





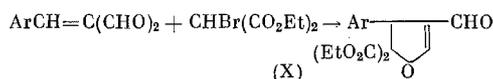
TABLE 2. Some Characteristics of the Carbanions Generated from Malonic and Cyanoacetic Acids

| Carbanion                    | $\pi$ Electron charge on the carbanion center | Coefficient in the HOMO | Energy of the HOMO, eV |
|------------------------------|---|-------------------------|------------------------|
| $\text{CH}(\text{COOH})_2^-$ | -0,435  | -0,634                  | -4,124                 |
| $\text{NCCHCOOH}^-$          | -0,479  | -0,660                  | -3,254                 |

TABLE 3. Some Characteristic of the Electronic Structure of the Enals

| Enal   | $\pi$ Electron charge |                | $\pi + \sigma$ Electron charge |                | Coefficient in the LUMO |                | Energy of the LUMO, eV |
|--|-----------------------|----------------|--------------------------------|----------------|-------------------------|----------------|------------------------|
|  | C <sup>1</sup>        | C <sup>3</sup> | C <sup>1</sup>                 | C <sup>3</sup> | C <sup>1</sup>          | C <sup>3</sup> |                        |
| $\text{CH}_2=\text{CHCH}=\text{O}$                         | 0,157                 | 0,051          | 0,225                          | 0,003          | 0,511                   | -0,576         | 2,176                  |
| $\text{MeCH}=\text{CHCH}=\text{O}$                         | 0,163                 | 0,091          | 0,225                          | 0,060          | 0,461                   | -0,579         | 2,118                  |
| $\text{Me}_2\text{C}=\text{CHCH}=\text{O}$                 | 0,166                 | 0,126          | 0,224                          | 0,101          | 0,461                   | -0,579         | 2,039                  |
| $\text{H}_2\text{C}=\text{C}(\text{Me})\text{CH}=\text{O}$ | 0,154                 | 0              | 0,217                          | -0,028         | 0,503                   | -0,576         | 2,143                  |
| $\text{MeCH}=\text{C}(\text{Me})\text{CH}=\text{O}$        | 0,159                 | 0,042          | 0,217                          | 0,029          | 0,449                   | -0,572         | 2,010                  |
| $\text{ClCH}=\text{CHCH}=\text{O}$                         | 0,155                 | 0,050          | 0,232                          | 0,124          | 0,485                   | -0,523         | 1,673                  |
| $\text{Cl}_2\text{C}=\text{CHCH}=\text{O}$                 | 0,155                 | 0,053          | 0,234                          | 0,221          | 0,453                   | -0,613         | 1,372                  |
| $\text{Cl}_2\text{C}=\text{CHCH}=\text{CHCH}=\text{O}$     | 0,220                 | 0,080          | 0,160                          | 0,090          | 0,336                   | -0,475         | 1,380                  |

Finally, we found that formylidihydrofurans (X) are formed in the reaction of arylidene malonic aldehydes with the bromomalonic ester in conditions of two-phase catalysis (DMF -  $\text{K}_2\text{CO}_3$  - TEBAC) [5]



Based on the previous studies [1-5] and as a result of the present study, it is thus possible to postulate the following features of the reaction of nucleophilic addition of CH acids of the  $\text{XCH}_2\text{CO}_2\text{Et}$  type ( $\text{X} = \text{CO}_2\text{Et}$ , COMe, CN) and  $\text{CHBr}(\text{CO}_2\text{Et})_2$  to enals in the conditions of two-phase catalysis. In the benzene -  $\text{Na}_2\text{CO}_3$  - TEBAC system: 1) Enals unsubstituted in position 3 (acrolein, metacrolein) react with  $\text{CH}_2\text{XCO}_2\text{Et}$  ( $\text{X} = \text{CO}_2\text{Et}$ , COMe, CN) only at the  $\text{C}=\text{C}$  bond (Michael reaction). 2) Enals monosubstituted in position 3 of the crotonaldehyde and cinnamaldehyde type, 3,3-dimethoxybuten-2-al, etc. react with  $\text{XCH}_2\text{CO}_2\text{Et}$  ( $\text{X} = \text{CO}_2\text{Et}$ , COMe) at the  $\text{C}=\text{C}$  bond; enals with manifest electron-donor substituents of the 3-(N-methyl-N-phenyl)- or 3-ethoxyacrolein type are decomposed, and polyenals of the  $\text{R}(\text{CH}=\text{CH})_n\text{CHO}$  type ( $\text{R} = \text{Me}$ , Ph,  $n = 2, 3$ ) do not react. 3) 2,3-Dimethylacrolein adds the malonic and acetoacetic esters at the  $\text{C}=\text{C}$  bond. In contrast to the above, 3,3-disubstituted enals react with  $\text{CH}_2\text{XCO}_2\text{Et}$  ( $\text{X} = \text{CO}_2\text{Et}$ , COMe, CN) at the  $\text{C}=\text{O}$  bond. 4) The reaction between 3-monosubstituted and 2,3-disubstituted enals and  $\text{NCCH}_2\text{CO}_2\text{Et}$  takes place at the  $\text{C}=\text{O}$  bond. 5) N,N-Dichloropolyenals react with  $\text{XCH}_2\text{CO}_2\text{Et}$  ( $\text{X} = \text{CO}_2\text{Et}$ , COMe), forming a mixture of the product of addition at the  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  bonds. 6) In the benzene - 50% NaOH - TEBAC system, acrolein, 3-monosubstituted enals, and dienals form formylcyclopropanes in the reaction with  $\text{CHBr}(\text{CO}_2\text{Et})_2$ .

In the DMF -  $\text{K}_2\text{CO}_3$  - TEBAC system: 7)  $\text{CHBr}(\text{CO}_2\text{Et})_2$  reacts with arylidenemalonic aldehydes with the formation of 3-formyl-2,3-dihydrofurans. 8) 3,3-Disubstituted enals add  $\text{CHBr}(\text{CO}_2\text{Et})_2$  at the  $\text{C}=\text{O}$  bond and yield oxides.

The formation of all of these products can be explained as follows. Addition of carbanions of the  $\text{XCH}^- \text{CO}_2\text{Et}$  and  $\text{BrC}^-(\text{CO}_2\text{Et})_2$  type, generated from  $\text{XCH}_2\text{CO}_2\text{Et}$  ( $\text{X} = \text{CO}_2\text{Et}$ , COMe, CN) or from  $\text{CHBr}(\text{CO}_2\text{Et})_2$ , to the bidentate system of the enal can result in oxanions A and B or C and D, which can be stabilized in different ways, as indicated below

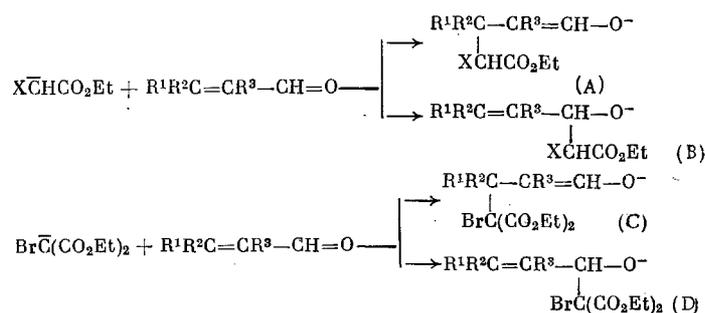
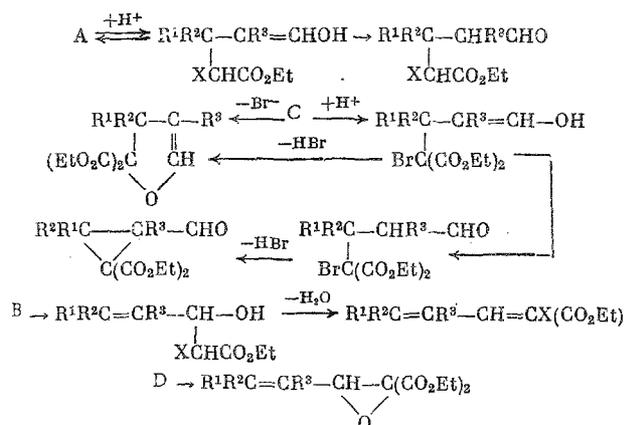


TABLE 4. Values of  $\Delta E$  ( $E_{\text{HOMO}} - E_{\text{LUMO}}$ ) for Some Enals and the Relative Value of Indexes  $I_1$  and  $I_2$

| Enal  | Carbanion                           | $\Delta E$ , eV | $I_1(C^1)/I_2(C^2)$ |      |
|---|-------------------------------------|-----------------|---------------------|------|
| $\text{CH}_2=\text{CHCH}=\text{O}$                  | $\text{CH}(\text{COOH})_2^-$        | -6,30           | 3,24                | 3,70 |
|   | $\text{CH}(\text{CN})\text{COOH}^-$ | -5,43           |                     |      |
| $\text{MeCH}=\text{CHCH}=\text{O}$                  | $\text{CH}(\text{COOH})_2^-$        | -6,24           | 3,30                | 3,55 |
|   | $\text{CH}(\text{CN})\text{COOH}^-$ | -5,37           |                     |      |
| $\text{Me}_2\text{C}=\text{CHCH}=\text{O}$          | $\text{CH}(\text{COOH})_2^-$        | -6,16           | 3,25                | 3,65 |
|   | $\text{CH}(\text{CN})\text{COOH}^-$ | -5,29           |                     |      |
| $\text{CH}_2=\text{C}(\text{Me})\text{CH}=\text{O}$ | $\text{CH}(\text{COOH})_2^-$        | -6,26           | 3,28                | 3,62 |
|   | $\text{CH}(\text{CN})\text{COOH}^-$ | -5,39           |                     |      |
| $\text{MeCH}=\text{C}(\text{Me})\text{CH}=\text{O}$ | $\text{CH}(\text{COOH})_2^-$        | -6,13           | 3,23                | 3,52 |
|   | $\text{CH}(\text{CN})\text{COOH}^-$ | -5,26           |                     |      |

TABLE 5. Relative Energies of Pyramidalization of the  $\text{C}^1$  Atom in  $\text{R}^1\text{R}^2\text{C}=\text{CHCH}=\text{O}$  Structures (the energy of the structure with a pyramidalized  $\text{C}^3$  atom is set at zero)

| $\text{R}^1$ | $\text{R}^2$ | $\Delta E$ , kcal/mole | $\text{R}^1$ | $\text{R}^2$ | $\Delta E$ , kcal/mole |
|--------------|--------------|------------------------|--------------|--------------|------------------------|
| H            | H            | 4                      | H            | Cl           | -1                     |
| H            | Me           | -3                     | Cl           | Cl           | -4                     |
| Me           | Me           | -9                     |              |              |                        |



The direction of the reaction should evidently be a function of the nature of the carbanion, the enal, and the conditions of the reaction. The different direction of the reaction of  $\beta$ -substituted aldehydes (crotonaldehyde, cinnamaldehyde, 3,3-dimethoxybuten-2-al, etc.) with the carbanions generated from malonic (or acetoacetic) esters and cyanoacetic ester in this case could be due to the preferred orbital control of the direction of the reaction in the first case and to preferred charge control in the second case. These explanations are very widely used by various investigators in similar reactions. The term "charge control" means the electrostatic interaction between the reagents. Its value is proportional to the product of the charges of the C atoms which directly participate in the formation of the bond between the carbanion and the aldehyde. The term "orbital control" means the energy of the interaction between the molecular orbitals of the reagents. This energy has a quantum mechanical origin and has no analog in classical mechanics and electrostatics. Its value in the approximation of boundary orbitals can be estimated with the following equation

$$E_{\text{orbit}} = \beta^2 C_N^2 C_E^{*2} S_{NE}^2 / (E_E^* - E_N)$$

where  $C_N$  and  $C_E^*$  are coefficients with the  $\pi$  orbitals of the C atoms which directly participate in the formation of a bond between the carbanion and the aldehyde in the  $\pi$ -electron higher occupied molecular orbital (HOMO) of the nucleophile and the lower unoccupied molecular orbital (LUMO) of the enal, respectively;  $S_{NE}$  is the integral of the overlap between these orbitals;  $E_N$  and  $E_E^*$  are their energy;  $\beta$  is a coefficient which has the dimensionality of the energy.

In the present article, the electronic structure of the methyl and chlorine derivatives of acrolein and the carbanions generated from malonic and cyanoacetic acids were calculated to determine whether it is possible

TABLE 6. Yields and Properties of the Products Obtained\* ed\*

| Compound                                     | T of the reaction, °C (time, h) | Yield, % | Bp, °C (P, mm Hg)<br>Mp, °C | $n_D^{20}$ | IR-spectrum, $\nu$ , $\text{cm}^{-1}$ | UV spectrum, $\lambda_{\text{max}}$ nm ( $\epsilon$ ) | PMR spectrum, $\delta$ , ppm (J, Hz)   |
|--|---------------------------------|----------|-----------------------------|------------|---------------------------------------|---|--|
| (II a)                                       | 40-45 (6)                       | 33       | 95-97 (0,7)                 | 1,4380     | 1736<br>1720                          |   | 1,12 d (3H, CH <sub>3</sub> , J=6), 1,2 t (6H, 2CH <sub>2</sub> ester J=7), 1,25-1,72 m (3H, CH <sub>2</sub> , CH), 3,25-3,5 m (1H, CH(CO <sub>2</sub> Et) <sub>2</sub> ), 4,15 q (4H, 2CH <sub>2</sub> ester J=7), 9,55 s (1H, CHO)   |
| (II b)                                       | 60-65 (3)                       | 75       | 150-152 (0,3)               | 1,4720     | 1736<br>1720                          |   | 1,12-1,6 m (1H, 3CH <sub>3</sub> , 2H ring), 2,4-2,6 m (1H, CH), 2,6-2,87 m (2H, CH <sub>2</sub> ), 3,65 q (1H, CH(CO <sub>2</sub> Et) <sub>2</sub> , J=7), 4,06 q (4H, 2CH <sub>2</sub> ester, J=7), 9,6 s (1H, CHO)  |
| (II m)                                       | 40-45 (6)                       |          | 105-107 (0,6)               | 1,4352     | 1736<br>1720                          |   | 0,85-1,4 m (12H, 2CH <sub>2</sub> ester, 2CH <sub>3</sub> ), 2,25-2,8 m (2H, 2CH, 3,3 d (1H, CH(CO <sub>2</sub> Et) <sub>2</sub> , J=6), 4,1 q (4H, 2CH <sub>2</sub> ester) 9,55 s (1H, CHO)   |
| (III b)                                      | 40-45 (0,5)                     | 54       | 135-138 (0,3)               | 1,5131     | 1736<br>1720                          |   | 1,24 m (8H, 2CH <sub>3</sub> , 2H ring), 2,12 s (3H, COCH <sub>3</sub> ), 2,5 m (1H, CH), 2,76 m (2H, CH <sub>2</sub> ), 3,7-3,9 m (1H, CH(COCH <sub>3</sub> )CO <sub>2</sub> Et), 4,16 q (2H, CH <sub>2</sub> ester, J=7), 9,6 s (1H, CHO)  |
| (IV j)                                       | 50 (4)                          | 48       | 104-105 (0,1)               | 1,5042     | 1730                                  | 280 (17600)   | 1,28 t (6H, 2CH <sub>3</sub> , J=7), 3,74-4,42 m (4H, 2CH <sub>2</sub> , J=7), 7,04 d 7,46 d (2H, =CH-CH=, J=12)   |
| (V a)  | -30 + -35 (4)                   | 12       | 97-98 (0,6)                 | 1,4590     | 1720<br>2245                          |   | 1,1-1,24 m (9H, 3CH <sub>3</sub> ), 1,7-2,7 m (3H, CH <sub>2</sub> , CH), 3,6-3,9 m (1H, CH(CN)CO <sub>2</sub> Et), 4,3 q (2H, CH <sub>2</sub> ester, J=7), 9,65 s (1H, CHO)   |
| (VI c)                                       | 20-25 (0,75)                    | 38       | 144-142 (10)                | 1,5150     | 1735<br>1755                          | 303 (18300)   | 1,28 t (3H, CH <sub>3</sub> ester J=7), 2,04 s (6H, (CH <sub>2</sub> ) <sub>2</sub> C=), 4,49 q (2H, CH <sub>2</sub> ester J=7), 6,31 d (1H, CH=, J=12), 7,95 d (1H, 2H, CH <sub>2</sub> ester, J=7), 3,35 s (3H, CH <sub>3</sub> ), 4,17 q (2H, CH <sub>2</sub> ester, J=7), 5,73 t (1H, CH=, J=12), 6,97-7,43 m (6H, =CH, C <sub>6</sub> H <sub>5</sub> ), 7,79 d (1H, CH=C(CN)CO <sub>2</sub> Et, J=12) |
| (VI h)                                       | 45 (0,5)                        | 86       | 130-131                     |            | 1726<br>2228                          | 382 (32800)   | 1,29 t (3H, CH <sub>3</sub> , J=7), 4,27 q (2H, CH <sub>2</sub> , J=7), 6,7-7,12 m 7,12-7,6 m (9H, 4CH=, C <sub>6</sub> H <sub>5</sub> ), 7,8 d (1H, CH=C(CN)CO <sub>2</sub> Et, J=12)   |
| (VI j)                                       | 5-10 (0,5)                      | 60       | 78-80 (0,01)                | 1,5540     | 1726<br>2230                          | 300 (21300)   | 1,32 t (3H, CH <sub>3</sub> , J=7), 4,27 q (2H, CH <sub>2</sub> , J=7), 6,43 d, 7,34 d (2H, =CH-CH=, J=12)   |
| (VI k)                                       | 15 (0,5)                        | 75       | 127-128                     |            | 1726<br>2230                          | 338 (33000)   | 1,22 t (3H, CH <sub>3</sub> , J=7), 4,26 q (2H, CH <sub>2</sub> , J=7), 6,93-7,09 m 7,9-8,08 m (4H, 4CH=)  |
| (VII l)                                      | 20 (1)                          | 75       | 119-120                     |            | 1726<br>2230                          | 370 (26000)   | 1,2 t (3H, CH <sub>3</sub> , J=7), 4,21 q (2H, CH <sub>2</sub> , J=7), 6,48-6,80 m (5H, 5CH=), 7,53 d (1H, CH(CN)CO <sub>2</sub> Et, J=12)   |
| (III k + (IV k)                              | 80 (3)                          | 25       | 135-137 (0,3)               | 1,4849     | 1735<br>1752                          | 320 (4430)  | 1,22 m (CH <sub>3</sub> ester), 2,63 m (CH <sub>2</sub> ), 3,50 m (CH), 4,06 q 4,1 q (CH ester, J=7), 5,54-6,16 m 7,1-7,26 m (CH=), 9,52 s (CHO)   |
| (III l <sup>k</sup> + (VII l <sup>k</sup> l) | 40 (3)                          | 42       | 133-134 (0,35)              | 1,5641     | 1690<br>1725                          | 320 (24400)   | 1,5-1,74 m (CH <sub>3</sub> ester), 2,0-2,3 m (COCH <sub>3</sub> ), 2,64 m (CH <sub>2</sub> ), 3,66 m (CH), 3,96-4,40 m (CH <sub>2</sub> ester), 5,73-6,12 m 6,50-6,83 m 7,10-7,30 m (CH=), 9,5 s (CHO)  |
| (III l + (VII l)                             | 50 (6)                          | 46       | 200-205 (0,5)               | 1,6176     | 1690<br>1725                          | 357 (19400)   | 1,3 m (CH <sub>3</sub> ester), 2,0-2,35 m (COCH <sub>3</sub> ), 2,62 m (CH <sub>2</sub> ), 3,2 m 3,6 m (CH), 3,93-4,3 m (CH <sub>2</sub> ester), 5,0-6,3 m 6,5 m 6,7-6,9 m 7,1-7,3 m (CH=), 9,4 s (CHO)  |

\* The results of the elemental analysis are in good agreement with the theoretical results.

to predict the direction of the reaction based on the competition of only two types of reaction (orbital and charge).

The results of the calculations of the electronic structure of the carbanions of malonic and cyanoacetic acids are reported in Table 2. A comparison of these data shows that the carbanion of cyanoacetic acid has a significantly higher coefficient  $C_N$  and a higher HOMO. As a consequence, it will be a more active reagent with respect to the orbital reaction. The charge on the carbanion center in this anion is also greater than in the carbanion of malonic acid. As a consequence, the carbanion of cyanoacetic acid will also be a more active reagent with respect to an electrostatic interaction. The calculations thus show that the carbanion of cyanoacetic acid will be a more active nucleophile than the malonic acid carbanion. This result is in total agreement with the experimental data.

The calculations of the electronic structure of the enals are reported in Table 3. It follows from these data that the highest positive charge is located on the  $C^1$  atom of the  $C=O$  group in all of the enals investigated. As a consequence, reactions whose direction is determined by an electrostatic interaction should primarily take place on this atom. The highest coefficient  $C_{E^*}$  in the LUMO of the enal corresponds to the  $\pi$  electron atomic orbital of the  $C^3$  atom, however. Reactions whose rate is determined by the  $C^3$  atom in orbital interactions should thus primarily take place on the  $C^3$  atom of the  $C=C$  bond.

It is experimentally known that the carbanions generated from the cyanoacetic ester primarily react in the  $C=O$  group. For this reason, it can be hypothesized that the direction of the reaction in the case of these anions is controlled by an electrostatic (charge) interaction. The reactions involving the malonic carbanion primarily take place at the  $C=C$  bond. Their direction is apparently controlled by an orbital interaction.

We attempted to estimate the relative contribution of the Coulomb (charge) and orbital interactions in molecules of the acrolein series and its methyl-substituted derivatives using the ratio of the indexes  $I_1/I_2$ , where  $I_1$  characterizes the Coulomb and  $I_2$  characterizes the orbital interaction.  $I_1 = q_N q_E (\pi, \pi + \sigma)$ , where  $q_N$  and  $q_E$  ( $\pi$  or  $\pi + \sigma$ ) are the charges on the atoms of the nucleophile and electrophile directly involved in the formation of a new bond.  $I_2 = C_N^2 C_{E^*}^2 / (E_{E^*} - E_N)$ . The data obtained are reported in Table 4, which indicates that methylation virtually does not alter the value of  $\Delta E$  or the ratio  $I_1/I_2$  in all cases. It is not possible to predict the change in the direction of the reaction based on the ratios obtained. It is also not possible to explain the change in the direction of the reaction on substitution of the H atoms in the acrolein by Cl atoms. The change in the direction of the reaction of nucleophilic addition on introduction of  $CH_3$  groups or Cl atoms in the enal thus cannot be explained based on concepts of the competition of orbital and electrostatic (charge) interactions.

This negative result could be due to the fact that some important factors which affect the direction of nucleophilic addition were not accounted for in our calculation. In the general case, the total energy of the reaction between reagents can be divided into contributions of three types: an electrostatic (Coulomb or charge) interaction, an orbital interaction, and steric stresses. The electrostatic and orbital interactions attract the reagents to each other, while the steric stresses prevent them from approaching. In addition, the reaction takes place in solution in the presence of a counterion, and the interactions with the solvent and counterion can also affect the direction of the reaction. The Coulomb and orbital interactions were examined above, and the contributions of steric stresses and the interaction with the solvent and counterion must now be compared.

In our case, the solvent and counterion apparently should not significantly affect the direction of the reaction. This reaction is conducted in the same conditions of interphase catalysis, which consists of the generation of an extremely active, weakly solvated carbanion. The interaction with the solvent and counterion reduces its reactivity, and the reaction is conducted so that these effects are minimal. In addition, as a result of the direct experimental study it was shown that the relative yields of the end products are not dependent on the choice of solvent in such reactions.

The steric hindrances related to the different volume of the H atom and  $CH_3$  group or Cl atom can significantly affect the direction of addition. In addition of carbanions to enals, there is a significant change in the structure of one of the C atoms in the enal: on approach of the carbanion, it changes from plane to pyramidal. We calculated the pyramidalization energies of the  $C^1$  and  $C^3$  sites in acrolein and its methyl and chlorine derivatives. The pyramidalization energies were calculated as the difference between the energies of the pyramidal and plane enal. All valence angles were assumed to be equal to their standard values of 120 and 109.5°. The valence angles in the pyramidalized C atom were assumed to be equal to 109.5°. All interatomic distances were optimized. The results obtained are reported in Table 5.

Table 5 shows that pyramidalization of the end C<sup>3</sup> atom in the C=C double bond is most advantageous in acrolein. Substitution of one of the H atoms on C<sup>3</sup> by a CH<sub>3</sub> group results in a qualitative change in the result. Pyramidalization of the C<sup>1</sup> atom in the C=O group becomes more advantageous. Substitution of a second H atom at C<sup>3</sup> by a CH<sub>3</sub> group increases this difference to 9 kcal/mole. Substitution of H atoms by Cl atoms results in the qualitatively identical result as methylation. Substitution of the H atoms on C<sup>3</sup> by CH<sub>3</sub> groups or Cl atoms thus favors a change in the direction of addition due to steric factors, and the value of this effect was high enough to result in a qualitative change in the yield of the final products.

#### EXPERIMENTAL

The structure of the compounds obtained was confirmed by the IR, UV, and PMR spectra and by elemental analysis. The individuality of the products was verified by GLC; the course of the reaction was monitored by the same method. The GLC analysis was conducted on a LKhM-8 MD-5 chromatograph with a flame ionization detector and N<sub>2</sub> carrier gas; glass column (1.4 × 0.003 m) packed with 5% SE-30 on Chromaton N-AW-DMCS. The PMR spectra were made on a Varian DA-60IL (60 MHz) for solutions in CCl<sub>4</sub>, the chemical shifts were given in the δ scale, and TMS was the internal standard. The IR spectra were made in CHCl<sub>3</sub> on a UR-20 spectrometer. The UV spectra were made in alcohol on a Specord spectrometer. Compounds (II)-(VII) were prepared as described in [1]. The yields and properties of the products obtained are reported in Table 6. The calculations were conducted by the CNDO/2 method [6].

#### CONCLUSIONS

1. The general mechanisms of the direction of addition of CH acids of the XCH<sub>2</sub>CO<sub>2</sub>Et and BrCH(CO<sub>2</sub>Et)<sub>2</sub> type to enals in conditions of two-phase catalysis were formulated: a) CH acids (X = CO<sub>2</sub>Et, COCH<sub>3</sub>, CN) are added to enals unsubstituted in position 3 only at the C=C bond; b) enals monosubstituted in position 3 add CH acids (X = CO<sub>2</sub>Et, COCH<sub>3</sub>) at the C=C bond and CH acids (X = CN) at the C=O bond; c) enals disubstituted at position 3 add CH acids (X = CO<sub>2</sub>Et, COCH<sub>3</sub>, CN) exclusively at the C=O bond.

2. Quantum-chemical calculations showed that the direction of the reaction of addition of CH acids to enals cannot be explained based on concepts concerning the competition of orbital and charge interactions.

3. The change in the direction of addition in methylation and chlorination of the enal is due to steric hindrances which arise when the structure of the enal is altered when the reagents converge.

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