CONJUGATED SCHIFF'S BASES—10[1]. CONTROL EFFECT OF CHARGE RESONANCE COUPLING ON 1,3-CYCLOADDITION OF HETEROCUMULENES TO SOME 1,4-DIAZABUTADIENES

JANUSZ MOSKAL and ALEXANDRA MOSKAL†
Department of Organic Chemistry, Jagiellonian University, 30060 Cracow, Poland

and

WŁADYSŁAW PIETRZYCKI
Department of Organic Chemistry, Silesian University, 40006 Katowice, Poland

Abstract—1,3-Dipolar cycloaddition of organic isocyanates to some 1,4-diazabutadienes has been investigated by theoretical and experimental methods. Analysis of HOMO, LUMO interactions indicated the reaction mechanism and the product structure. Cycloaddition proved to be combined with 1,4 sigmatropic-type hydrogen shift and elimination of the initial 1,4-diazabutadiene fragment.

Although conjugated Schiff's bases containing the 1,4-diazabutadiene system[2,3] are atypical 1,3-dipoles, their chemical behaviour[3,5] suggests that these compounds could react with some polarophiles. Therefore a theoretical model of 1,3-dipolar cycloaddition employing the α,β-diimine of α,β-diketobutyric acid amide and isocyanic acid has been considered. According to general rules[6] regarding 1,3-cycloaddition formulated in terms of charge resonance and reverse charge resonance coupling[7,8] contact of the reactants involves formation of a π complex-type transition state in which the $\delta(2p_\pi - 2p_\pi)$ overlap of the terminal atom orbitals plays the chief rôle. However, if the initial molecules contain atoms bearing unshared electrons and/or possess nonplanar conformation these HOMO, LUMO interactions sometimes give results inconsistent with experiments. Orbitals occupied by unshared electrons although they do not take part directly in cycloaddition, contribute to a high degree to HOMO, LUMO transitions. Hence, the necessity to calculate interactions of all occupied and unoccupied MO's of both 1,3-dipole and polarophile. Nonplanar conformation enhances a variety of orbital interactions so the generally accepted $\sigma(2p_\pi - 2p_\pi)$ overlap describes inadequately acceptor, donor coupling. In such cases overlap in the whole valence basis, i.e. $2p_x$, $2p_y$, $2p_z$ and 1s of hydrogen must be taken into account.

Interaction of an occupied χ_i orbital of 1,3-dipole with an unoccupied $\chi_{\not{j}}$ orbital of dipolarophile (the crossed out index of the orbital shows that it belongs to dipolarophile) can be expressed by the equation of the ground state function of the charge transfer complex. This equation is formulated in the perturbation method[9,10] as below:

$$\chi_i^{(\not{j})} = \chi_i^0 + b_{i,\not{j}} \chi_{\not{j}}^0. \tag{1}$$

Index "0" designates the unperturbed function, "$\not{j}$" is the perturbing orbital index. The energy gain of this interaction is estimated by the following expression:

$$\Delta E_{i,\not{j}} = \frac{-(H_{i,\not{j}} - S_{i,\not{j}} E_i)^2}{E_{\not{j}} - E_i}$$
$$= \frac{-[\beta_{i,\not{j}} + 1/2(E_{\not{j}} - E_i)S_{i,\not{j}}]^2}{E_{\not{j}} - E_i} \tag{2}$$

where $H_{i,\not{j}} = \langle \chi_i | \hat{H} | \chi_{\not{j}} \rangle$, $\hat{H}$ is the perturbation hamiltonian, E_i and $E_{\not{j}}$ are energies of the i and $\not{j}$ orbitals, respectively, $S_{i,\not{j}}$ is the overlap integral, and $\beta_{i,\not{j}}$ the core integral. The latter is defined by the formula:

$$\beta_{i,\not{j}} = \frac{1}{2} \sum_{\mu,\nu} (\beta_X^0 + \beta_Y^0) C_{\mu,i} C_{\nu,\not{j}} S_{\mu,\nu} \tag{3}$$

β_X^0 and β_Y^0 designate empiric parameters characteristic for the given atoms, used in the CNDO and INDO methods.[11,12] They are equal to $-21\,\text{eV}$, $-9\,\text{eV}$, $-31\,\text{eV}$ and $-25\,\text{eV}$ for carbon, hydrogen, oxygen, and nitrogen, respectively. The overlap integral $S_{\mu,\nu}$ is evaluated for the Slater's orbitals (indexes μ and ν designate atomic orbitals in the valence basis). The overlap integral $S_{i,\not{j}}$ considering linear combination of the i and $\not{j}$ MO's, is described by the eqn (4) in which $C_{\mu,i}$ and $C_{\nu,\not{j}}$ are the LCAO coefficients:

$$S_{i,\not{j}} = \sum_{\mu,\nu} C_{\mu,i} C_{\nu,\not{j}} S_{\mu,\nu} \tag{4}$$

The resonance energy gain estimated by the formula (2) is connected with charge transfer expressed by the Sakurai's equation:[16]

†Present address: Polish Academy of Sciences, Institute of Pharmacology, 31920 Cracow, Poland.

$$Q_{i,\not{j}} \cong b_{i,\not{j}} \frac{H_{i,\not{j}} - S_{i,\not{j}} E_i}{E_{\not{j}} - E_i}. \tag{5}$$

Total charge resonance energy equals to summ of the resonance energy gains of the particular orbital inter-actions:

$$\Delta E = -2 \sum_{i}^{occ} \sum_{+}^{unoc} \Delta E_{i,+} - 2 \sum_{+}^{occ} \sum_{j}^{unoc} \Delta E_{+,j}. \qquad (6)$$

Values of $\Delta E_{i,+}$ and $\Delta E_{+,j}$ are from the formula (2). Similarly, total charge accepted or released by an atom X of 1,3-dipole is the summ of the particular charges:

$$q_X = 2 \sum_{i}^{occ} \sum_{+}^{unoc} Q_{i,+} \left(\sum_{\mu}^{(X)} c_{\mu,i}^2 \right)$$

$$+ 2 \sum_{+}^{occ} \sum_{j}^{unoc} Q_{+,j} \left(\sum_{\mu}^{(X)} C_{\mu,j}^2 \right). \qquad (7)$$

Values of $Q_{i,+}$ and $Q_{+,j}$ are calculated using the expression (5). Negative sign of q_X designates an increase of the negative charge on the atom X and reversely, positive sign of q_X designates a decrease of the negative charge on the chosen atom.

In order to find the most favourable steric arrangement of both reacting molecules in the π complex-type transition state two probable conformations of the initial diimine molecule were taken into consideration. In the "planar conformation" azomethine groups were situated coplanar in trans position in relation to the carbon, carbon linkage (analogously as in dianil diacetyl[13]). The amide group was in the perpendicular plane as in the other vicinal polycarbonyl compounds.[14] The "twisted conformation" was characterized by arrangement of azomethine and amide groups in three perpendicular planes (such a conformation called "pseudo-gauche" is adopted by α,β-dianils of α,β-diketobutyric acid anilides due to an expanding effect of bulky substituents[15]). Distance of the reacting centres was considered in two variants: 1.75 Å and 2.5 Å. The former was adjusted to the $\sigma(2p_\pi - 2p_\pi)$ overlap connected with the maximal MO interactions. This correctly reproduced stabilization

energy in the reduced valence basis. The latter was comparable with that occurring in molecular complexes coupled by charge resonance forces and reproduced well stabilization energy in the enhanced valence basis. Charge resonance coupling accompanying the contact process of α,β-diimine in question and isocyanic acid was limited to interactions of occupied MO's of diimine with unoccupied MO's of isocyanic acid and reversely, occupied MO's of isocyanic acid with unoccupied MO's of diimine because these interactions defined mechanism and value of charge transfer. Interactions of occupied MO's of both reactants were neglected for they were not connected with charge transfer and did not estimate its value. Analysis of HOMO, LUMO interactions appearing in the π complex-type transition state containing either the planar or the twisted diimine molecule was performed by the INDO method using the Pople, Beveridge and Dobosh parametrization.[12] The planar conformation of diimine proved to be less profitable than the twisted one. According to the Sustmann's classification[17] the π complex transition state possessing the planar diimine molecule corresponded to the LUMO controlled reactions whereas the π complex transition state consisting of the twisted diimine molecule described the more favourable HOMO, LUMO controlled process.

Then the twisted conformation of α,β-diimine of α,β-diketobutyric acid amide was accepted for further consideration. Steric arrangement of both reacting molecules in the transition state is shown in Fig. 1:

Inspection of the data regarding distribution of the charge resonance energies (Table 1) and charges transferred due to the orbital interactions (Table 2) characterized the contact π complex. Thus it was found to be rather weak (the total charge resonance energy and the global charge transfer were equal to -1.2106 eV and $+0.2998$ charge unit, respectively for 1.75 Å and -0.1289 eV and $+0.1263$ charge unit, respectively for 2.5 Å). Donating function was fulfilled by nitrogen N_4 and N_7 atoms (Fig. 1) and by the oxygen O_5 atom. The carbon skeleton of diimine (C_1, C_2 and C_3 carbons) and

planar diimine
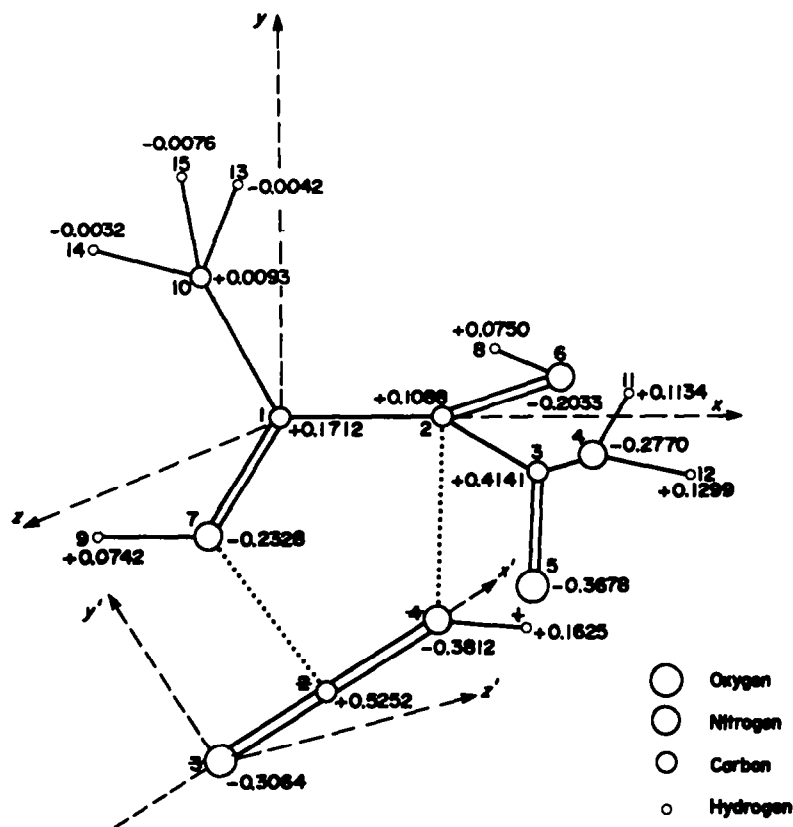

twisted diimine

Scheme 1.
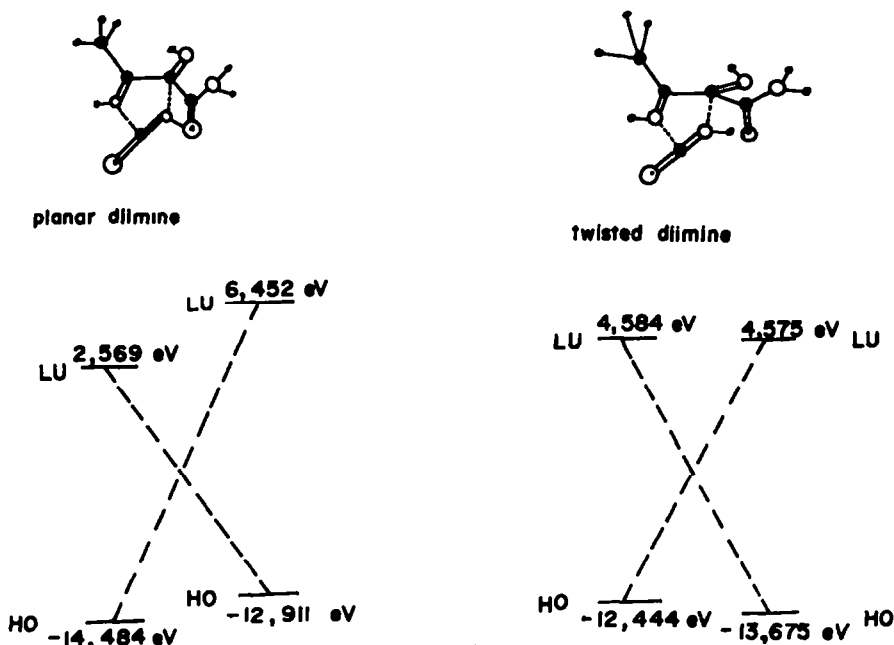
Fig. 1. Steric arrangement of diimine and isocyanic acid in the π-complex transition state. Numbering of the atoms and the atom electron densities calculated by the INDO method (net charges).

the isocyanic acid carbonyl atom C_3 played accepting function. Hydrogen atoms of the amide group (H_{11} and H_{12}) behaved in a similar fashion, i.e. revealed accepting character. This suggested formation of the intermolecular $N_4 \rightarrow C_2$, $N_7 \rightarrow C_9$ and $O_5 \rightarrow H_4$ two-centre interactions.

The strongest charge resonance coupling corresponded to the diimine LUMO, the isocyanic acid NHOMO and to the diimine NHOMO, the isocyanic acid LUMO interactions. Considering LCAO coefficients (Table 3) of these fundamental transitions it could be deduced that in the former case the orbital performing donating function showed mainly n orbital character of N_4 nitrogen:

$$\Phi n(N_4) = -0.616\Phi(2p_y) + 0.326\Phi(2p_x) + 0.519\Phi(2s)$$

$2p_z$ orbital of the diimine C_2 carbon atom was the acceptor. Then this transition characterized $N_4 \rightarrow C_2$ two-centre interaction. It could be found that N_6 nitrogen or rather its $2p_z$ orbital overlapping the n orbital of N_4 nitrogen caused a weakening effect on the contact in question.

The second strong coupling NHOMO, LUMO included two-centre interactions $N_7 \rightarrow C_9$ and $O_5 \rightarrow H_4$. Similarly, the donating orbital had the n orbital character of N_7 nitrogen:

$$\Phi n(N_7) = -0.463\Phi(2p_z) + 0.266\Phi(2p_x) + 0.196\Phi(2s)$$

and $2p_z$ orbital of the C_9 carbon atom played accepting function. The contact $O_5 \rightarrow H_4$ showed H-bond formation and was specific for the model accepted.

Table 1. Distribution of the charge resonance energy $E_{i,j}$ and the charges $Q_{i,j}$ transferred due to the orbital interactions in the π complex state

Orbital number		Orbital energies		Values of $E_{i,j}$		Values of $Q_{i,j}$	
Diimine	Isoc.Acid	E_i	E_j	1.75 Å	2.5 Å	1.75 Å	2.5 Å
23 /LU/	7 /NHO/	4.421	-13.675	-0.1295	-0.0188	-0.0723	-0.0228
21 /NHO/	9 /LU/	-12.444	4.575	-0.1734	-0.0254	0.0547	0.0207
22 /HO/	9 /LU/	-10.708	4.575	-0.0915	-0.0131	0.0713	0.0273
17	9 /LU/	-15.309	4.575	-0.0739	-0.0037	0.0431	0.0096
24 /NLU/	7 /NHO/	4.584	-13.675	-0.0476	-0.0059	-0.0225	-0.0031
19	9 /LU/	-13.571	4.575	-0.0470	-0.0098	0.0359	0.0164
23 /LU/	8 /HO/	4.421	-12.911	-0.0176	-0.0035	-0.0361	-0.0126

Table 2. Values of the negative charge q_X (el. charge units) induced on particular atoms by charge resonance coupling

Atom	1.75 Å	2.5 Å
C_1	−0.0559	−0.0066
C_2	−0.0310	−0.0098
C_3	−0.0443	−0.0147
N_4	+0.0569	+0.0233
O_5	+0.2086	+0.0671
N_6	+0.0690	+0.0196
N_7	+0.1097	+0.0441
H_8	−0.0024	+0.0006
H_9	+0.0024	+0.0025
C_{10}	+0.0017	+0.0056
H_{11}	−0.0117	−0.0026
H_{12}	−0.0133	−0.0028
H_{13}	−0.0057	−0.0006
H_{14}	−0.0027	−0.0002
H_{15}	−0.0015	−0.0007
N_4	+0.1848	+0.0525
C_2	−0.4712	−0.1581
O_5	+0.2064	+0.0490
H_4	−0.2198	−0.0696

"−" designates accepting and "+" donating character.

The main transition of the diimine LUMO, the isocyanic acid HOMO proved to be very weak even in comparison with the diimine NLUMO, the isocyanic acid NHOMO coupling which was more than twice as strong (Table 1). This anomaly was from the structure of the diimine LUMO in which $2p_z$ orbital of N_6 nitrogen not participating directly in two-centre interactions, contributed to the highest degree. The rôle of the N_6 nitrogen atom is interesting. Generally this atom revealed donating function (Table 2) connected chiefly with its $2p_x$ and $2p_y$ orbitals possessing a distinct contributions in HO and NHO MO's (Table 4). Hence N_6 nitrogen could act as an electron releasing centre in HOMO, LUMO and NHOMO, LUMO interactions.

Table 3. MO LCAO characteristics for fundamental transitions the diimine LUMO, the isocyanic acid NHOMO and the diimine NHOMO, the isocyanic acid LUMO. $Q_{LUMO,NHOMO} = -0.0723$ el. charge unit, $Q_{NHOMO,LUMO} = +0.0713$ el. charge unit

Atom	Orbital	LUMO LCAO	NHOMO LCAO	Atom	NHOMO LCAO	LUMO LCAO
O_2	s	0.084	−0.155	N_4	0.319	0.319
	p_x	0.008	−0.002		0.326	0.092
	p_y	−0.075	0.205		−0.616	0.001
	p_z	−0.514	−0.042		0.000	0.000
O_5	s	−0.024	−0.002	C_2	−0.084	−0.149
	p_x	0.148	−0.355		−0.104	−0.054
	p_y	−0.005	0.362		−0.002	0.650
	p_z	−0.001	−0.245		0.000	0.000
N_6	s	0.027	0.071	O_5	−0.012	0.033
	p_x	−0.045	0.042		−0.113	0.098
	p_y	−0.024	−0.112		0.587	−0.432
	p_z	0.528	−0.076		0.000	0.000
N_7	s	−0.074	0.196	H_4	−0.191	−0.494
	p_x	−0.002	0.226			
	p_y	0.235	−0.176			
	p_z	−0.064	−0.463			

Table 4. LCAO coefficients of LU, NLU, HO, and NHO MO's of diimine N_6 nitrogen

Orbital	LUMO LCAO	NLUMO LCAO	HOMO LCAO	NHOMO LCAO
2s	0.027	0.148	−0.203	0.071
$2p_x$	−0.045	−0.136	−0.438	0.042
$2p_y$	−0.023	−0.055	0.032	−0.112
$2p_z$	0.528	−0.269	−0.065	−0.076

On the other hand $2p_z$ orbital contributed in NLU and LUMO's. This implied strong accepting activity in LUMO, HOMO, LUMO, NHOMO and NLUMO, NHOMO transitions. Since $2p_z$ orbital composed π bond (Fig. 1) its accepting character involved an increase of the π electron density on N_6 nitrogen in the cycloaddition process. It suggested the possibility of an intramolecular coupling between N_6 nitrogen and one of the amide hydrogens. ($N_6 \rightarrow H_{11}$ or $N_6 \rightarrow H_{12}$).

To compare theoretical results with the experimental reaction of α,β-dianils of α,β-diketobutyric acid anilides with aryl isocyanates has been investigated. According to expectations the reaction proved to be thermally induced and practically independent of solvent polarity. It was found out that the product formation was accompanied by aryl isocyanate elimination from the anilide group. For the sake of assignment the spectra of the product was measured and analysed. The NMR spectra suggested the presence of the MeCH group in the molecule (doublet and quartet at approximately 1.08 and 5.05 ppm, respectively). The origin of the methine proton was clarified carrying out the reaction using α,β-dianil deuterium labelled in the anilide fragment. The product contained the MeCD group. The aromatic proton

multiplet exhibited three aryl rings in the molecule. The IR spectra showed two sharp absorptions in the CO stretching vibration region at 1670 and 1740 cm^{-1}. There was no NH absorption. Similarly the NMR spectra did not reveal any NH signals. Since analytical data showed that only one O was present in the molecule the band at 1670 cm^{-1} could be either from C=N or C=C double bond stretching vibrations. Differentiation did not afford any difficulties because the azomethine bond should be strongly affected by acids. In fact the products hydrolyzed easily losing the arylamine molecule invested in α-azomethine group of the initial dianil. The new CO group absorption appeared at 1780 cm^{-1} in the IR spectra of the hydrolysis products. The spectral properties of these products corresponded well with the predicted heterocyclic structure of imidazolidine-2,4-dione derivatives.[18] Arguments proving this structure were provided by synthesis.[19] Thus α-bromopropionic acid and an arylamine yielded α-arylaminopropionic acid which further reacted with a corresponding aryl isocyanate to give the imidazolidine-2,4-dione derivative required.

The cycloaddition in question yielded 1,3 - diarylo - 4 - arylimino - 5 - methylimidazolidine - 2 - ones which hydrolysed to 1,3 - diarylo - 5 - methylimidazolidine - 2,4 -
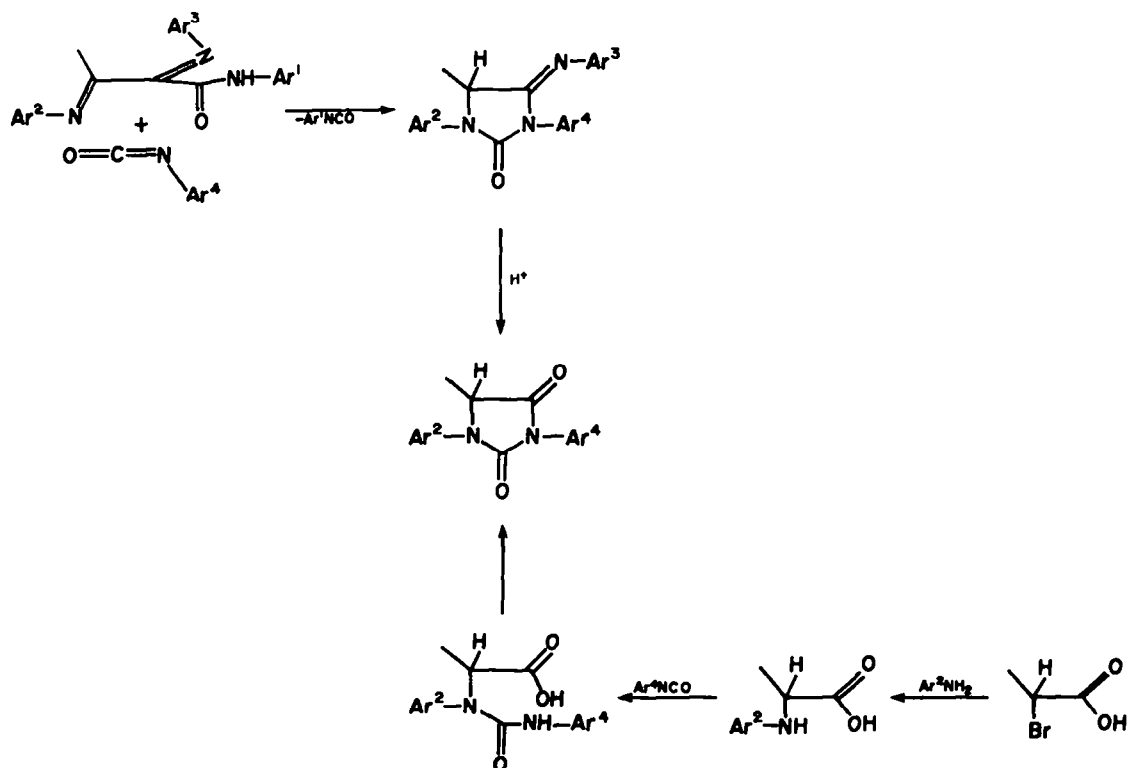
Scheme 2.

diones (hydantoine derivatives). This reaction can be useful as a convenient synthesis of new hydantoine-type compounds. Experimental observations are consistent with theoretical predictions regarding the two-centre interactions $N_4 \rightarrow C_2$ and $N_7 \rightarrow C_2$. However, hydrogen migration occurring in the course of cycloaddition was rather obscure. In order to find more evidence of the mechanism, UV and NMR kinetic measurements were performed. The UV spectra of the dianils exhibited intense absorption at approx. $43,200\ cm^{-1}$ ($\epsilon_{max} = 25,000$) and $34,000\ cm^{-1}$ ($\epsilon_{max} = 12,500$)[20] whereas imidazolidine - 2 - ones absorbed at approximately $39,600\ cm^{-1}$ ($\epsilon_{max} = 25,000$) and $35,200\ cm^{-1}$ ($\epsilon_{max} = 7000$). The data found were not clear showing great complexity. Nevertheless, two different reactions could be suspected to follow one another. The first one occurred at a high rate even at relatively low temperature ($-10°$) and was evidenced by almost immediate disappearance of the absorption at $34,000\ cm^{-1}$ and formation of a new absorption at $34,800\ cm^{-1}$ ($\epsilon_{max} = 14,500$). The second reaction was slow enough to be measured. It was demonstrated by decrease of the absorption intensity at $34,800\ cm^{-1}$ and appearance of the absorption at $35,200\ cm^{-1}$. Intensity changes showed the I-st order dependence (rate constant $k = 0.572 \mp 0.03\ min^{-1}$ at $20 \mp 0.5°$, correlation coeff. $r = 0.998$). The UV data suggested that the rapid process as a kinetically controlled reaction yielded a compound which isomerised into the more stable end-product. The NMR measurements shed more light on nature of the cycloaddition. Inspection of the spectra determined at $20°$ immediately after preparation of the equimolar mixture of the appropriate dianil and phenyl isocyanate revealed reduction.[21] There were only singlets at 1.88 and 5.08 ppm, and the distinctly reduced multiplet of aromatic proton signals. Singlets faded slowly with passage of time and the doublet at 1.03 and quartet at 5.03 ppm appeared simultaneously. Singlets disappeared after approximately 120 min and the spectrum assumed a shape identical to that determined for the isolated reaction product. Considering resonance frequencies of these signals it was found that the singlet positioning at 1.88 was from the Me group attached to the C=C double bond.[20] This at 5.08 ppm corresponded to the enamine NH proton.[4] The cycloaddition therefore, yielded first 1,3 - diarylo - 4 - arylamino - 5 - methyl - Δ^4 - imidazoline - 2 - ones which further isomerized to the more stable (about 17 kcal/mole[21]) 1,3 - diarylo - 4 - arylimino - 5 - methylimidazolidine - 2 - ones. Such a cycloaddition route agreed well with the theoretical predictions suggesting intramolecular coupling between α-azomethine nitrogen N_6 and anilide hydrogen H_{11}. In other words the cycloaddition process was accompanied by 1,4 sigmatropic shift of anilide hydrogen combined with elimination of the anilide group as aryl isocyanate. Its mechanism is shown on Scheme 3.

Substituent effects were also consistent with theoretical considerations. Thus substituents joining N_7 nitrogen exhibited donating activity (Table 2) whereas those at N_6 nitrogen behaved reversely. In fact electron releasing groups located in β-anilo ring facilitated the reaction and electron withdrawing substituents made it difficult to occur. Similarly, introduction of strong electron releasing groups to α-anilo ring impeded the cycloaddition.

α,β-Dianils of α,β-diketobutyric acid anilides were obtained by condensation of corresponding β-anils of acetoacetic acid anilides with nitrosobenzenes in t-BuOH as a solvent in the presence of small amounts of KOH as a catalyst.[3] The following compounds were prepared (anilide ring, α-anilo, β-anilo rings, m.ps, and yield are given): Phenyl, phenyl, p-N,N-dimethylaminophenyl, 204°, 70%; phenyl, p-N,N - diethylaminophenyl, phenyl, 161–3°, 79%. (Found: C, 75.8; H, 6.5; N, 13.6. $C_{26}H_{28}N_4O$, m.w. 412, Calc.: C, 75.7; H, 6.8; N, 13.6%). Phenyl, p-methoxyphenyl, phenyl, 144–6°, 75%; p-methoxyphenyl, p-methoxyphenyl, phenyl, 144–5°, 77%. (Found: C, 71.4, H, 5.8, N, 10.9; $C_{24}H_{23}N_3O_3$, m.w. 401, Calc.: C, 71.8, H, 5.7, N, 10.5%). 2,5 - Dichlorophenyl, phenyl, phenyl, 161–4°, 82%; 2,5 - dichlorophenyl, p-chlorophenyl, phenyl, 146–8°, 71%. (Found: C, 59.6, H, 3.7, N, 9.2, Cl, 23.9; $C_{22}H_{16}N_3OCl_3$, m.w. 444.5, Calc.: C, 59.4, H, 3.6, N, 9.4, Cl 24.0%); 2,5 - Dichlorophenyl, p-methoxyphenyl, phenyl, 147–9°, 79%; 2,5 - dichlorophenyl, p - bromophenyl, phenyl, 163–7°, 72%; 2,5 - dichlorophenyl, p-acetylophenyl, phenyl, 196–7°, 75%. (Found: C, 64.1; H, 4.4, N, 9.0; Cl, 15.4. $C_{24}H_{19}N_3O_2Cl_2$, m.w. 452, Calc.: C, 63.7; H, 4.2; N, 9.3; Cl, 15.7%) Analyses of the other compounds were reported before.[3,22]

β-Anils of acetoacetic acid anilides were prepared using the azeotropic method described previously.[22,23] The following β-anils were obtained (anilide ring, β-anilo ring, m.p., and yields are given): Phenyl, phenyl, oil, 73%; phenyl, p-methoxyphenyl, 108°, 77%; phenyl, p-N,N-diethylaminophenyl, 122°, 81%. (Found: C, 74.1; H, 7.6; N, 13.3; $C_{20}H_{23}N_3O$; m.w. 323, Calc.: C, 74.3, H, 7.7, N, 13.0%), Phenyl, p-nitrophenyl, 163°, 46%; p-nitrophenyl, p-methoxyphenyl, 166°, 67%. (Found: C, 62.4; H, 5.2; N, 12.8; $C_{17}H_{17}N_3O_4$, m.w. 327, Calc.: C, 62.4; H, 5.2; N, 12.9%); p-Methoxyphenyl, p-methoxyphenyl, 114°, 76%. (Found: C, 69.1; H, 6.4; N, 8.8; $C_{18}H_{20}N_2O_3$, m.w. 312, Calc.: C, 69.2; H, 6.4; N, 9.0%) 2,5 - Dichlorophenyl, p-methoxyphenyl, 131°, 84%; 2,5 - dichlorophenyl, phenyl, 132°, 82%; 2,5 - dichlorophenyl, p-bromophenyl, 103°, 69%; 2,5 - dichlorophenyl, p- acetylophenyl, 144°, 75%. (Found: C, 59.3; N, 7.8; Cl, 19.7; H, 4.3%). $C_{18}H_{16}N_2O_2Cl_2$, m.w. 363, Calc.: C, 59.5; H, 4.4; N, 7.7; Cl, 19.5%. Analyses of the other compounds were reported before.[22,23]
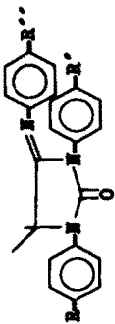
1,3 - Diarylo - 4 - arylimino - 5 - methylimidazolidine - 2 - ones

A corresponding α,β - dianil of α,β - diketobutyric acid anilide was dissolved in dry aprotic solvent (n-hexane, benzene, dioxane, ets.) to obtain a concentrated soln. An equimolar amount of aryl isocyanate was then added and the mixture was warmed. The mixture decolorised and thick, white crystals began to precipitate. In some cases addition of small amounts of petrol ether was desirable to facilitate the crystallization process. The product was filtered off, washed with petrol ether and purified by
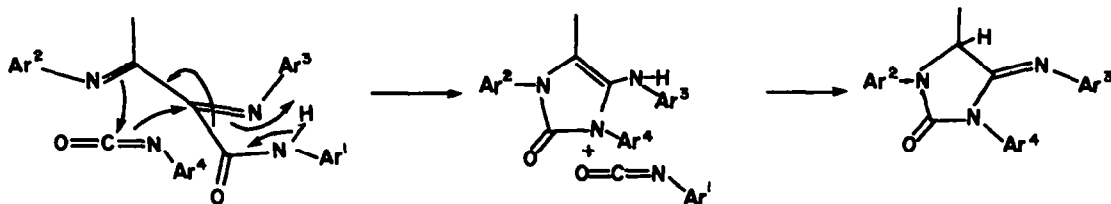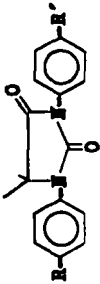

Scheme 3.

Table 5. Spectral and physical properties of 1,3-diaryl-4-arylimino-5-methylimidazolidine-2-ones

R	R'	R''	M.p. °C	Yield %	Formula	Analyses % Calc. Found		I.R. data, cm⁻¹	N.M.R. data, ppm[a]	M.S. data, m/e, /% of the base peak/
H	H	H	144–5	73	$C_{22}H_{19}N_3O$	C 77.2 / 77.0 H 5.8 / 5.6 N 12.5 / 12.5		2985,2960,2930 C–H aliph., 1740 2-C=O, 1675 C=N	1.05 d, 3H, ΔJ=6.7; 5.05 q, 1H, ΔJ=6.7; 7.45–6.82, m, 15H	M^+ 341 /100/, M+1 /23.8/,
OMe	H	H	142–3	76	$C_{25}H_{21}N_3O_2$	C 74.4 / 74.2 H 5.7 / 5.8 N 11.5 / 10.9		2992,2982,2965 C–H aliph., 2838 OMe, 1738 2-C=O, 1678 C=N	1.05 d, 3H, ΔJ=6.6; 5.64 s, 3H; 5.05 q, 1H, ΔJ=6.6, 7.60–6.75, m, 14H	M^+ 371 /100/, M+1 /26.9/
Br	H	H	162–3	70	$C_{22}H_{18}N_3OBr$	C 62.9 / 65.4 H 4.3 / 4.4 N 9.0 / 9.3 Br 19.0 / 19.3		2985,2970,2935 C–H aliph., 1742 2-C=O, 1660 C=N, 538 C–Br	1.11 d, 3H, ΔJ=6.4; 5.05 q, 1H, ΔJ=6.4; 6.76–6.65, m, 4H; 7.01–7.45, m, 10H	M^+ 419 /100/, M+1 /52.9/, M+2 /94.1/, M+3 /27.7/
Me₂	H	H	110–1	79	$C_{26}H_{28}N_4O$	C 75.2 / 75.5 H 6.8 / 6.7 N 15.6 / 13.6		2960,2930 C–H aliph., 2875 NMe₂, 1740 2-C=O, 1675 C=N	1.04 d, 3H, ΔJ=6.7; 1.08 t, 1H, ΔJ=6.5; 3.27 q, 4H, ΔJ=6.5; 5.00 q, 1H, ΔJ=6.7; 6.55–7.60, m, 14H	M^+ 412 /100/, M+1 /33.8/
OMe	H	H	141–2	76	$C_{24}H_{25}N_5O_3$	C 71.8 / 71.9 H 5.7 / 5.8 N 10.5 / 10.1		2985,2965,2955 C–H aliph., 2838 OMe, 1738 2-C=O, 1670 C=N	1.11 d, 3H, ΔJ=6.7; 3.78 s, 3H; 3.81 s, 5.12 q, 1H, ΔJ=6.7; 7.50–6.88, m, 13H	M^+ 401 /66.2/, M+1 /18.4/
OMe	H	Cl	161–2	71	$C_{25}H_{20}N_3O_2Cl$	C 68.1 / 68.5 H 4.9 / 5.2 N 10.4 / 10.4 Cl 9.3 / 9.5		2982,2940 C–H aliph., 2840 OMe, 1742 2-C=O, 1678 C=N, 752 C–Cl	1.03 d, 3H, ΔJ=6.5; 5.01 q, 1H, ΔJ=6.5; 3.69 s, 3H; 7.45–6.77, m, 13H	M^+ 405 /71.4/, M+1 /21.3/, M+2 /23.8/
H	H	Cl	176–8	75	$C_{22}H_{18}N_3OCl$	C 70.4 / 70.0 H 4.8 / 4.9 N 11.2 / 11.5 Cl 9.3 / 9.7		2960,2930 C–H aliph., 2-C=O, 1675 C=N, 1748 C–Cl	1.04 d, 3H, ΔJ=6.5; 5.02 q, 1H, ΔJ=6.5; 7.52–6.75, m, 14H	M^+ 375 /76.0/, M+1 /26.3/, M+2 /30.5/
OMe	H	H	145–6	69	$C_{22}H_{18}NN_3O$	C 77.2 / 77.1 H 5.8 / 5.8 N 12.5 / 12.2		2985,2960,2930 C–H aliph., 2570 C–D, 1740 2-C=O, 1675 C=N	1.12 d, 3H, ΔJ=1.8; 7.54–6.86, m, 15H	M^+ 342 /16.4/, M+1 /9.5/,
OMe[b]	H	H	148–50°d	76	$C_{25}H_{21}N_3O_2$	C 74.4 / 74.1 H 5.7 / 5.5 N 11.5 / 11.5		3250 N–H, 2960,2935 C–H aliph., 2840 OMe, 1695 2-C=O, 1655 C=N	1.88 s, 3H; 3.75 s, 3H; 5.06 s; 6.45–7.75, m, 14H	M^+ 371 /22.5/, M+1 6.2/

a/ s – singlet, d – doublet, t – triplet, q – quartet, and m – multiplet.   b/ 1-p-Methoxyphenyl-3-Phenyl-4-Aniline-5-Methyl- Δ⁴-imidazoline-2-one.

Table 6. Spectral and physical properties of 1,3-diarylo-5-methylimidazolidine-2,4-diones obtained

R	R'	M.p. °C	Yield %	Formula	Analyses % Calc. Found			I.R. data, cm⁻¹	N.M.R. data, ppm [a]	M.S. data, m/e /% of the base peak/
H	H	104-5	78	$C_{16}H_{14}N_2O_2$	C 72.2 71.8	H 5.3 5.3	N 10.5 10.5	2990,2965,2955 C-H aliph., 1785 4-C=O, 1775 2-C=O	1.50 d, 3H, ΔJ=8.7 4.66 q, 1H, ΔJ=8.7 7.40-7.12, m, 10H	M⁺ 266 /45.9/, M+1 /8.2/, 104 /100/
OMe	H	134-5	82	$C_{17}H_{16}N_2O_3$	C 68.9 68.8	H 5.4 5.4	N 9.5 9.5	2960,2935,2910 C-H aliph., 2850 OMe, 1785 4-C=O, 1728 2-C=O	1.49 d, 3H, ΔJ=8.6 3.80 s, 3H, 4.63 q, 1H, ΔJ=8.6, 7.19 d,4H,4H, ΔJ=11.2,Δν=31.2, 7.51 s, 5H	M⁺ 296 /100/, M+1 /22.2/
OMe	OMe	156-7	80	$C_{18}H_{18}N_2O_4$	C 66.3 66.3	H 5.5 5.6	N 8.6 8.6	2975,2945,2910 C-H aliph., 2842 OMe, 1781 4-C=O, 1725 2-C=O	1.44 d, 3H, ΔJ=8.7 3.74 s, 6H, 4.55 q, 1H ΔJ=8.7, 7.07 d,4H,4H ΔJ=12.0,Δν=29.0, 7.12 d,4H, 4H, ΔJ=12.0, Δν =29.0	M⁺ 326 /64.0/, M+1 /15.4/, 149 /100/
OMe	Cl	129-30	76	$C_{17}H_{15}N_2O_3Cl$	C 61.8 62.2	H 4.6 4.7	N 8.5 8.5 / Cl 10.7 10.6	2970,2940,2915 C-H aliph., 2845 OMe, 1785 4-C=O, 1740 2-C=O, 748 C-Cl	1.47 d, 3H, ΔJ=8.5 3.74 s, 3H, 4.54 q, 1H ΔJ=8.5, 7.06 d,4H, 4H, ΔJ=11.2,Δν=27.5, 7.56 s, 5H	M⁺ 330 /76.3/, M+2 /26.7/, 149 /100/
NMe₂	H	94-5	80	$C_{20}H_{23}N_3O_2$	C 71.2 71.2	H 6.9 6.9	N 12.5 12.5	2970,2955 C-H aliph., 2895, 2870 NMe₂, 1770 4-C=O, 1725 2-C=O	1.09 t, 6H, ΔJ=9.2, 1.43 d, 3H, ΔJ=8.7, 3.29 q,4H, ΔJ=9.2, 4.46 q, 1H, ΔJ=8.7, 6.67-6.55, 7.38-7.09 m, 5H	M⁺ 337 /54.3/, M+1 /18.5/, 322 /100/
Br	H	119-20	76	$C_{16}H_{15}N_2O_2Br$	C 55.8 55.9	H 3.8 3.8	N 8.2 8.5 / Br 23.0 22.8	2965,2935,2918 C-H aliph., 1778 4-C=O, 1735 2-C=O, 550 C-Br	1.45 d, 3H, ΔJ=8.7, 4.61 q, 1H, ΔJ=8.7, 7.22 d,4H,4H,ΔJ=11.8 Δν=27.9, 7.48 s, 5H	M⁺ 344 /100/, M+1 /20.5/, M+3 /17.3/

[a]/ s - singlet, d - doublet, t - triplet, q - quartet, and m - multiplet

repeated crystallization from benzene or EtOH. Yields, spectral and physical properties, and analyses are listed in Table 5.

1,3 - Diarylo - 5 - methylimidazolidine - 2,4 - diones

1 g of an appropriate 1,3 - diarylo - 4 - arylimino - 5 - methylimidazolidine - 2 - one was suspended in 80 ml water containing 20 ml conc HCl and the mixture was refluxed for 0.5 hr. The yellow oil solidified after cooling. The product was filtered off, washed with cold water and crystallized from 80% EtOH. Yields, analyses, spectral and physical properties are collected in Table 6.

Synthesis of 1 - p - methoxyphenylo - 3 - phenylo - 5 - methylimidazolidine - 2,4 - dione

p-Anizidine (3 g) and α-bromopropionic acid (3.7 g) were mixed in 35 ml EtOH containing a few drops of triethylamine. The mixture was refluxed for 10 min. The product precipitated after cooling. It was purified by repeated crystallization from EtOH, yield 71%. m.p. 195–7° deco. (Found: C, 61.6; H, 6.7; N, 7.5. $C_{10}H_{13}O_3N$, m.w. 195, Calc.: C, 61.5; H, 6.7; N, 7.2%).

The α-*p*-anizidinopropionic acid was dissolved in 30 ml of dry xylene containing 2.5 g phenyl isocyanate. The mixture was refluxed for 3 hr. The product was separated after cooling and addition of some petrol ether. It was crystallized from 80% EtOH, yield 65%, m.p. 134–5°. (Found: C, 68.7; H, 5.3; N, 9.6. $C_{17}H_{16}O_3N_2$, m.w. 296, Calc.: C, 68.9; H, 5.4; N, 9.5%).

Deuteration of the α,β-dianil of α,β-diketobutyric acid 2,5-dichloroanilide was performed with the help of deuterated t-BuOH. The degree of the deuterium exchange was estimated by means of the IR and NMR measurements. It was equal to 89%.

The UV measurements were recorded on a VSU-2P Zeiss Jena spectrophotometer using 1-cm spectrosil transmission cells. The

Fig. 2. Diagram of log C vs time drafted with the help of the UV data. Temperature $20 \mp 0.5°$, the correlation coefficient r = 0.998, rate constant k = 0.572 ∓ 0.03 min^{-1}.

NMR spectra were determined on a Tesla BS-487 spectrometer using $CDCl_3$ as a solvent and TMS as internal standard. The IR spectra were recorded on an UR-10 Zeiss Jena spectrophotometer using Nujol and Hexachlorobutadiene mulls. The MS spectra were determined on an LKB-9000S spectrometer using a direct insertion probe. Electron voltage 70 eV. Fragmentation pathways will be discussed separately. The isomerization rate constant was determined in n-hexane at $20 \mp 0.5°$. The soln containing reactants was prepared in a concentration 10^{-4} M and was kept in a thermostat. The concentration variations were calculated from the absorption measurements by the usual methods.[24] The UV results were consistent with those found using the NMR method.

Theoretical calculations were performed on an ODRA-1305 computer using the author's own programms.

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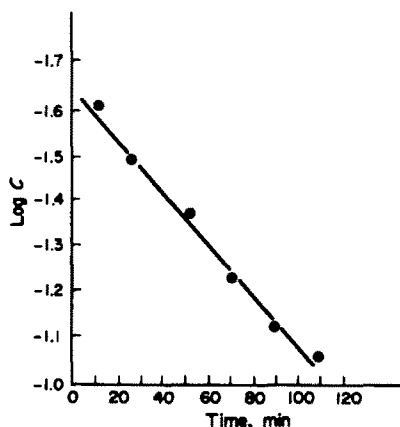[24]J. Świętosławska, *Spektrofotometria absorpcyjna*, PWN, Warsaw (1962).