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Alkylation of 3,4-Dibromo-4-methyltetrahydropyran with Diethyl Malonate as a Key to Understanding the Electronic Nature of Chemo- and Regioselectivity of Molecules

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Abstract—The reaction of 3,4-dibromo-4-methyltetrahydropyran with diethyl malonate in the presence of sodium butoxide leads to formation of the corresponding cross-coupling product rather than of tetraethyl ethane-1,1,2,2-tetracarboxylate (product of dehydrodimerization of diethyl malonate) which is formed in the presence of sodium ethoxide. An explanation was proposed, which may be regarded as a key to understanding the nature of the driving force for one- and two-electron transfer, as well as chemo- and regioselectivity of organic molecules.

It was recently shown that the dehydrobromination–substitution pattern (Scheme 1, path *1*: **I** → **II** → **III**), which is typical of reactions of 3,4-dibromo-4-methyltetrahydropyran (**I**) with a series of nucleophiles (such as amines, phenols, alcohols, organic acid salts, etc.) [1–3], is not followed in reactions with enolates derived from β-dicarbonyl compounds [4]. In the latter case, dehydrodimers **IV** of β-dicarbonyl compounds (path *2*) and dihydropyran **V** are formed instead of cross-coupling products **III**. It may seem that we revealed just one more example of radical nucleophilic substitution whose general relations have long been known [5–10].

However, it becomes clear that this fact also contains important information on both driving forces of radical nucleophilic substitution itself and chemo- and regiochemistry of molecules on the whole [11–13]. This information can be revealed by considering the problem in terms of the ion-pair version of mechanisms of organic reactions, which distinctly differentiates the roles of reagent and substrate [14–20]. Without going into details (for more information, see [15–18]), we should note that such refinement of the behavior of a reagent and a substrate rules out possible arbitrary treatment of nucleophilic or electrophilic properties of reagents [11–13]. Another specific feature of the above version is that it implies the charge on an atom in a reagent, estimated in the chemical bond ionic character units, as a measure of the ability of a C–nucleofuge bond to undergo heterolysis and the degree of extension of the C–nucleofuge bond in the substrate as a measure of regio- and stereochemistry [16–18]. In addition, it is believed that heterolytic dissociation of a C–nucleofuge bond is a three- rather than two-step process, each step corresponding to one type of ion pairs. These types include contact, loose, and solvent-separated ion pairs (IP_c, IP_l, and IP_{ss}), the two latter possessing electrophilic properties [16]. Each type of ion pairs is characterized by specific regio- and stereochemical transformations, regardless of the type of chemical bond and transformation mode.

Success of the approach is achieved due to the fact that the most important source of information on the nature of the driving force of a reaction is the product structure. This belief originates from the assumption that structure of a molecule contains so much important and reliable information on the properties of its precursors (ion pairs and molecules as a whole) that cannot be obtained by any other method for studying mechanisms of organic reactions.

On the basis of the above concepts we were able to reveal and solve many problems whose existence could

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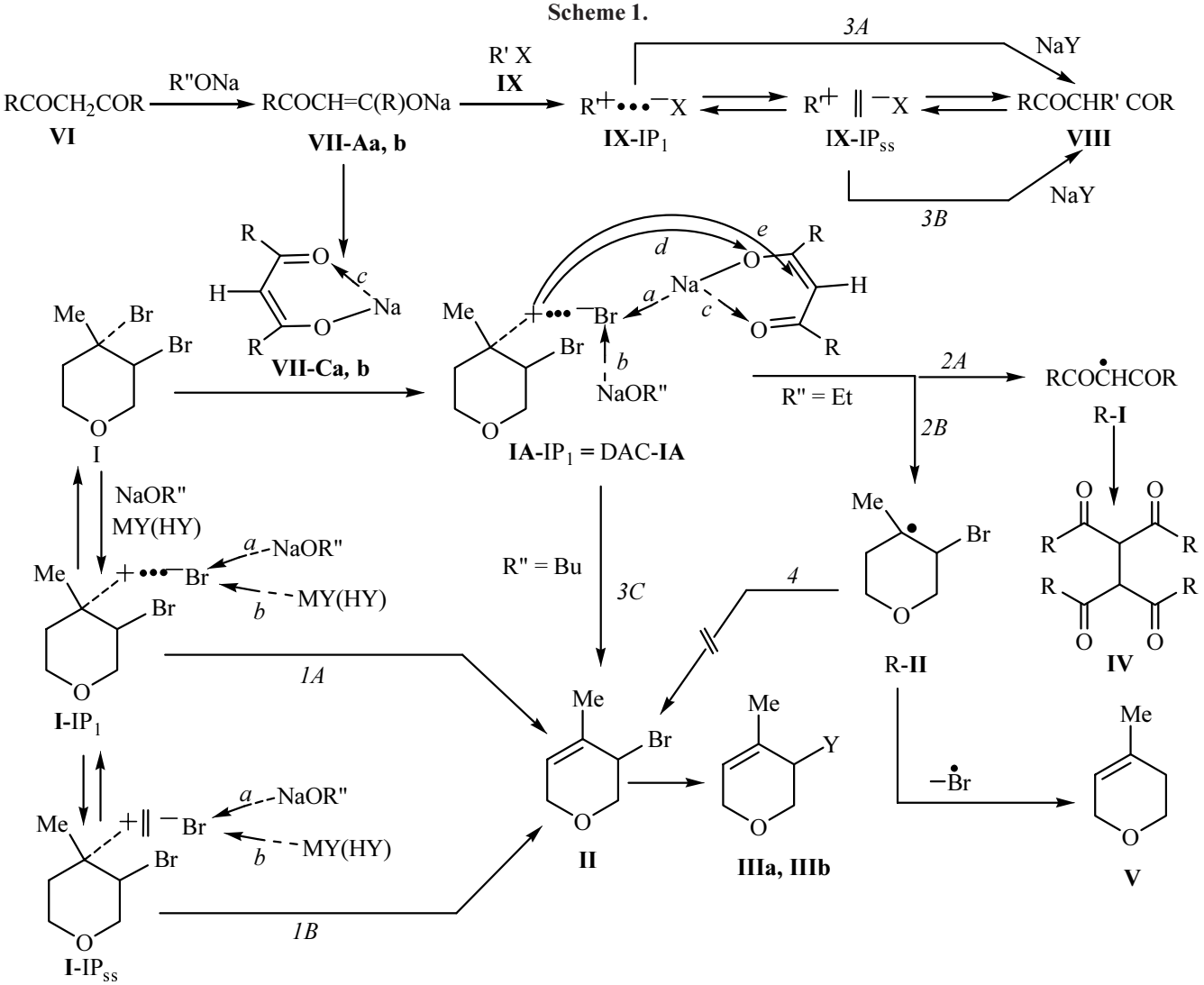
not be surmised in terms of the modern organic chemistry principles [19, 20], especially in the given case, taking into account that dicarbonyl compounds **VI** under analogous conditions (while being converted into sodium enolate **VII**) give rise to normal alkylation products **VIII**.

Let us demonstrate once more the possibilities of the proposed approach by revealing the reason for dehydrodimerization of sodium enolates by the action of dibromide **I** as an example [4]. We start the discussion by noting that since the discovery of nucleophilic radical substitution [5–10] some authors presumed classical nucleophilic substitution to be a process including two steps of transfer of one electron.

However, it became clear that such simplification of the problem gives only an illusion of its solution. While touching one aspect of the problem, the others fall out from the scope of attention, though just the latter should be revised to understand the true cause for change in the behavior of a molecule. Therefore, conclusions and predictions drawn on the basis of this concept are often confusing rather than reliable. An illustrative example is the suggestion to consider radical nucleophilic reactions to be a specific kind of transformation without assigning them to electrophilic or nucleophilic type, for supposedly there is no clear differentiation between these terms. For the same reason, rigorous classification of molecules into reagents and substrates [10] etc., seems to make no sense. As a result, no answers were given so far to the following questions: why some halogen derivatives react according to the classical nucleophilic substitution scheme

Scheme 1.



HY = $HNAlk_2$, H_2NAlk; MY = MOAlk, MOAr, MOAc, $M[CH(COR)_2]$; **III**, R = OEt (**a**), OBu (**b**); M = Na, K; X = Hlg; **IV**, **VII**, R = OEt (**a**), Me (**b**).

(paths *1* and *3*) while reactions of others under the same conditions involve formation of radical species (path *2*)? Which factors (and according to which scheme) are responsible for such difference in the properties of similar molecules?

In order to elucidate the reason for the above ambiguity and to answer the above questions, we focused on some relevant data [14, 15, 21, 22]. The most important of these are the following. First, the reason for elimination of hydrogen halide according to the Zaitsev rule is not the conjugation effect but emergence of electrophilic species [22]; second, elimination of a hydrogen atom capable of departing as hydride ion from secondary γ-halo ethers cannot be prevented even in superbasic medium [14].

Taking into account the above stated, let us to determine those properties of reagent and substrate, which control one- and two-electron transfer, in particular the formation of dimeric molecules **IV**. It is known that compounds **IV** are also formed in the oxidation of enolates derived from β-dicarbonyl compounds with iodine, silver oxide, copper(II) trifluoromethanesulfonate, etc. [23]. The specificity of the described reaction is that dibromide **I** acts here as oxidant, while with other nucleophiles it reacts according to the dehydrobromination–substitution pattern to afford products **III**. How can this occur? The simplest answer is that the oxidant is not dibromide **I** itself but one of its electrophilic ion pairs, **IA**-IP_l or **IA**-IP_{ss}. Nevertheless, it cannot be regarded as an answer to the above questions; this is only a description of the cause of one-electron transfer in some molecules but not of the cause of behavior of other related molecules which are not involved in analogous reaction.

We succeeded in noticing that information necessary for solution of this problem is contained in the mere fact of alteration of the reaction direction upon replacement of reagent of one type by another. This obviously indicates that emergence of ion pairs responsible for product formation involves both base (NaOR) and reagent molecule (reactions *a* and *b*). Formalistically, this resembles a trimolecular process of dissociation of Swain's electrofuge–nucleofuge bond [24] occurring with participation of the solvent and reagent. Apart from similarity, the proposed version is characterized by a radical difference. It does not imply stabilization of already developed cationoid species by the solvent but participation of the latter (or a co-reagent) just in the extension of the electrofuge–nucleofuge bond in the substrate.

In fact, had the NaOR base alone (i.e., without participation of co-reagent **VII**) been capable of playing this role (reaction *a*), such reaction, as well as in the presence of co-reagents like MY (HY) (reaction *b*), would lead to formation of monobromide **II**. This is not the case. Compounds **IV** and **V** are formed instead. Their precursors could be only radical species R-**I** and R-**II**, respectively. Although this version is justified to a sufficient extent, it is not irreproachable as well, for it does not answer the fundamental question of organic chemistry: which forces and in which way induce homolytic dissociation of the C–nucleofuge bond in one molecule but heterolytic dissociation of the same bond in the others?

We succeeded in answering this question by calling our attention to the following two facts. First, radical species R-**I** and R-**II** are also formed as a result of extension and rupture of the C–Br bond, although this scheme requires smaller energy than does heterolytic dissociation. Second, electrophilic power of a species increases in parallel with the degree of extension of the C–nucleofuge bond. From the latter statement it follows that the degrees of extension of the C–nucleofuge bond in monohaloalkanes **IX** and the C–Br bond in dibromide **I** should be different. The extension of the C–nucleofuge bond in **IX** should be greater since dibromide **I** contains two γ-alkoxy substituents (one of which also possesses a β-bromine atom) hampering heterolytic dissociation. Therefore, ion pair derived from dibromide **I** should be less electrophilic than that formed from haloalkanes **IX**. We can state that ion pair **IA**-IP_l undergoes one-electron oxidation just because it is less electrophilic than ion pairs derived from **IX**. Presumably, this is the reason why the latter are capable of effecting two- rather than one-electron transfer (transfer of anionic ligand), which is interpreted as nucleophilic substitution.

In fact, even γ-haloalkyl ethers react mainly according to the electrophilic substitution pattern (see above) under conditions less favorable for heterolysis (in a concentrated solution of a base), whereas monohaloalkanes **IX** which are more prone to heterolytic dissociation give rise to electrophilic ion pairs under more favorable conditions. This also follows from the fact that base-catalyzed alkylation of β-dicarbonyl compounds with haloalkanes **IX** is sometimes accompanied by formation of dialkylated products in an amount comparable to the monoalkylated product [25, 26].

Although it is difficult to disagree with the above stated, we cannot believe it to answer the raised questions. The reason is that the assumption involving formation of **IA**-IP_l ion pair with reduced electrophilicity contradicts the Pauling principle which implies ionic character of

a chemical bond [27, 28]. Here, the main point is the following. Although the sodium atom in the O–Na fragment possesses a greater positive charge (+2.51), it induces lesser extension of the C–Br bond (interaction *b*) than does the N–H proton which bears a charge of +0.84 (the ionic orders of the O–Na and N–H bonds are 2.51 and 0.84, respectively). Estimation of atomic charges in chemical bond ionic character units (hereinafter, c.b.i.c.) can be regarded as valid, for these values correlate with those determined by electronic spectroscopy [28]. In addition, a direct relation was revealed between the charges on atoms in the reagent and degree of extension of the C–nucleofuge bond in the substrate [17–20]. Therefore, to draw a final conclusion on the nature of this anomaly it was necessary to elucidate (1) whether such reduction in atomic properties is possible or not and (2) if it is possible, why it is observed for the enolate sodium atom of β-dicarbonyl compounds and not for its unidentate analogs?

We have succeeded in answering these questions. First, we have succeeded in findings arguments in support of the possibility of the presumed effect and, second, we have succeeded in demonstrating that this effect results from the well-known intramolecular donor–acceptor interaction [8, 11–13] which in the given case occurs between the sodium cation and carbonyl oxygen atom of enolate **VII** (intramolecular interaction *c*). Analogous influence (reduction of the acceptor power of, e.g., aluminum atom in alanes) is observed even in going from a solution in benzene to more basic diethyl ether [18, 29]. This effect is so strong that it leads to complete inversion of stereoselectivity in the addition of alane at the carbonyl group (88 : 12 against 17 : 83). It is assumed that analogous reduction of the acceptor power of the enolate sodium atom precedes its contact with bromine electrons at the C–Br bond (RONa···Br···NaOC=C). There are published data on a wide variety of molecules which are characterized by a similar solvent effect on the behavior of other metal atoms [5–10, 26].

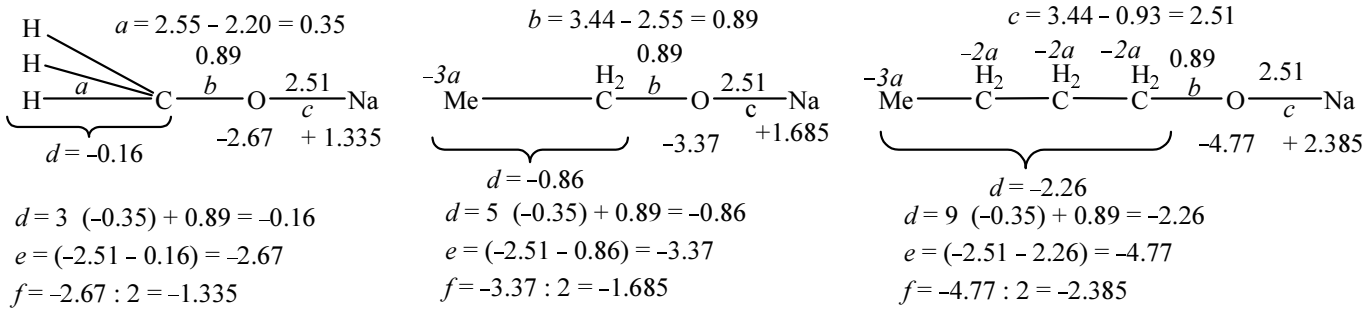
The conclusion is obvious: the reason for one-electron oxidation of enolates **VII** is not electrophilicity alone but the reduced electrophilicity of ion pair **IA** due to low degree of heterolysis of the C–Br bond in dibromide **I**. If the proposed version correctly describes the nature of driving forces governing the behavior of dibromide **I**, increase in the ability of the medium to favor heterolytic dissociation (e.g., by raising its polarity) should change the reaction direction (chemoselectivity). However, contrary to expectations, replacement of ethanolic sodium ethoxide by a more polar reagent, a solution of sodium hydroxide in ethanol (in essence, by sodium hydroxide and water) gave no desired result. Under these conditions, dibromide **I** almost failed to react and was recovered from the reaction mixture.

Seemingly, this failure indicates that the problem could not be solved with the use of a base in which the counterion is sodium. This also follows from published data according to which the polarity of alcohols (and hence of the corresponding alkoxides) decreases within a homologous series [30]. By contrast, a radically different solution results from the new version of organic reaction mechanisms [16–20]. In the framework of this version, the positive charge on the sodium atom in an alkoxide group and therefore its ability to favor heterolytic dissociation increase rather than decrease within a homologous series. This information is usually revealed starting from determination of local polarity which, according to the electronegativities of atoms [17, 18, 27, 28], is induced by hydrogen and oxygen atoms on each carbon atom of the alkoxide group. It is assumed that the induced polarity (charges on atoms are expressed in c.b.i.c. units) is then transmitted along the atom chain toward the most electronegative atom of a functional group. This effect can be estimated on a semiquantitative level if the algebraic sum of charges induced on each atom in the chain is used as a measure of polarity (Scheme 2). In order to simplify the calculation, the loss in the polarity with increase in the distance from a bond to the reaction center (functional group) is neglected. Scheme 2 shows an appreciable increase of the electron-donor power of the alkyl group in the given alkoxide series ($-0.16 < -0.86 < -2.26$ for methyl, ethyl, and butyl, respectively). As this polarity is transmitted to the oxygen atom, we obtain a "refined" series of ionic characters of the O–Na bonds (or charges on the sodium atom in c.b.i.c. units; $1.335 < 1.685 < 2.385$) against the basis value equal to 2.51.

The application of such a simple (and inaccurate) procedure for estimation of the ionic character of a chemical bond and atomic charge is justified by the facts that the obtained results are confirmed by other data [28] and that they possess a predictive power [16–20]. Therefore, we presumed that the difference between the acceptor powers of sodium butoxide and sodium ethoxide (2.385 against 1.685 c.b.i.c. units) is too large to ensure dehydrobromination–alkylation of dibromide **I** even with β-dicarbonyl compounds.

These theoretical predictions turned out to be valid. In the reaction of dibromide **I** with diethyl malonate in a solution of sodium butoxide in butyl alcohol we observed

Scheme 2. Estimation of the acceptor power (charge, in c.b.i.c. units) of the sodium atom in sodium methoxide, ethoxide, and butoxide



$d = 3\ (-0.35) + 0.89 = -0.16$
$e = (-2.51 - 0.16) = -2.67$
$f = -2.67 : 2 = -1.335$

$d = 5\ (-0.35) + 0.89 = -0.86$
$e = (-2.51 - 0.86) = -3.37$
$f = -3.37 : 2 = -1.685$

$d = 9\ (-0.35) + 0.89 = -2.26$
$e = (-2.51 - 2.26) = -4.77$
$f = -4.77 : 2 = -2.385$

a, *b*, and *c* are the initial ionic characters of bonds and charges (in c.b.i.c. units) estimated from the tabulated electronegativities of the hydrogen (2.20), carbon (2.55), and oxygen atoms (3.44) [27, 28]; *d* is the total charge induced on the carbon atom of the C–O bond by the oxygen atom and hydrogen atoms of the entire alkyl group; *e* is the total charge induced by the alkyl group and sodium atom on the oxygen atom; and *f* are the average (refined) charges on the sodium atom in alkoxides.

formation of cross coupling products as a mixture of diethyl and dibutyl malonates **IIIa** and **IIIb** at a ratio of 1 : 9 with an overall yield of ~90%.

Finally, let us consider driving forces which control chemoselectivity in a reaction medium consisting of numerous molecules and ion pairs. The problem is that transformations of these species follow paths contradicting traditional concepts of organic chemistry. For example, what is the reason for the fact that the reaction in a medium consisting of an alcoholic solution of a haloalkane, β-dicarbonyl compound sodium salt, and sodium alkoxide involves enolate derived from the β-dicarbonyl compound rather than alkoxide? This is the riddle which has not been solved so far. At best, attempts were made to reveal some relations for particular classes of molecules but not for the phenomenon as a whole [31].

Despite the apparent complexity of the problem, it can be solved fairly simply on the basis of the above stated principles. In this respect, the most important information is obtained from the statement that a chemical reaction occurs only when the affinity of a reagent exceeds the force preventing rupture of the electrofuge–nucleofuge bond in a substrate [32]. Otherwise, the interaction stops at the stage of formation of a metastable donor–acceptor complex like DAC-**IA** which occurs in equilibrium with the initial reactants. Analysis of numerous data [5–10, 23–26] (including those given above) led us to the following simple rules. Let us consider these rules as applied to reactions where the reagent is an electrophile.

First, reactions of an electrophile (reagent), regardless of its power, always begin with attack on an electron donor possessing the highest electron density. Therefore, when a reaction mixture consisting of ethanol, sodium ethoxide, and enolate derived from a dicarbonyl compound gives rise to an electrophilic ion pair, the latter necessarily attacks the alkoxide oxygen atom (i.e., oxygen atom in the C–O–Na fragment). None of the other atoms in molecules present in the reaction medium, including the enolate oxygen atom (see above) possesses such electron density. If a reagent is capable of overcoming counteraction of substrate atoms (i.e., of the sodium and C–O–Na carbon atoms in sodium ethoxide), a new chemical bond is formed (in our case, with the oxygen atom). Only when electron transfer from the oxygen atom to an atom in the reagent becomes impossible, either decomposition of the complex occurs or the reaction center in the reagent undergoes reorientation (certainly, the affinity of the reagent weakens upon complex formation) toward other electron donors. The direction of attack by the "weakened" reagent is determined by decreasing power of electron donor. Therefore, the next electron-donor center to which the attack by the reagent is directed (interaction *e*) is *p* electrons of the enolate oxygen atom (C=C–O–Na). In other words, the contact of the reagent with electron-rich reaction center is completed not by automatic replacement of the metal by electrophile but only by formation of a donor–acceptor complex like DAC-**IA**, as was shown with **IA**-IP_1 as an example. If this interaction is not completed by electron transfer as well, the electrophilic center is reoriented again (predominant interaction *f* in DAC-**IA**) toward energetically more accessible electrons of the neighboring group, in our case toward *p* electrons of the C=C bond; a new stage of comparison of the reagent and substrate powers begins until charge deficit on the reagent be eliminated via for-

mation of a stable molecule. In the given series of electron donors, the greater ability of *p* electrons of the C=C bond to undergo cleavage results from the fact that the ionic character of this bond is entirely determined by a small difference in the electronic properties of its atoms due to effect of substituents.

Nevertheless, difficulties appear even in the transfer of such electrons of substrate to reagent. As shown above, these difficulties arise in the case of weak but not strong electrophiles. For that reason, the power of ion pairs derived from haloalkanes **IX** is sufficient to ensure two-electron transfer and formation of a new bond with participation of both oxygen atom (O-alkylation products) and carbon atom of the enolate moiety. This factor is also responsible for the fact that O-alkylation occurs just with those electrophiles in which the maximal extenstion of the C–nucleofuge bond is achieved [11–13, 25, 26]. For example, acid chlorides, α-chloro ethers, chlorosilanes, and other related reagents, in which the electrofuge–nucleofuge bond undergoes heterolytic dissociation especialy readily, give rise mainly (or almost exclusively) to O-alkylation products. This also follows from the data on the regiochemistry of molecules affording radical nucleophilic substitution reaction [5–10]. For instance, the alkylation of 2-nitropropane sodium salt with *p*-nitrobenzyl chloride gives C- and O-alkylation products (92 and 6%, respectively), while an analogous reaction with benzyl chlorides having no electron-acceptor nitro group leads to almost exclusive formation of O-alkylation products [33].

The general applicability of the proposed approach and its use in the solution of other theoretical and synthetic problems will be reported elsewhere.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrophotometer in mineral oil. The ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury-300 spectrometer (300 MHz for ^{1}H) from solutions in DMSO-d_6–CCl_4 (1 : 3) using TMS as internal reference.

1,1,2,2-Tetrakis(ethoxycarbonyl)ethane (IVa). Diethyl malonate, 13 g (0.081 mol), was gradually added to a solution of sodium methoxide prepared by standard procedure from 15 ml of anhydrous ethanol and 1.85 g (0.08 mol) of metallic sodium. The mixture was stirred for 15 min and heated to 70–75°C, and 5.2 g (0.02 mol) of 3,4-dibromo-4-methyltetrahydropyran was added over a period of 1.5 h to the resulting suspension. The mixture was stirred for 5 h at that temperature, about 10 ml of ethanol was distiled off, and the residue was cooled, neutralized with hydrochloric acid, and extracted with diethyl ether. The extract was dried over Na_2SO_4, the solvent was distilled off, and the product was distilled under reduced pressure. Yield 4.2 g (70.5%), bp 125–133°C (1 mm). The product solidified on storage to form colorless crystals with mp 74–75°C. ^{1}H NMR spectrum, δ, ppm: 1.27 t (12H, J = 7.1 Hz), 3.93 s (2H), 4.17 q (8H). ^{13}C NMR spectrum, δ_C, ppm: 13.4 (Me), 50.6 (CH), 60.9 (CH_2), 165.8 (C=O). The product was identical to a known sample [34]. In addition, from the low-boiling fraction we isolated 4-methyl-3,6-dihydropyran, bp 114–116°C (680 mm).

3,4-Diacetyl-2,5-hexanedione (IVb). The reaction was carried out following the above procedure with the use of 1.85 g (0.08 mol) of sodium, 8 g (0.08 mol) of acetylacetone, and 5.2 g (0.02 mol) of 3,4-dibromo-4-methyltetrahydropyran. Yield 2 g (50.5%). bp 120–122°C (18 mm). The product solidified to give colorless crystals with mp 192–193°C. ^{1}H NMR spectrum, δ, ppm: 1.99 s (12H), 12.74 s (2H). ^{13}C NMR spectrum, δ_C, ppm: 22.81 (Me), 191.66 (C=O). The product was identical to that described in [35].

3-Bis(ethoxycarbonyl)methyl- and 3-bis(butoxycarbonyl)methyl-4-methyl-3,6-dihydro-2*H*-pyrans IIIa and IIIb. A solution of sodium butoxide in 1-butanol was prepared from 40 ml of 1-butanol and 3.68 g (0.16 mol) of metallic sodium at 100°C. The solution was cooled to 50–60°C, and 13 g (0.081 mol) of diethyl malonate was addede. The mixture was stirred for 15 min, heated to 70–75°C (the mixture became homogeneous), and 10.4 g (0.04 mol) of 3,4-dibromo-4-methyltetrahydropyran was added dropwise over a period of 25 min. The mixture was stirred for 5 h at that temperature, cooled, neutralized with hydrochloric acid, and extracted with ether. The extracts were washed with water and dried over sodium sulfate, the solvent was removed, and the residue was distilled under reduced pressure, a fraction boiling in the temperature range from 160 to 175°C (3 mm) being collected (about 16 g). Repeated fractional distillation of that fraction gave 11.1 g (88.9%) of a product with bp 168–175°C (3 mm) which, according to the ^{1}H NMR data, was a mixture of 3-bis(ethoxycarbonyl)methyl- and 3-bis(butoxycarbonyl)methyl-4-methyl-3,6-dihydro-2*H*-pyrans **IIIa** and **IIIb** at a ratio of 16:84.

Ester **IIIa**. ^{1}H NMR spectrum, δ, ppm: 0.94 t and 0.95 t (6H, C**H**$_3$CH$_2$, J = 7.3 Hz), 1.31 m and 1.45 m (4H, CH$_3$C**H**$_2$, CH$_2$), 1.54–1.66 m (4H, CH$_3$C**H**$_2$, CH$_2$),

1.69 q (3H, =CCH$_3$, J = 1.9 Hz), 2.55 br.s (1H, =CCH), 3.51 d (1H, O=C–CH–C=O, J = 6.0 Hz), 3.84–4.17 m (8H, OCH$_2$), 5.48 br.s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 13.1 (CH$_3$); 21.3 (=C**C**H$_3$); 18.4, 29.8, and 29.9 (CH$_2$, ester); 64.1 and 64.1 (OCH$_2$, heteroring); 64.7 and 65.3 (OCH$_2$, ester); 123.0 (=CH); 130.9 (Me**C**=C); 167.0 and 167.9 (C=O).

Ester **IIIb**. ^{1}H NMR spectrum, δ, ppm: 1.24 t and 1.27 t (6H, C**H**$_3$CH$_2$, J = 7.1 Hz), 1.69 q (3H, =CCH$_3$, J = 1.9 Hz), 3.51 br.s (1H, =CCH), 3.55 d (1H, O=CCHC=O, J = 3.4 Hz), 3.84–4.17 m (8H, OCH$_2$), 5.48 br.s (1H, =CH).

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