0.541	-0.071	0.052	0.401	0.075
Thiophene	S_0	0.627	0.715	0.635	-0.315	-0.028	-0.400
	S_1	-0.101	-0.275	-0.211	0.344	0.001	0.348
	S_2	-0.241	-0.282	-0.180	0.122	0.011	0.732
	T_1	-0.243	-0.349	0.102	0.112	0.003	0.736
	T_2	-0.018	-0.070	-0.831	0.375	0.064	0.092

*The corresponding P_{ik} are given for the ground state S_0 .

TABLE 2. Reactivity Indices in Photoisomerization Reactions of Azoles

Compound	State	$K^*_{1,3}$	$K_{1,4}$	$K_{2,4}$	$K_{2,5}$	$K_{3,5}$
Oxazole	S_0	-0.201	-0.184	-0.167	-0.446	-0.108
	S_1	0.209	-0.008	0.460	0.365	-0.131
	S_2	-0.005	0.155	-0.111	0.713	0.280
	T_1	0.087	0.082	0.076	0.762	-0.030
	T_2	0.035	0.052	0.465	0.036	0.367
Imidazole	S_0	-0.223	-0.204	-0.188	-0.409	-0.131
	S_1	0.208	0.018	0.431	0.356	-0.110
	S_2	0.007	0.175	-0.079	0.686	0.256
	T_1	0.094	0.096	0.079	0.750	-0.025
	T_2	0.028	0.052	0.500	0.043	0.372
Thiazole	S_0	-0.312	-0.274	-0.094	-0.400	-0.040
	S_1	0.326	0.292	0.212	0.348	-0.056
	S_2	0.195	0.230	0.054	0.544	0.037
	T_1	0.128	0.146	0.061	0.726	-0.050
	T_2	0.361	0.252	0.497	0.175	-0.175
Isodazole	S_0	-0.190	-0.240	-0.136	-0.390	0.051
	S_1	0.261	0.158	0.257	0.489	-0.478
	S_2	-0.045	0.201	-0.064	0.493	0.347
	T_1	0.086	0.184	0.070	0.763	-0.150
	T_2	0.059	0.176	0.302	0.039	0.110
Pyrazole	S_0	-0.241	-0.238	-0.179	-0.378	-0.014
	S_1	0.358	0.208	0.189	0.352	-0.456
	S_2	-0.153	0.282	-0.024	0.559	0.355
	T_1	0.092	0.058	0.180	0.758	-0.064
	T_2	0.305	0.125	0.535	0.047	-0.102
Isothiazole	S_0	-0.291	-0.350	-0.058	-0.386	0.065
	S_1	0.514	0.500	0.067	0.344	-0.310
	S_2	-0.068	0.207	-0.107	0.672	0.201
	T_1	0.070	0.196	0.055	0.742	-0.080
	T_2	0.332	0.604	-0.127	0.144	-0.035

*The corresponding P_{ik} are given for the S_0 ground state.

There are still no experimental data on the reactions of thiophene derivatives in these states. Nevertheless, in the case of the S_1 and T_2 states, Scheme 2 is confirmed by all the data available in the literature (see monographs [19, 22, 29] etc.).

4. Table 2 presents the indices K_{ik} and P_{ik} for photoisomerization reactions of azoles. It is seen that the isoxazole molecule (VII) should readily isomerize to oxazole, the value of $P_{ik} + K_{ik}$ in the S_1 state being greater than 0 for both the 2-4 bond and for the 2-5 and 1-3 bonds. When the weakness of the 1-2 bond is taken into account, this implies the possibility of the occurrence of a reaction both along the ring-opening-contraction-formation

path and along the path of intramolecular cyclization with isomerization (with the intermediate formation of IX and X) or isomerization with the formation of a zwitterionic tricyclic intermediate. However, as follows from the calculation, the main reaction path should involve the intermediate formation of azirine VIII (path b, Scheme 3).

Path b should also be predominant in the T_2 state, although there is already another isomerization path with cyclization at positions 3 and 5, which, incidentally, does not result in isomerization to oxazole.

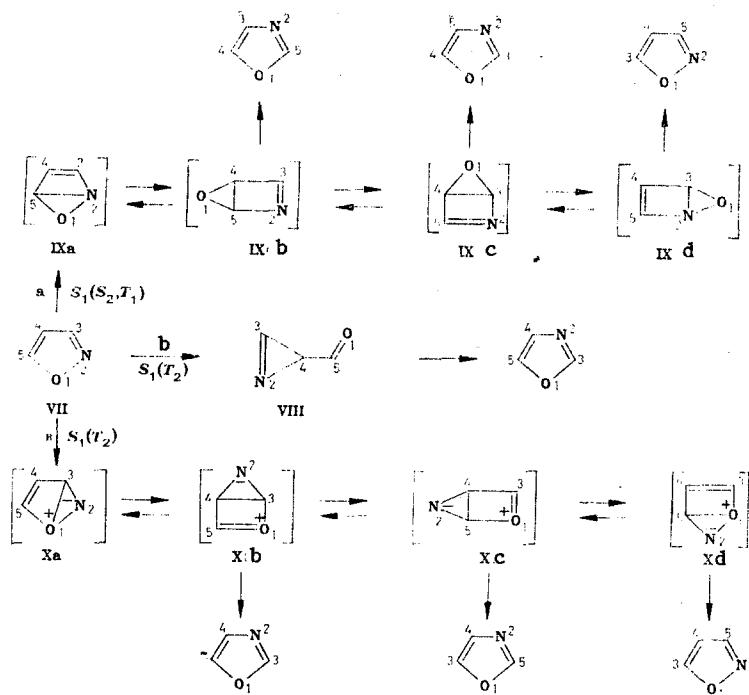
Since the values of $P_{ik} + K_{ik}$ for the S_1 state of molecule VII are significantly greater than zero, the introduction of substituents should not alter the predominant direction of the reaction. Experimental data confirming the conclusions drawn are found in monographs and reviews [19, 22, 29, 30] and the literature cited therein.

The isomerization of isoxazole (VII) to oxazole (XI) is reversible, photoisomerization through azirine intermediate VIII (Scheme 4, path a) being preferable for the oxazole molecule in the S_1 and T_2 states, according to the data from the calculation.

As is seen from Table 2, in contrast to the case of the S_2 and T_1 states, bonding between positions 2 and 5 (the formation of intermediate XIII) should not occur in this reaction, in agreement with the data from the experiment and the nonempirical calculations with consideration of the configuration interaction in [31]. In the second triplet state the reaction can follow path b in Scheme 4 with the intermediate formation of XII.

The influence of the functional groups on the direction of the photoisomerization of oxazole is more pronounced than in the case of isoxazole, although the value of $P_{24} + K_{24}$ in the S_1 state is fairly high. From the calculation in [22] it follows that the introduction of phenyl and/or methyl groups into positions 2 and/or 5 of the oxazole ring results in initial electrocyclization at positions 2-5 (intermediate XIII). It is curious that not only substituents, but also the reaction conditions, particularly the solvent, have a significant influence. For the experimental data on this reaction see [19, 22, 29, 30, etc.].

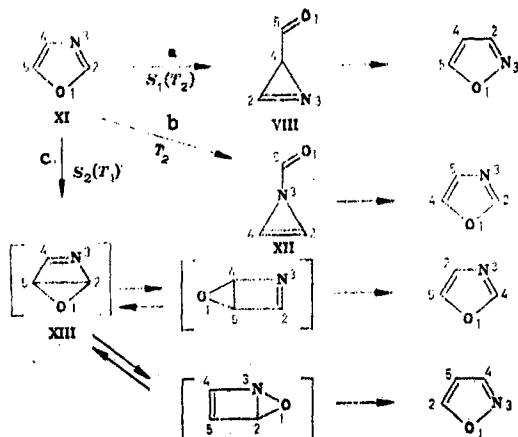
Scheme 3



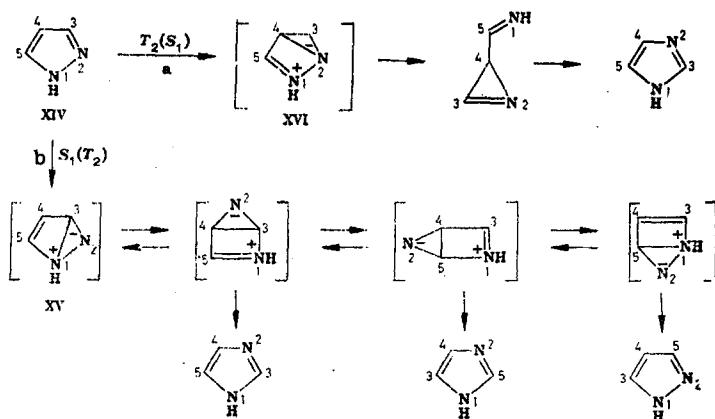
The photoisomerization of pyrazole XIV is distinguished from the isomerization of isoxazole by the fact that in this case, according to the data in Table 2, electrocyclization at positions 1 and 3 (intermediate XV), rather than at 2 and 4 (intermediate XVI), is predominant in the S_1 state, while the reaction should proceed predominantly by means of bonding between positions 2 and 4 in the T_2 state. We stress that, although this mechanism differs somewhat from that adopted in [22], it gives the same products, as is seen from Scheme 5.

The photoisomerization paths of pyrazole in the S_1 and T_1 states are not presented in the scheme, since there are no experimental data on these reactions. With respect to the reverse isomerization of imidazole to pyrazole, it follows from the calculated data that it should be completely analogous to the isomerization of oxazole.

Scheme 4

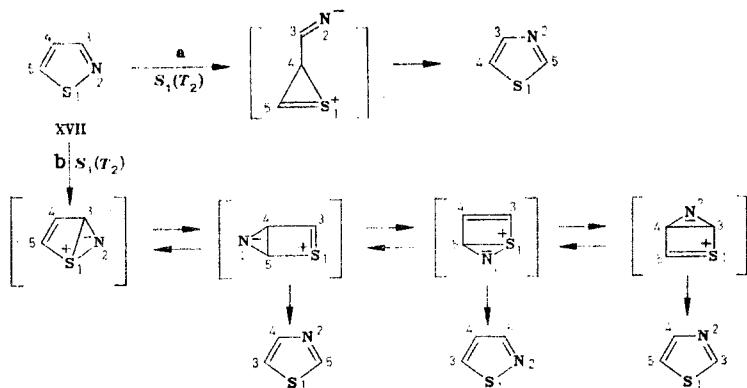


Scheme 5



As was noted in [22], at the present time 95% of all the isomerization products of isothiazole and thiazole in the lowest singlet state (see [19, 22, 29, 32, 33]) can be explained either by a tricyclic zwitterionic mechanism or by an intramolecular cyclization-isomerization mechanism. In the framework of the scheme developed here, this is manifested by the presence of large positive values of K_{ik}^S for the 1-3, 1-4, and 2-4 positions of thiazole and isothiazole in the lowest singlet state (see Table 2). The possible photorecyclization paths of the S_1 state of isothiazole (XVII) under the assumption of a bicyclic transition complex are presented in Scheme 6. As we have already stated above, the predominance of a particular transition state is greatly dependent on the nature of the substituents and the reaction conditions.

Scheme 6



According to the calculated data, in the S_2 and T_1 states this reaction should involve bonding between positions 2 and 5. We note that the existence of large positive values of $K_{1,4}S$ for the S_1 state is also an indication of the possibility of the elimination of an HCN fragment with the formation of a potentially antiaromatic C_2H_2S system. Photoreactions of this type were studied in [34].

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SYNTHESIS OF 5-SUBSTITUTED CYANOFURANS AND THEIR REACTION WITH HYDRAZINE

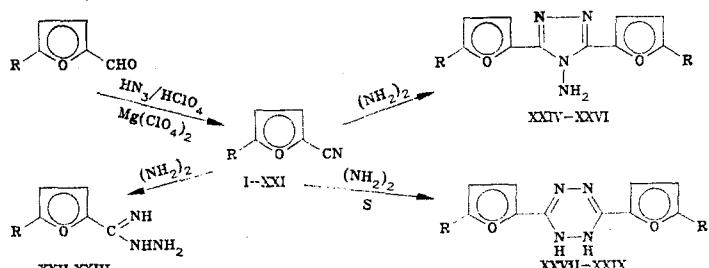
P. A. Pavlov and V. G. Kul'nevich

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722.2+547.882'722.2

Based on the Schmidt reaction, a new method has been developed for the preparation of nitriles in furan series from the corresponding furfural derivatives. Depending on conditions, the reaction of 5-substituted cyanofurans with hydrazine leads to amidrazone, N-aminotriazoles, or 1,2,4,5-dihydrotetrazines.

The known methods for the preparation of cyanofurans from furancarboxaldehydes [1-6] have several disadvantages: multiplicity of stages, difficulties related to the regeneration of the reagents, limited number of suitable methods, because of scarcity of starting materials, as well as impossibility of their use for the preparation of individual compounds, for example, 5-nitro-2-cyanofuran [5].

For this purpose we used the Schmidt reaction [7], considered to be unsuitable for the preparation of nitriles of the furan series. Instead of sulfuric, phosphoric, hydrochloric and other mineral acids, and also Lewis acids [7], we used 72% perchloric acid, with which it was possible to avoid resinification of furancarboxaldehydes, but the yield of the nitrile did not exceed 50%. When anhydrous magnesium perchlorate was introduced, it was possible to reduce the amount of perchloric acid to catalytic quantities, and thus the yield of products I-XXI increased to 76-96%, while the time of the reaction was shortened.



I, XXIV, XXVII R = H, II, XXV, XXVII R = CH₃, III R = C₆H₅, IV R = -C ≡ CC₆H₅, V, XXII, XXVI, XXIX R = Br, VI R = I, VII, XXIII R = NO₂, VIII R = CH₂Cl, IX R = 4-C₆H₄NO₂, X R = 4-OC₆H₄CH₃, XI R = OC₆H₄Cl, XII R = SCH₃, XIII R = SCH₂COOC₂H₅, XIV R = 2,4-SC₆H₃(NO₂)₂, XV R = 5-thio-2-cyanofuran, XVI R = 5-thio-2-oxo-furan, XVII R = S-C(=O)-C₆H₅, XVIII R = 3-S-C(=O)-C₆H₄Br, XIX R = thio-furo-5-yl, XX R = SO₂C₆H₅, XXI R = 4-SO₂C₆H₄CH₃

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