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PARTICIPATION OF THE ClO_4^- ANION IN ADDITION REACTIONS OF ArSCl AND HALOGENS WITH UNSATURATED DERIVATIVES OF TRICYCLO[4,2,2,$0^{2,5}$]DECANE. SYNTHESIS OF STABLE COVALENT PERCHLORATES

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Abstract—New reactions, halogenoperchloration and arylsulfenylperchloration of olefins of the tricyclo[4,2,2,$0^{2,5}$]decane series are described. Stable covalent perchlorates have been isolated in pure form in these reactions. Some important mechanistic and stereochemical features of these processes are discussed.

Few methods exist for the preparation of covalent esters of perchloric acid.[1-3] The most useful involves the nucleophilic substitution reaction of an alkyl iodide with silver perchlorate.[1-2] Several secondary alkyl perchlorates have been obtained via addition of $HClO_4$ in the presence of H_2SO_4 to unbranched olefins, which have been used either as such or generated *in situ* from the corresponding secondary alcohols.[4] The main disadvantages of this synthetic approach are the formation of the mixture of isomeric perchlorates and difficulties in purification and isolation of the products. The synthesis of perchlorates has also been achieved by the reaction of dichlorine heptoxide with alcohols.[5]

It is not surprising that little is known about the chemical properties of the esters of $HClO_4$ because of their extremely explosive properties.[1-3,6] In most cases covalent perchlorates have not actually been isolated and analysed in pure form with one exception, the relatively stable sulfonylmethyl perchlorates, $RSO_2CH_2OClO_3$,[7] the structure of one of them being proved by X-ray diffraction.[8] We should emphasize that the stability of this type of perchlorates was due to stabilizing substituents. Organic covalent perchlorates, in contrast with their ionic counterparts,[2] have not received much attention despite the obvious theoretical and synthetic interest.

Our previous studies have shown that the course of the addition of ArSCl to olefins is drastically changed in the presence of strong electrolytes, e.g. $LiClO_4$. The addition of $LiClO_4$ to the reaction mixture leads to a strong increase of the effective electrophilicity of the electrophile and this addition reaction could be made to yield products typically formed in carbenium ion like processes.[9-17] This phenomenon, referred to as doping-addition, is of synthetic importance because it permits access to the products of the incorporation of external nucleophiles,[11,12] skeletal rearrangements,[10,11,13-15] and hydride shifts.[16] The amazing point of these investigations is the demonstration of the formation of covalent perchlorates in doping addition of ArSCl.[11,15,17] The covalent perchlorates of tetracyclo[6,1,1,$0^{2,7}$,$0^{5,10}$]decane and tetracyclo[5,3,0,$0^{2,5}$,$0^{3,8}$]decane systems are sufficiently stable to be isolated in pure form[11,17] and to determine for some of them melting points (!) and X-ray diffraction patterns.[18-21]

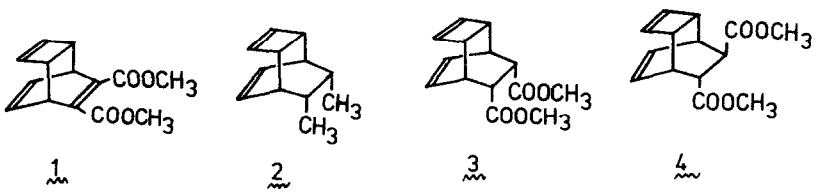
In this paper we describe in detail a new and facile preparation of relatively stable secondary perchlorates of some cage structures for a number of electrophilic additions (for preliminary communications see Refs. 17-22).

RESULTS

Taking into account our preliminary results[17-22] the present investigation has been carried out using the olefins **1-4** of the tricyclo[4,2,2,$0^{2,5}$]decane series as a model compounds. These readily available compounds contain two proximal unsubstituted double C=C bonds with sharply different reactivity. The structure of addition products to **1-4** depends on the electrophilicity of reagent: (i) weak electrophiles, including RSCl, interact with the cyclobutene double bond to give the trans-adducts;[23] (ii) the increase of reagent electrophilicity leads to the cross-type participation of the second double bond and in some cases is followed by 1,2-shift(s).[11,14,15] For the diester **3** the addition of strong electrophiles leads to δ-lactone closure after the cross-bonding step.[24] We have previously elaborated the criteria of structural and configurational assignment in these series[11] which have been of indispensable help for this study.

We have studied the addition of chlorine, bromine, iodine, 2-nitrobenzenesulfenyl (NBSC) and 2,4-dinitrophenylsulfenyl (DNBSC) chlorides in presence of variable amounts of $LiClO_4$ in non-nucleophilic solvents, namely in diethyl ether, ethyl acetate and methylene chloride. The former two solvents are able to dissolve $LiClO_4$ at 30° (up to 6 M concentration in Et_2O[25]). Usually the good results were obtained only under a large excess of $LiClO_4$ (up to 10 moles for 1 mol of reagents). Lithium perchlorate is scarcely soluble in CH_2Cl_2 (1.2×10^{-6} mol/l[26]) and we used its suspension for the addition processes. Reactions with iodine and sulfenyl chlorides were performed at 25°, those with chlorine and bromine at −78°.

The separation and preparative isolation of products have been performed using preparative tlc on silica gel following the procedure of Refs. 11 and 13. The processes were also monitored by tlc on silica gel: the perchlorates are conveniently detected by this method since the heating of the tlc plate induces a characteristic decay with formation of a black spot. The yields and product distribution are shown in Table 1.



1 2 3 4

Table 1. Reactions of compounds **1–4** with electrophilic agents and lithium perchlorate under various conditions

Olefin	Electrophilic agent	Solvent	Temp., °C	$LiClO_4$ mol-eq.	Reaction products (yield, %)
1	I_2	ether	25	16	5a(54)
	Br_2	ether	-78	16	5b(53), 7a(25)
	Cl_2	ether	-78	16	5c(26), 7b(41)
	I_2	CH_2Cl_2	25	2	5a(25)
	DNBSC	AcOEt	25	10	5d(26), 7c(31)
	DNBSC	CH_2Cl_2	25	2	5d(18), 6a(39)
	NBSC	ether	25	10	5e(47), 6b(16), 7d(8)
	NBSC	AcOEt	25	10	5e(76)
	NBSC	CH_2Cl_2	25	2	6b(54)
2	I_2	ether	25	10	8a(80)
	Br_2	ether	-78	10	8b(68)
	Cl_2	ether	-78	10	8c(35)
	DNBSC	ether	25	10	8d(89)
	NBSC	ether	25	10	8e(76)
3	I_2	ether	25	10	9a(35), 10a(37)
	Br_2	ether	-78	10	9b(46), 10b(41)
	Cl_2	ether	-78	10	9c(46), 10c(30)
	DNBSC	ether	25	10	9d(53), 10d(21), 11a(6)
	NBSC	ether	25	10	9e(53), 10e(18), 11b*
	NBSC	AcOEt	25	10	9e(83)
4	I_2	ether	25	10	12(6), 13(33), 14(17)

* This compound was contaminated with some other unidentified perchlorates (see Experimental).

Addition to triene **1**. Reaction of triene **1** with iodine and $LiClO_4$ in ether at 25° proceeds smoothly to give the iodoperchlorate **5a** as a major product. Its structure (including the proof of covalent bonding of $OClO_3$ group with the skeleton) has been unambiguously determined by X-ray diffraction.[18] ^1H NMR spectrum of **5a** contains the signals of seven skeletal protons at δ 2.3–3.7 ppm, two singlets of OCH_3 groups and characteristic low field doublet of H–$COClO_3$ proton at δ 5.0 ppm (J = 6.3 Hz). Previously we have shown that this value of coupling constant corresponds of the *endo*-configuration of substituent at C^6.[11] The same reaction in CH_2Cl_2 proceeds analogously but more slowly and the yield of **5a** is substantially reduced.

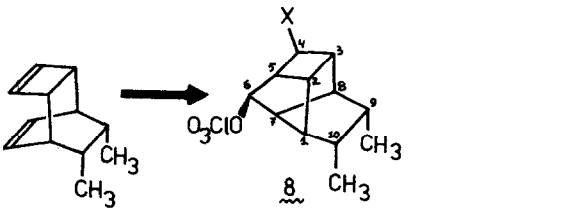
Reactions of triene **1** with chlorine and bromine and $LiClO_4$ in ether proceed very rapidly even at −78° to give a mixture of two major products, corresponding halogenoperchlorates **5b** and **5c** and dihalogenides **7a** and **7b**. The structure of perchlorates **5b** and **5c** have been supported by ^1H NMR spectra, which contain the signals of H–CHal protons at δ 3.9–3.8 ppm and low field quadruplet of H–$COClO_3$ proton near δ 5 ppm (J_1 = 6.2–6.4 Hz and J_2 = L ~ 1 Hz) which indicates the *endo*-configuration. The dihalogenides **7a** and **7b** have the skeleton of tetracyclo[4,4,0,$0^{2,4}0^{3,7}$]decane: the structure of **7a** has been definitely determined by X-ray analysis,[22] and the structure of **7b** has been elucidated on the basis of the pictoral resemblance of its ^1H NMR spectrum with that

of **7a**. Indeed their spectra contain three upfield signals of cyclopropane rings at 1.7–2.1 ppm, narrow multuplet of H–C^5-Hal at 4.2 ppm and low field doublets (δ 5.3 ppm, J = 5.4 Hz) of allylic H–C^{10}-Hal proton (see data of Ref. 11 and 27).

Let us consider now the reactions of triene **1** with arylsulfenyl chlorides in presence of $LiClO_4$. In contrast with reactions with halogens these additions proceed relatively slow (24–48 hr) the product ratio being sharply dependent on a solvent. We have not succeeded in isolating any product from the complex mixture when the reaction of **1** with DNBSC was performed in ether. In ethyl acetate the addition of DNBSC proceeds to give *endo*-perchlorate **5d** (26% yield) and rearranged chloride **7c** (31% yield). Their structures have been established by ^{1}H NMR in accordance with previously discussed data for **5a–c** and **7a–b**. However this addition in CH_2Cl_2 proceeds with formation of a mixture of the epimeric *endo* (**5d**) and *exo* (**6b**) perchlorates in 1:2 ratio (configurational assignment *vide infra*).

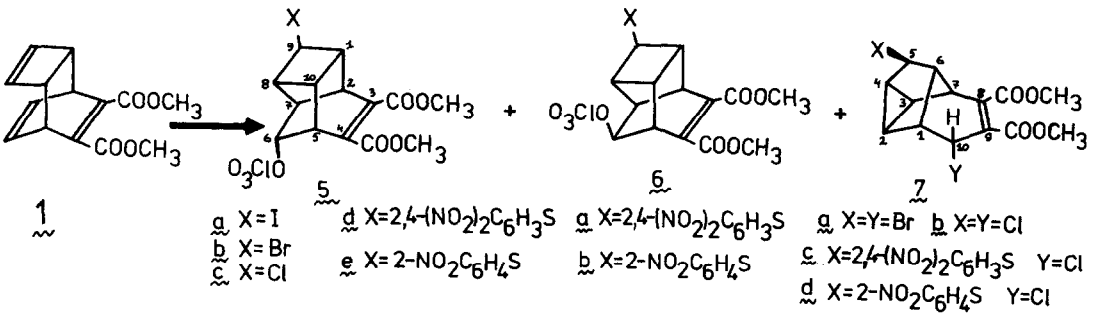
The reaction of triene **1** with NBSC in ether in presence of 10 mol of $LiClO_4$ gave the mixture of epimeric perchlorates **5e** and **6b** (3:1) which have been separated and isolated (total yield 60%, TLC indicates also the formation of traces of **7d**). Decreasing the amount of $LiClO_4$ (to 1 mol) leads to increase in the relative content of *exo*-epimer **6b**. Stereoselectivity of NBSC addition to triene **1** may be regulated by the proper choice of the solvent. Indeed this reaction in ethyl acetate proceeded to give 76% of *endo*-perchlorate **5e**. In contrast, this reaction in CH_2Cl_2 gave epimeric *exo*-perchlorate **6b** with 50% yield.

Addition to diene **2**. The additions of electrophiles in presence of $LiClO_4$ proceed more rapidly and at lower temperatures, compared with triene **1**. With exclusion of the chloroperchloration reaction, tlc indicates for all the cases the formation of a single product, which can be isolated and purified by crystallization (Table 1). All perchlorates of this series are relatively less stable during storage or chromatography on silica gel. Nevertheless we have been able to obtain sufficiently good analytical data for **8a**, **8b** and **8d**. We could not isolate the perchlorate **8c** in a pure form and its yield has been determined by ^{1}H NMR.



2 **8**

a X=I d X=2,4-$(NO_2)_2C_6H_3S$
b X=Br
c X=Cl e X=2-$NO_2C_6H_4S$



1 **5** **6** **7**

a X=I d X=2,4-$(NO_2)_2C_6H_3S$ a X=2,4-$(NO_2)_2C_6H_3S$ a X=Y=Br b X=Y=Cl
b X=Br
c X=Cl e X=2-$NO_2C_6H_4S$ b X=2-$NO_2C_6H_4S$ c X=2,4-$(NO_2)_2C_6H_3S$ Y=Cl
d X=2-$NO_2C_6H_4S$ Y=Cl

Configurational assignments to perchlorates **5e** and **6b** has been performed on the basis of their ^{1}H NMR spectra in accordance with previously discussed criteria.[11] The general pattern of the skeletal protons for these compounds at 2–4 ppm is very similar to that of the iodoperchlorate **5a**, the location and coupling of H–$COClO_3$ proton in epimeric perchlorates **5e** and **6b** being substantially different. The respective signal for epimer **5e** appears as a doublet at 5.0 ppm with J = 6.4 Hz which is in close analogy with the data for iodoperchlorate **5a**. The doublet signal of H–$COClO_3$ for the epimer **6b** is shifted up to 4.7 ppm with J = 2.5 Hz. These data clearly point to the *exo*-configuration of perchlorate group for epimer **6b** with the small coupling constant and *endo*-configuration for epimer **5e**, having a larger coupling constant.[11] The configurational assignment for the mixture of **5d** and **6a** has been achieved in a similar manner on the basis of $J_H{}^6$ value (6.2 Hz for **5d** and 2.5 Hz for **6a**).

The structures of two of the perchlorates, **8a** and **8d**, have been unambiguously proved by X-ray data.[20,21] These perchlorates have not the cross-bonded structure of type **5–7**, but the skeleton of tetracyclo [5,3,0,$0^{2,5}$,$0^{3,8}$]decane, the perchlorate group at C^6 being in *anti*-position in respect with the framework, relative to the electrophilic reagent (arylthiogroup or halogen atom). The structures of the other perchlorates of this series, **8b**, **8c** and **8e**, have been elucidated by ^{1}H NMR spectra by comparison with NMR data for perchlorates **8a** and **8d**. All show the same patterns of signals of skeletal protons and contain low field signal of H–$COClO_3$ proton at 5.1–5.4 ppm. Diagnostic criterion for the configurational assignment of this proton is again the coupling constant.[11] For all of these perchlorates this signal is a singlet which permits to assign to these compounds *anti*-configuration at C^6. In the case of *syn*-configuration of the substituent at C^6 the proton at this

centre appears in NMR spectrum as a doublet of doublets with J = 8.0–8.5 and 3.0–3.5 Hz.[11]

Addition to the dienes **3** *and* **4**. Diene **3** is the most readily available compound of the whole series of unsaturated derivatives of tricyclo[4,2,2,$0^{2,5}$]decane and hence the most fully investigated. It was mentioned above that electrophilic additions of strong electrophiles to diene **3** lead to the formation of δ-lactones.[24] To the best of our knowledge electrophilic addition to the *trans*-diester **4** has not been studied at all.

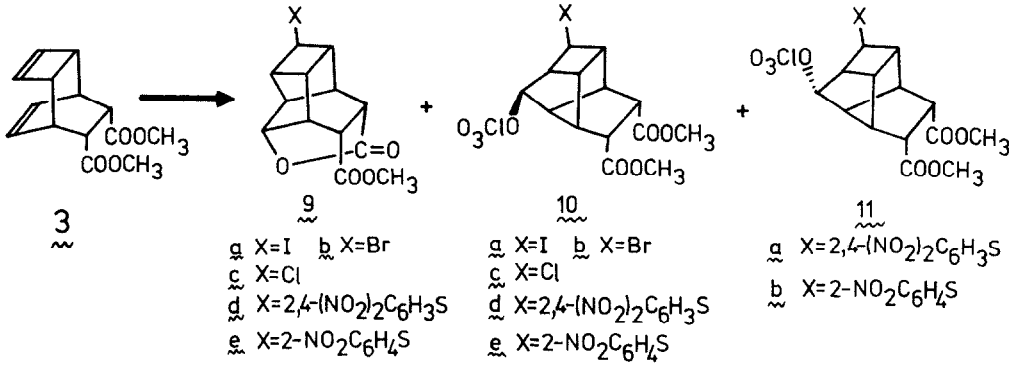
We have found that the addition of halogens to diene **3** in presence of a large amount of $LiClO_4$ in ether proceeds to give a 1:1 mixture of lactones **9a–c** and perchlorates **10a–c** with a total yield of 70–90%. The use of CH_2Cl_2 as a solvent gave worse results. The structure of lactones has been supported by comparison of IR and ^1H NMR data with previously prepared compounds of δ-lactone series, which structures have been elucidated unambiguously by X-ray diffraction.[24] The perchlorates **10a–c** are stable at room temperature, melt without decomposition, are inert to striking and explode only under rapid heating up to 200°. Their structures have been elucidated on the basis of ^1H NMR spectra, which contain two low field signals at δ5.2 ppm (H–$COClO_3$) and δ 3.8 ppm (H-CHal). The signals of skeletal protons (several multiplets at 2.0–3.4 ppm) have a good pictorial resemblance with the same part of ^1H NMR spectra of compounds **8a–e**. On this basis we suggest for these perchlorates **10a–c** the structures with skeleton of tetracyclo[5,3,0,$0^{2,5}$,$0^{3,8}$]decane and with *anti*-configuration of $OClO_3$ group.

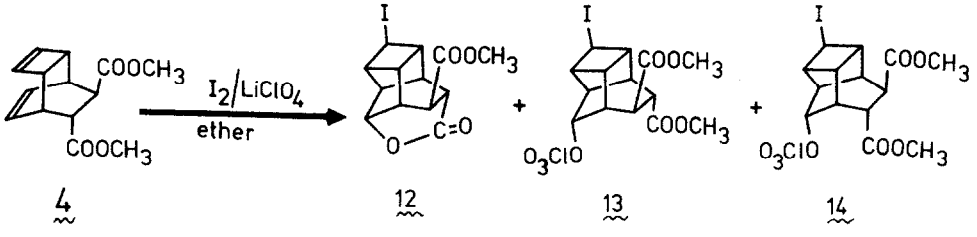
The reaction of diene **3** with DNBSC in presence of $LiClO_4$ in ether proceeds to give predominantly lactone **9d** and the 3:1 mixture of *anti* (**10d**) and *syn* (**11a**) perchlorates (see Table 1). The configurational assignments have been made on the basis of NMR spectra of these isomers in accordance with our previous data:[11] *anti*-isomer **10d** shows H^6 resonance as a singlet whereas this signal for *syn*-isomer **11a** appears as doublet of doublets with J = 8.0 and 2.5 Hz. Addition of NBSC to diene **3** in presence of $LiClO_4$ in ethyl acetate gave lactone **9e** as the main product and only traces of perchlorate **10e** identified by tlc. However the same addition in ether gave 71% of a mixture of **10e** and **9e**, the yield of the former being 18%. Reaction mixture contains also a small amount of an other perchlorate which has been identified as *syn*-perchlorate **11b** by NMR. Unfortunately it was contaminated with other perchlorates and was too unstable to be isolated. The structures of both isolated compounds **9e** and **10e** have been determined analogously by ^1H NMR spectra.

Preliminary study of the additions to diene **4** reveals rather more complex course of the reactions, and we have studied in detail only iodoperchloration of **4** in ether. The product ratio for this reaction is completely different from the one of the analogous addition to diester **3** (see Table 1). First, the δ-lactone **12** is a minor product, obtained with a yield of only 6%. After its separation by column chromatography the mixture of perchlorates (50%) was obtained. Partial crystallization of this mixture permitted the isolation of two perchlorates **13** and **14** in a pure form. Single crystal X-ray data for **13** revealed cross-bonded skeleton of tetracyclo[6,1,1,$0^{2,7}$,$0^{5,10}$]decane and *endo*-configuration of $OClO_3$ group.[19] Taking into account the ^1H NMR data for **13** and **14**, namely the close resemblance of skeleton and H-C^6 signals, we suggest for **14** analogous cross-bonded structure with *endo*-position of perchlorate group.

DISCUSSION

Before discussing the main results it is expedient to consider briefly the rationalisation of mechanistic pathways to grasp the structural features of the rearranged



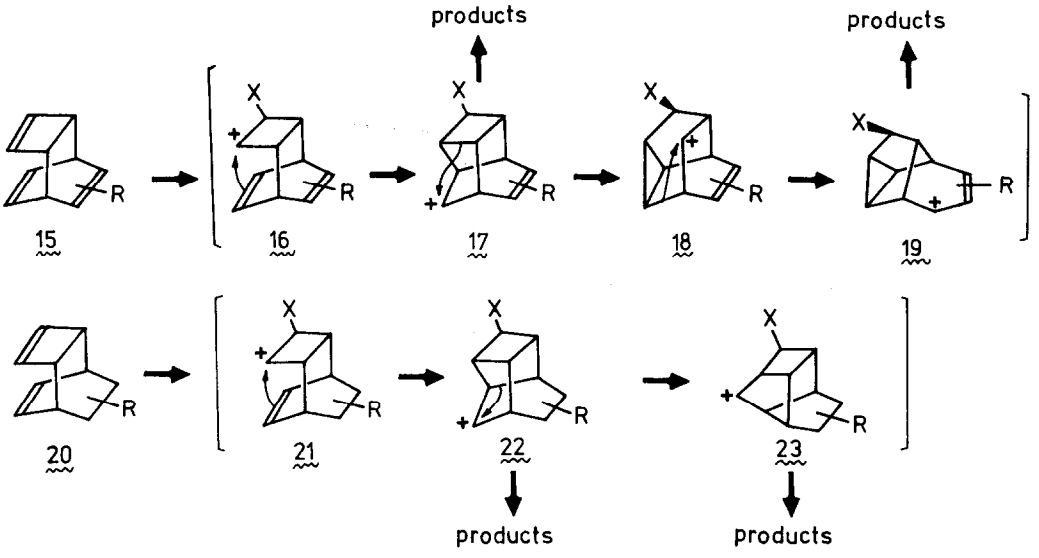


products. For the sake of simplicity we shall use the pictures of pure distinct carbocations for the illustration of pathways of skeletal rearrangements. All observed reactions include *exo*-attack of electrophiles on cyclobutene double bond, which results in a generation of transient positive charge and the participation of the second proximal double bond in a six-membered ring (**15**→**16**→**17** and **20**→**21**→**22**) and the transannular bond formation affording the cationic species of types **17** and **22**. Trapping by a nucleophile leads to final products of the tetracyclo[6,1,1,$0^{2,7}$,$0^{5,10}$]decane series. In the case of esters **3** and **4** there exists a chance to trap this carbocation by internal nucleophile, namely COOR group to give δ-lactones.[24] However this pathway is realized predominantly in the case of the former ester **3**. The formation of the products possessing the skeleton of tetracyclo[4,4,0,$0^{2,4}$,$0^{3,7}$]decane in the case of the triene **1** can be rationalized by the sequence **15**→**19** in accordance with our previous data.[11] This pathway also includes *exo*-attack on cyclobutene double bond, (**15**→**16**), cross-bond formation (**16**→**17**) and two subsequent 1,2-shifts of C_8–C_{10} and C_5–C_6-bonds affording the cationic species of type **18** and **19** respectively. The formation of the products possessing the skeleton of tetracyclo[5,3,0,$0^{2,5}$,$0^{3,8}$]decane from the species of type **22** involve 1,2 shift of C_2–C_7-bond affording the species of type **23**. The competition of these two rearranged pathways and structural factors determined it have also been discussed.[11] It is not well understood why the additions to diester **3** gave the rearranged perchlorates **10**, while iodoperchloration of diester **4** gave the cross-bonded perchlorates **13** and **14**. The presence of electron-withdrawing COOR groups must in principle hamper the 1,2-shift of the adjacent C–C bond; this phenomenon has been studied in detail for the norbornane[28] and 7-oxabicyclo[2,2,1]heptane[29–31] systems and rationalized in terms of electrostatic[32] interactions (see also orbital rationalization of the related long range effects[33]). However the position of COOR groups in **3** and **4** seems to be sufficiently far to exclude their influence. Anyhow the experiments show an easier occurrence of the skeletal rearrangement in the case of **3**.

The chief result of the present investigation is the demonstration that the formation of perchlorates (i) occurs for a number of typical electrophilic additions and (ii) represents major pathway of these additions. In other words our serendipitious discovery of perchlorate formation in electrophilic addition of ArSCl to olefins of tricyclo[4,2,2,$0^{2,5}$]decane series[11,15,17] receives the status of general phenomenon in this paper (see also Refs. 34 and 35). It is worth reminding that the addition of $LiClO_4$ to a reaction mixture is a generally accepted tool to increase the ionic power of media without danger of contamination with additional nucleophilic species. However the important result of the present work is that participation of ClO_4^- in the final step of the electrophilic addition takes place *in the presence of other more reactive nucleophilic species*, such as Cl^-, Br^- and I^- or even nucleophilic solvents (AcOH in our previous work[11,15,17]). This is in obvious contrast with the general accepted super-low nucleophilicity of the perchlorate anion.

It is well understood now that it is impossible to introduce the universal order of nucleophilicity[36] (e.g. using Swain-Scott equation[37]). In other words the order of nucleophilicity can be changed to the opposite one depending on the substrate (see for example, the orders of basicity, nucleophilicity in S_N2 and nucleophilicity in addition to C=O[38]) and the HSAB theory,[39] Edwards equation[40] and PMO consideration[38] are widely used as a guide line to explain the reactivity effects in nucleophilic reactions. In fact the ions ClO_4^-, AcO^- and Cl^- are altogether regarded as hard bases[39] (Cl^- is regarded sometimes as a borderline case), and the general HSAB approach seems to be too rough to divide their reactivity.

In our work concerning doping addition we presented proof for an ion pair mechanism for ArSCl addition,[9–13,16] elaborated the criteria of the involvement of



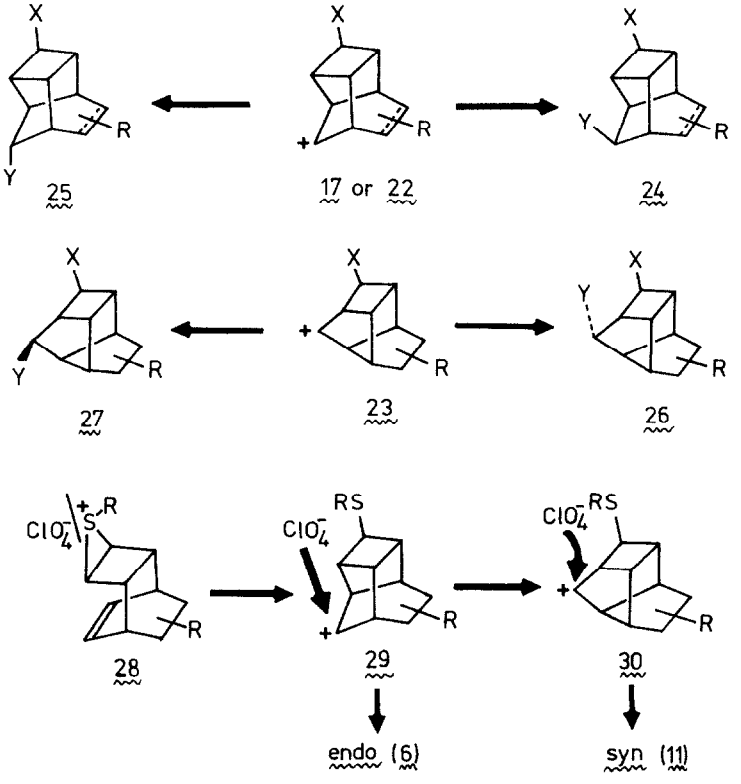
ion pair of different types and discussed in detail the chemical (including stereochemical) consequences of ion-pair mechanism.[10,11] Particularly it was shown that the involvement of ion-pair may lead to a different configuration of the products as compared with the attack by external nucleophile.[10,11,13] Hence, the stereochemistry of perchloration reactions and its variation depending on conditions need to be discussed.

Our previous investigations[11] clearly showed that the attack of the ions of type **17** or **22** by nucleophile may proceed in two ways either from *exo*-side to give *exo*-structure of type **24** or from *endo*-side to give *endo*-structure of type **25**, depending on the partial bonding of the nucleophilic and electrophilic moieties in an intermediate. The attack by *external* nucleophile leads to the *endo*-structure: in contrast the ion-pair mechanism including some sort of bonding of the counter ion Y with X framework in the intermediate leads to *exo*-attack at carbocationic center to give *exo*-adduct of type **24**.[11] Analogously, the attack of the ion of type **23** by an external nucleophile proceeds to give the addition products of type **27** with *anti*-configuration while the intermediacy of the ion-pairs leads to the *syn*-configuration (structure **26**).[11]

With two exclusions (reactions of triene **1** and diester **3** with ArSCl) the stereochemistry of all perchlorates obtained (*endo*-**5**, **13** and **14** and *anti*-**8** and **10**) shows that ClO_4^- plays role of the external nucleophile. One may regard these electrophilic additions as stepwise processes where the final step is an attack by ClO_4^- ion from the media. The great excess of lithium perchlorate added (doping condition, see Refs. 9–15) surrounds an intermediate, which leads to the stabilization of the positive charge in it, to a separation of counterion, which disappears in a solvent pool, as a result, to the highly polar intermediate, which is sufficiently "hot" to react in non-selective manner, even with super-low nucleophilic ClO_4^- ions. In other words, the general picture of these reactions is that in presence of a substantial concentration of $LiClO_4$ the formation of intermediate which behaves like more or less free ions (perhaps like ionic aggregates with lithium perchlorates) is indicated.

The stereochemistry of the additions of ArSCl to triene **1** is in apparent contrast with the one observed for all other additions, being drastically dependent on the solvent (see Table 1). The use of the nonpolar solvent, CH_2Cl_2, leads to a predominant (exclusive in the case of NBSC) formation of the *exo*-perchlorates **6**, while the application of more polar solvents gave *endo*-perchlorates.

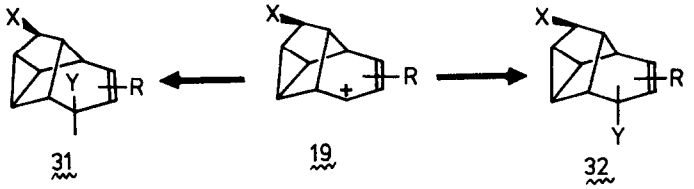
Two origins in principle may be accounted for this difference in stereochemistry of products. First, the formation of *exo*-epimers may be due to a side reaction of S_N2 type of *endo*-perchlorate with excess of $LiClO_4$ (*vide infra*). However, this explanation has to be rejected, because we especially demonstrated the absence of the epimerization process in the treatment of *endo*-perchlorate **5a** by $LiClO_4$. Second explanation associates this difference in stereochemistry of the addition products with ion pairing phenomena. In analogy with previous consideration of ion-pair mechanism[9–13] one may assume the formation of perchlorate ion-pair of type **28** (see Ref. 11) and then the attack at the incipient carbocationic centre by the ClO_4^- ion, incorporated in the structure of ion-pair **29** and **30**. Evidently, this pathway should lead to *exo*-perchlorate of type **24** and *syn*-perchlorate of type **26**. This ion pairing with ClO_4^- or the formation of some other type of ionic aggregates should



be more pronounced in CH_2Cl_2 as compared with more polar solvents. However, at present we have no indications whether or not the electrophiles are indeed still the halogen or ArSCl in the media with a large concentration of $LiClO_4$ and the mechanism of the perchlorate formation needs a special investigation. The investigation of the isotope exchange between ArSCl and labelled $LiCl^{35}$ in AcOH reveals its fast occurrence only in the case of DNBSC and NBSC; phenylsulfenyl chloride does not exchange its chlorine atom in these conditions.[41] These data indirectly support the possibility of the transient formation of highly reactive species of type RS^+/ClO_4^- or more complex ionic aggregates in the case of ArSCl used in the present work.

While for this particular study the side reaction of the formation of the compounds of type **7** is annoying, it is of considerable interest when considered by itself. Previously we have found that the rearranged products possessing the skeleton of tetracyclo[4,4,0,$0^{2,4}$,$0^{3,7}$]decane have the *exo*-configuration at C^{10} (e.g. formula **31**) *via* attack by external nucleophile. At the same time the halogenation products **7a–b** and products of chlorosulfenylation **7c–d** have the *endo*-position of the chlorine atom (see formula **32**). Hence, the configuration of the nucleophilic group for the compounds of the present study is the opposite as compared with the ones of the previous publications.[11,27] We suggest the following explanation for this observation: it is reasonable to accept the formation of the allylic perchlorate of type **31** (Y = $OClO_3$) with *exo*-configuration of perchlorate group in accordance with previous data as the one of the addition products. However, having allylic structure, this perchlorate has to be very reactive (much more than other perchlorate obtained) in nucleophilic substitution of S_N2 type by Cl^-. This process gives the inversion of configuration at C-10 leading to the compounds of type **32** (Y = Cl). We have found that the substitution of $OClO_3$ group in perchlorates of types **5**, **6**, **8** and **10** by halide or p-nitrophenylsulfonyl ion in acetone proceeds with the inversion of configuration. These data support S_N2 mechanism of substitution. These results will be published separately.

In conclusion it might be said that the present work together with our preliminary studies point out the surprising utility of lithium perchlorate as a reagent in electrophilic addition reactions.



EXPERIMENTAL

General. Melting points were determined with a micromelting point apparatus in open capillary tubes and are uncorrected. The NMR spectra were obtained in the indicated solvents on Varian ST-60 or Jeol XL-100 spectrometers. Tetramethylsilane was used as an internal standard and the chemical shifts are expressed in δ values. The IR spectra were taken with an UR-10 IR spectrophotometer as Nujol suspensions. Analytical and preparative thin layer chromatography was carried out using silica gel 5 × 40 or 40 × 100 or Silufol plates. Microanalyses were performed in the Laboratory of Microanalyses of the Moscow State University. The starting olefins were prepared according to Refs. 42 and 43 and purified by recrystallization.

Reactions of dimethyl tricyclo[4,2,2,$0^{2,5}$]*deca* - 3,7,9 - *triene* - 9,10 - *dicarboxylate* (**1**). (A) *With iodine in ether.* A mixture of triene **1** (0.3 g), lithium perchlorate (2.14 g) and iodine (0.51 g) in 5 ml of ether was stirred for 48 hr and washed with a saturated solution sodium thiosulfate (3 × 10 ml) and then with water (2 × 15 ml) and was dried (Na_2SO_4). The solvent was removed by evaporation and the oily residue was chromatographed on a silica gel column. Elution with 1:4 mixture of ethyl acetate–hexane gave **5a** (0.31 g), R_f 0.52, m.p. 117–118° (decomp); IR: 1725, 1710, 1637, 1610, 1290, 1270 and 1230 cm^{-1}; NMR (100 MHz, $CDCl_3$): 5.00 (1H, d, J = 6.3 Hz, H–$COClO_3$), 3.87 and 3.80 (6H, 2s, 2 $COOCH_3$), 3.70 (1H, dd, J = 6.4 and 5.4 Hz), 3.66 (1H, s, CHI), 3.39 (1H, m), 3.23 (1H, m), 2.90 (1H, m), 2.75 (1H, m), 2.36 (1H, m). (Found: C, 36.08; H, 3.10. $C_{14}H_{14}ClIO_8$ requires C, 35.58; H, 2.99%). X-ray data see Ref. 18.

(B) *With iodine in* CH_2Cl_2. Repeating this procedure in methylene chloride (5 ml) for 4 days gave perchlorate **5a** (0.15 g).

(C) *With bromine in ether.* A bromine (0.2 g) was added dropwise to the stirred solution of **1** (0.3 g) and lithium perchlorate (2.14 g) in ether (5 ml) at −78°. The mixture was kept at this temperature for 10 hr. Usual work-up as described in A gave the oil which was chromatographed on a silica gel column. Elution with 1:4 mixture of ethyl acetate–hexane gave **5b** (0.27 g) and **7a** (0.12 g).

For **5b**: R_f 0.28; m.p. 120°; IR: 1730, 1645, 1285, 1270, 1232 and 1220 cm^{-1}; NMR (100 MHz, $CDCl_3$): 4.96 (1H, dd, J = 6.2 and 1.0 Hz, H–$COClO_3$), 3.84, 3.80 and 3.77 (3s, 7H, 2 $COOCH_3$ and CHBr), 3.68 (1H, dd, J = 6.0 and 5.0 Hz), 3.34 (2H, m), 2.87 (1H, m), 2.74 (1H, m) and 2.37 (1H, m). (Found: C, 39.92; H, 3.40. $C_{14}H_{14}BrClO_8$ requires C, 39.51; H, 3.32%).

For **7a**: R_f 0.20; m.p. 155–157°; IR: 1730 and 1650 cm^{-1}; NMR (100 MHz, $CDCl_3$): 5.34 (1H, d, J = 5.4 Hz, C^{10}HBr), 4.21 (1H, dd, J = 1.8 and 1.4 Hz, C^5HBr), 3.87 and 3.81 (6H, 2s, 2 $COOCH_3$), 3.23 (1H, m), 2.61 (1H, m), 2.26 (1H, m) and 2.05–1.75 (3H, m). (Found: C, 41.30; H, 3.39. $C_{14}H_{14}Br_2O_4$ requires C, 41.41; H, 3.48%).

(D) *With chlorine in ether.* A solution of **1** (0.3 g) and lithium perchlorate (2.14 g) in ether (10 ml) were saturated with gaseous chlorine at −78° to appearance of stable yellow colaration. The usual treatment which was described in A gave the oil which was chromatographed on a silica gel column. The partial crystallization of fraction with R_f 0.8 from a 1:3 mixture of ether–hexane gave **5c** (0.12 g) and **7b** (0.16 g).

For **5c**: m.p. 123°; IR: 1740, 1653, 1290, 1267, 1240 and 1223 cm^{-1}; NMR (100 MHz, $CDCl_3$): 4.95 (1H, dd, J = 6.4 and 1.2 Hz, H–$COClO_3$), 3.89 (1H, s, CHCl), 3.84 and 3.78 (6H, 2s, 2 $COOCH_3$), 3.67 (1H, dd, J = 6.4 and 5.4 Hz), 3.38 (2H, m), 2.85 (1H, m), 2.66 (1H, m) and 2.34 (1H, m). (Found: C, 44.46; H, 3.76. $C_{14}H_{14}Cl_2O_8$ requires C, 44.12; H, 3.70%).

For **7b**: m.p. 145°; IR: 1728 and 1650 cm^{-1}; NMR (100 MHz, $CDCl_3$): 5.30 (1H, d, J = 5.4 Hz, C^{10}HCl), 4.17 (1H, dd, J = 1.8 and 1.5 Hz, C^5HCl), 3.84 and 3.80 (6H, 2s, 2 $COOCH_3$), 3.16 (1H, m), 2.64 (1H, m), 2.28 (1H, m), 2.07 (1H, m), 1.87 (1H, m) and 1.72 (1H, m). (Found: C, 52.98; H, 4.18. $C_{14}H_{14}Cl_2O_4$ requires C, 53.02; H, 4.45%). X-ray data see Ref. 22.

(E) *With DNBSC in* AcOEt. A solution of **1** (0.24 g), lithium

perchlorate (1.07 g) and DNBSC (0.24 g) in ethyl acetate (5 ml) was stirred for 24 h at room temperature, then washed with water (2 × 15 ml) and was dried (Na_2SO_4). The solvent was removed by evaporation and an oily residue was chromatographed on a column. Elution with 2:3 mixture ethyl acetate–hexane gave **5d** (0.14 g) and **7c** (0.15 g).

For **5d**: R_f 0.37; m.p. 151–153° (decompos.); IR: 1723, 1650, 1605, 1540, 1355, 1300, 1280, 1245 and 1230 cm^{-1}; NMR (60 MHz, $CDCl_3$): 9.0–7.2 (3H, m, C_6H_3), 5.0 (1H, d, J = 6.2 Hz, H–$COClO_3$), 3.87 and 3.77 (6H, 2s, 2 $COOCH_3$), 3.46 (1H, s, CHS) and 3.7–2.2 (6H, m). (Found: C, 43.93; H, 3.15; N, 5.17. $C_{20}H_{17}ClN_2O_{12}S$ requires C, 44.09; H, 3.14; N, 5.14%).

For **7c**: R_f 0.25; m.p. 195–196°; IR, 1755, 1720, 1650, 1610, 1530 and 1350 cm^{-1}; NMR (60 MHz, $CDCl_3$): 9.0–7.2 (3H, m, C_6H_3), 5.1 (1H, d, J = 5.8 Hz, CHCl), 3.73 (6H, s, 2 $COOCH_3$), 3.61 (1H, dd, J = 1.8 and 1.5 Hz, CHS) and 3.1–1.6 (6H, m). (Found: C, 49.95; H, 3.30; N, 6.35. $C_{20}H_{17}ClN_2O_8S$ requires C, 49.95; H, 3.56; N, 5.83%).

(F) *With DNBSC in* CH_2Cl_2. A mixture of **1** (0.49 g), DNBSC (0.47 g), lithium perchlorate (0.43 g) and methylene chloride (10 ml) was stirred for 3 days at room temperature. Usual workup as described in E gave **5d** (0.2 g) and **6a** (0.42 g), R_f 0.30; oil; IR: 1720, 1645, 1600, 1540, 1350, 1300, 1280, 1250 and 1235 cm^{-1}; NMR (60 MHz, $CDCl_3$): 9.0–7.3 (3H, m, C_6H_3), 4.8 (1H, d, J = 2.5 Hz, H–$COClO_3$), 3.92 and 3.87 (6H, 2s, 2 $COOCH_3$) and 3.6–2.5 (7H, m).

(G) *With NBSC in ether.* A solution of **1** (0.12 g), lithium perchlorate (0.55 g) and NBSC (0.095 g) in ether (2 ml) was kept for 10 h at room temperature. Usual work-up gave an oil which was chromatographed on a column. Elution with 1:3 mixture of ethyl acetate–hexane gave **5e** (0.12 g), **6b** (0.04 g) and **7d** (0.01 g).

For **5e**: R_f 0.27; m.p. 122–123° (decompos.); IR: 1735, 1650, 1600, 1525, 1350, 1290 and 1265 cm^{-1}; NMR (100 MHz, $CDCl_3$): 8.3–7.2 (4H, m, C_6H_4), 5.04 (1H, d, J = 6.4 Hz, H–$COClO_3$), 3.90 and 3.80 (6H, 2s, 2 $COOCH_3$), 3.75–3.30 (4H, m), 3.05 (1H, m), 2.75 (1H, m) and 2.35 (1H, m). (Found: C, 48.00; H, 3.47; Cl, 7.67; N, 3.04; S, 6.13. $C_{20}H_{18}ClNO_{10}S$ requires C, 48.06; H, 3.63; Cl, 7.09; N, 2.80; S, 6.41%).

For **6b**: R_f 0.23; m.p. 123–124° (decompos.); IR: 1735, 1650, 1600, 1530, 1345, 1287, 1270 and 1260 cm^{-1}; NMR (100 MHz, $CDCl_3$): 8.3–7.2 (4H, m, C_6H_4), 4.70 (1H, d, J = 2.5 Hz, H–$COClO_3$), 3.89 and 3.84 (6H, 2s, 2 $COOCH_3$), 3.55–3.35 (4H, m), 3.18 (1H, m), 2.84 (1H, m) and 2.48 (1H, m). (Found: C, 48.71; H, 3.64; Cl, 7.19; N, 2.87; S, 5.41. $C_{20}H_{18}ClNO_{10}S$ requires C, 48.06; H, 3.63; Cl, 7.09; N, 2.80; S, 6.41%).

For **7d**: R_f 0.2; NMR (60 MHz, $CDCl_3$): 8.3–7.1 (4H, m, C_6H_4), 5.15 (1H, d, J = 5.5 Hz, CHCl), 3.70 (6H, s, 2 CO_2CH_3), 3.60 (1H, m, CHS) and 3.1–1.6 (6H, m).

(H) *With NBSC in* AcOEt. A solution of **1** (0.24 g), lithium perchlorate (1.07 g) and NBSC (0.19 g) in ethyl acetate (10 ml) was kept for 24 hr at 25° and was chromatographed as described in G. This procedure gave **5e** (0.38 g).

(I) *With NBSC in* CH_2Cl_2. A mixture of **1** (0.24 g), lithium perchlorate (0.21 g) NBSC (0.19 g) and methylene chloride (10 ml) was stirred for 40 hr at room temperature, washed with water (20 ml) and dried (Na_2SO_4). The resulting solution was filtered through a thin silica gel layer. Removal of the solvent by evaporation and subsequent recrystallization from 2:1 mixture hexane–ethyl acetate gave **6b** (0.27 g).

Reactions of 9,10 - *cis* - *endo* - *dimethyl* - *tricyclo*[4,2,2,$0^{2,5}$]*deca* - 3,7 - *diene* (**2**). (A) *With iodine.* A solution of **2** (0.32 g), iodine (1.02 g) and lithium perchlorate in ether (10 ml) was held at room temperature for 1 hr. Removal of the solvent in *vacuo* afforded crystalline perchlorate **8a** (0.62 g), m.p. 100–102° (pentane); IR: 1265, 1242, 1228 and 1215 cm^{-1}; NMR (60 MHz, CCl_4): 5.12 (1H, s, H–$COClO_3$), 3.73 (1H, s, CHI), 3.35–1.70 (8H, m) and 0.9 (6H, m, 2 CH_3). (Found: C, 37.26; H, 4.15. $C_{12}H_{16}ClIO_4$ required C, 37.28; H, 4.17%). X-ray data see Ref. 21.

(B) *With Bromine.* Diene **2** (0.32 g) and lithium perchlorate (2.14 g) were dissolved in ether (10 ml) and bromine (0.31 g) was added at −78°. The usual work-up of resulting solution and subsequent recrystallization of solid residue from a 2:1 mixture hexane–ethyl acetate gave perchlorate **8b** (0.46 g), m.p. 82–83°; IR: 1298, 1260, 1240 and 1225 cm^{-1}; NMR (60 MHz, CCl_4): 5.11 (1H, s, H–$COClO_3$), 3.73 (1H, s, CHBr), 3.30–1.60 (8H, m) and 0.90 (6H, m, 2 CH_3). (Found: C, 42.02; H, 4.97. $C_{12}H_{16}BrClO_4$ requires C, 42.44; H, 4.75%).

(C) *With chlorine.* A solution of **2** (0.32 g) and lithium perchlorate in ether (10 ml) was saturated with gaseous chlorine at −78° to appearance of stable yellow coloration. The mixture was washed with water and was dried (Na_2SO_4). The evaporation of the solvent gave the perchlorate **8c** (0.21 g) as an unstable oil; R_f 0.23 (silufol, hexane); IR: 1290, 1270, 1243 and 1225 cm^{-1}; NMR (60 MHz, CCl_4): 5.17 (1H, s, H–$COClO_3$), 3.90 (1H, s, CHCl), 3.40–1.60 (8H, m) and 0.90 (6H, m, 2 CH_3).

(D) *With DNBSC.* A solution of diene **2** (0.32 g), DNBSC (0.47 g) and lithium perchlorate (2.14 g) in ether (10 ml) was held from −20° to 0° for 1.5 hr. The solution was washed with water (20 ml) and dried. The evaporation of solvent gave perchlorate **8d** (0.75 g), R_f 0.5 (ethyl acetate–hexane 1:4), m.p. 110–115° (decompos.); IR: 1600, 1520, 1340, 1280, 1260, 1240 and 1205 cm^{-1}; NMR (60 MHz, $CDCl_3$): 9.0–7.2 (3H, m, C_6H_3), 5.40 (1H, s, H–$COClO_3$), 3.30 (1H, s, CHS), 3.2–1.5 (8H, m) and 0.95 (6H, m, $2CH_3$). (Found: C, 46.63; H, 4.03. $C_{18}H_{16}ClN_2O_8S$ requires C, 47.12; H, 4.17%). X-ray data see Ref. 20.

(E) *With NBSC.* A solution of **2** (0.32 g), NBSC (0.38 g) and lithium perchlorate (2.14 g) in ether (10 ml) was held at −20° for 1 hr. The usual work-up gave perchlorate **8e** (0.63 g), R_f 0.6 (chloroform), m.p. 80° (decomp); IR: 1600, 1520, 1340, 1300, 1260, 1230 and 1220 cm^{-1}; NMR (60 MHz, $CDCl_3$): 8.4–7.0 (4H, m, C_6H_4), 5.3 (1H, s, H–$COClO_3$), 3.3 (1H, s, CHS), 3.3–1.6 (8H, m) and 1.0 (6H, m, 2 CH_3).

Reactions of dimethyl tricyclo[4,2,2,$0^{2,5}$]*deca* - 3,7 - *diene* - 9,10 - *cis* - *endo* - *dicarboxylate* (**3**). (A) *With iodine.* A mixture of **3** (0.49 g), iodine (0.76 g), lithium perchlorate (2.14 g) and ether (10 ml) was stirred at room temperature for 20 hr and then washed with a saturated solution of sodium thiosulfate. The solvent was removed by evaporation and the oily residue was adsorbed on a silica gel column and chromatographed. Elution with 2:3 mixture ethyl acetate–hexane gave **9a** (0.25 g), R_f 0.35, m.p. 152–155° (hexane)[44] and **10a** (0.35 g), R_f 0.53; m.p. 134–136°; IR: 1758, 1730, 1275 and 1230 cm^{-1}; NMR (100 MHz, $CDCl_3$): 5.26 (1H, s, H–$COClO_3$), 3.84 (1H, s, CHI), 3.69 (6H, s, 2 $COOCH_3$), 3.50 (2H, m), 3.1–2.7 (5H, m) and 2.29 (1H, t, J = 5.0 Hz). (Found: C, 35.30; H, 3.35. $C_{14}H_{16}ClIO_8$ requires C, 35.43; H, 3.40%).

Repeating this procedure in methylene chloride for 4 days gave **9a** (0.23 g) and **10a** (0.11 g).

(B) *With bromine.* Bromine (0.32 g) was added dropwise to the stirred solution of **3** (0.49 g) and lithium perchlorate (2.14 g) in ether (10 ml) at −78°. The mixture was kept at this temperature for 1 hr. Usual work-up gave an oily residue which was chromatographed on a silica gel column. Elution with ethyl acetate-chloroform (1:4) gave **9b** (0.29 g), R_f 0.62, m.p. 170–172°[44] and **10b** (0.35 g), R_f 0.83, m.p. 139–140°; IR: 1753, 1728, 1275 and 1230 cm^{-1}; NMR (100 MHz, $CDCl_3$): 5.21 (1H, s, H–$COClO_3$), 3.83 (1H, s, CHBr), 3.67 (6H, s, 2 $COOCH_3$), 3.35 (2H, m), 3.04 (1H, m), 2.90 and 2.84 (2H, 2s), 2.78 (1H, m), 2.68 (1H, m) and 2.20 (1H, t, J = 5.0 Hz). (Found: C, 39.16; H, 3.89. $C_{14}H_{16}BrClO_8$ requires C, 39.32; H, 3.77%).

(C) *With chlorine.* A solution of **3** (0.49 g) and lithium perchlorate (2.14 g) in ether (10 ml) was saturated with gaseous chlorine at −78° to appearance of stable yellow coloration. Usual work-up gave an oil which was chromatographed on a silica gel column. Elution with ethyl acetate–hexane, 2:3, gave **9c** (0.25 g), R_f 0.75, m.p. 178–180°[44] and **10c** (0.23 g), R_f 0.65; m.p. 121–122°; IR: 1750, 1730, 1275 and 1230 cm^{-1}; NMR (100 MHz, $CDCl_3$): 5.20 (1H, s, H–$COClO_3$), 3.76 (1H, s, CHCl), 3.64 (6H, s, 2 $COOCH_3$), 3.20 (2H, m), 3.0–2.6 (5H, m) and 2.09 (1H, t, J = 5 Hz). (Found: C, 44.04; H, 4.18. $C_{14}H_{16}Cl_2O_8$ requires C, 43.88; H, 4.21%).

(D) *With DNBSC.* A mixture of **3** (0.49 g), lithium perchlorate (2.14 g), DNBSC (0.47 g) and ether (10 ml) was stirred for 3 hr at room temperature, was poured into water (20 ml) and then was extracted with chloroform (100 ml). The evaporation of the solvent gave an oily residue. Preparative tlc on a silica gel plate (ethyl acetate–hexane 1:1) gave **9d** (0.46 g), R_f 0.25, m.p. 258–260°[24b], **10d** (0.23 g) and **11a** (0.14 g).

For **10d**: R_f 0.62; m.p. 151–155° (decomp); IR: 1750, 1730, 1610, 1540, 1360, 1290, 1280, 1260, 1250, 1230 and 1220 cm^{-1}; NMR (60 MHz, $CDCl_3$): 9.0–7.3 (3H, m, C_6H_3), 5.37 (1H, s, H–$COClO_3$), 3.6 (6H, s, 2 $COOCH_3$), 3.5–2.8 (8H, m) and 2.05 (1H, m). (Found: C, 44.46; H, 3.63. $C_{20}H_{19}ClN_2O_{12}S$ requires C, 43.92; H, 3.50%).

For **11a**: R_f 0.57; m.p. 134–136° (decomp); IR: 1745, 1600, 1530, 1350, 1270 and 1230 cm^{-1}; NMR (60 MHz, $CDCl_3$): 9.1–7.2 (3H, m, C_6H_3), 5.80 (1H, dd, J = 8.0 and 2.5 Hz, H–$COClO_3$), 3.7 (7H, m, CHS and 2 $COOCH_3$), 3.6–2.7 (8H, m) and 2.0 (1H, m). (Found: C, 44.00; H, 3.36. $C_{20}H_{19}ClN_2O_{12}S$ requires C, 43.92; H, 3.50%).

(E) *With NBSC.* A solution of **3** (0.49 g), NBSC (0.38 g) and lithium perchlorate (2.14 g) in ether (5 ml) was kept for 1 hr. Usual work-up gave the oily residue which was chromatographed on a silica gel plate. Elution with ethyl acetate–hexane (1:1) gave **9e** (0.41) g), R_f 0.1, m.p. 230–232°[24b] and **10e** (0.18 g), R_f 0.42; m.p. 110–112° (decomp); IR: 1750, 1650, 1610, 1530, 1350, 1270, 1250, 1220 and 1210 cm^{-1}; NMR (60 MHz, $CDCl_3$): 8.2–6.9 (4H, m, C_6H_4), 5.3 (1H, s, H–$COClO_3$), 3.6 (6H, s, 2 CO_2CH_3), 3.5–2.7 (8H, m) and 2.0 (1H, m). (Found: C, 48.10; H, 3.98. $C_{20}H_{20}ClNO_{10}S$ required C, 47.86; H, 4.02).

In this procedure an unstable oil (0.13 g) was obtained as a result of chromatography (R_f 0.33). This material contains mainly **11b** and traces of other unidentified perchlorates. For **11b**: NMR (60 MHz, $CDCl_3$): 8.3–7.0 (4H, m, C_6H_4), 5.90 (1H, dd, J = 8.5 and 3.0 Hz, H–$COClO_3$), 3.7 (7H, m, CHS and 2 $COOCH_3$), 3.6–2.7 (8H, m) and 2.0 (1H, m). Repeating this procedure in ethyl acetate gave **9e** (0.65 g).

Reaction of dimethyl tricyclo[4,2,2,$0^{2,5}$]*deca - 3,7 - diene - 9,10 - trans - dicarboxylate* (**4**) *with iodine.* A mixture of **4** (0.99 g), iodine (2.03 g), lithium perchlorate (4.28 g) and ether (20 ml) was stirred for 24 hr at room temperature and then was washed with a saturated solution of sodium thiosulfate then with water and was dried (Na_2SO_4) and stripped of solvent. The oily residue was adsorbed on a silica gel column and chromatographed. Elution with ethyl acetate–hexane, 1:2, gave **12** (0.08 g) and a mixture of the perchlorates **13** and **14** with R_f 0.58. Partial crystallization from a 1:3 mixture ether–hexane permitted to obtain **13** and **14** in a pure form and in a ratio 2:1.

For **12**: m.p. 184° (chloroform–hexane 1:2); IR 1775 and 1735 cm^{-1}; NMR (60 MHz, $CDCl_3$): 4.85 (1H, dd, J = 6.0 and 2.5 Hz), 3.82 (3H, s, $COOCH_3$), 3.69 (1H, s, CHI), 3.46 (2H, m) and 2.8–2.5 (6H, m). (Found: C, 43.25; H, 3.65. $C_{13}H_{13}IO_4$ requires C, 43.35; H, 3.64%).

For **13**: m.p. 127–128°; IR: 1750, 1738, 1270, 1250, 1220 and 1205 cm^{-1}; NMR (100 MHz, $CDCl_3$): 4.85 (1H, dd, J = 7.0 and 1.5 Hz, H–$COClO_3$), 3.77 (6H, s, 2 $COOCH_3$), 3.68 (1H, s, CHI), 3.50 (1H, m), 3.41 (1H, m), 3.19 (1H, m), 2.84 (3H, m), 2.63 (1H, m), 2.36 (1H, dd, J = 7.0 and 2.6 Hz). (Found: C, 35.48; H, 3.75. $C_{14}H_{16}ClIO_8$ requires C, 35.43; H, 3.40%). X-ray data see Ref. 19.

For **14**: m.p. 122–123°; IR: 1742, 1733, 1270, 1257, 1240 and 1207 cm^{-1}; NMR (100 MHz, $CDCl_3$): 4.90 (1H, dd, J = 7.1 and 1.6 Hz, H–$COClO_3$), 3.79 and 3.70 (6H, 2s, 2 $COOCH_3$), 3.62 (1H, s, CHI), 3.49 (1H, m), 3.36 (1H, m), 2.94 (3H, m), 2.64 (2H, m) and 2.50 (1H, dd, J = 7.0 and 3.0 Hz). (Found: C, 35.63; H, 3.60. $C_{14}H_{16}ClIO_8$ requires C, 35.43; H, 3.40%).

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