the formal triple bond are centered on both the N and S atoms. In contrast in NSF_3 these orbitals are localized on the nitrogen atom. In addition the nitrogen lone pair in NSF_3 is more strongly localized on the nitrogen atom than in NSF.

We wish to thank Prof. *R. N. Dixon* for communicating his results on NSF prior to publication.

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240. The Loss of CH_3COCH_2 Moieties from Methylketo Esters upon Electron Impact: A Discussion of Possible Long-Range Functional Group Interaction

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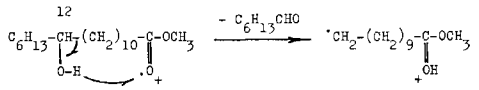
(3. VII. 72)

Summary. Methyl 10-oxoundecanoate and related long-chain methylketo esters exhibit loss of the terminal CH_3COCH_2 moiety as one of the most prominent modes of fragmentation in analogy to comparable long-chain diketones. In view of its absence in simple monoketonic analogues this process is thought to be induced by the distant ester function, e.g. *via* hydrogen abstraction from a suitable site (C(7)) within the alkyl portion of the molecule to be retained in the fragment. Rearrangement indicative of functional group interaction is thus concealed, and the attempt is made to unravel its incidence and true course by analysis of the further decomposition of the $(M - CH_3COCH_2)$ fragment *via* sequential losses of MeOH and CO, with the emphasis on establishing the origin of the —OH hydrogen of the former of these two particles. Extensive deuterium labelling of most of the positions of the central chain, as well as analysis of pertinent high-resolution data and metastable transitions, is employed in the pursuit of this objective.

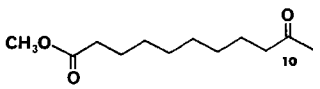
Introduction. – *Long-range interaction* of two functional groups within linear organic molecules frequently represents one of the more latent facets of mass spectrometric fragmentation, more amenable to conjecture by extrapolation from monofunctional compound behaviour than to experimental proof and elucidation. The occurrence of this phenomenon appears, however, to be the rule rather than the exception[1]). In few a instances, interaction of remote functions was readily recognized and

[1]) For leading references see *M. Sheehan, R. J. Spangler & C. Djerassi* [1].

explored in sufficient mechanistic detail, as exemplified by the ejection of a neutral $C_6H_{13}CH{=}O$ molecule[2]) from methyl 12-hydroxyoctadecanoate [3] *via* specific hydrogen transfer[3]) from the –OH group to the distant ester function:



Compared to such interaction directly reflected in the transfer of atoms between the neutral and the charged fragment concomitantly formed, *interaction by hidden rearrangement* within only one of these products is, quite naturally, subject to more uncertainty. This seems to be the case, *e.g.*, for various classes of bifunctional aliphatic compounds carrying exclusively carbonyl moieties such as oxo- and carboxyl groups, i.e. diketones, oxo- and di-carboxylic esters with sufficing chain-length and separation of their functionalities. The flexibility of the saturated carbon backbone and the pronounced reactivity of the oxygenated sites should indeed favour their interaction suspected since long [6]. The present work, using *methyl 10-oxoundecanoate* (I) as a typical representative of the class of oxo esters [7]–[10] [14], is an attempt to gain an insight into the mechanistic path along which keto- and ester functions of the ionized molecule can interact and thus alter the fragmentation behaviour commonly observed when these groups react as isolated sites[4]):



I

Indeed, inspection of the spectrum of I (Fig. 1) reveals a sequence of prominent fragmentation processes appearing, at a first glance, to be induced by participative interaction of the two functional groups: loss of the terminal CH_3COCH_2 moiety from the molecular ion[5]), highly uncommon in monoketones, is followed by sequential losses of neutral CH_3OH and CO molecules. The corresponding ions **A**, **B** and **C**, respectively, carry most of the ion current of the upper and medium mass range. Irrespective of whether this CH_3COCH_2 moiety is lost as an intact unit or as a combination of $CH_3/CH_2{=}C{=}O$ particles, formation of **A** corresponds to a β-cleavage with respect to the oxo-function (the charge remains at the non-ketonic portion of the molecule), and thus formally to a 'simple' C–C bond cleavage. Consequently, only

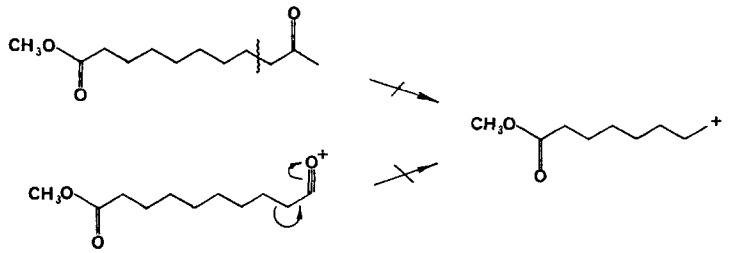
[2]) Whereas loss of RCH=O (not surprising since it results from a 'short range' *McLafferty* rearrangement) is abundant in 3-hydroxyalkanoates [2], it is, of course, totally absent in simple secondary alcohols, i.e. in absence of a carboxyl group functioning as a hydrogen acceptor.

[3]) Analogous processes are also observed upon replacement of the —OH hydrogen atom by Me_3Si- [4] and Me_2HSi- [5] substituents, enacting long-range transfer of even larger itinerant moieties.

[4]) Processes common to I *and* to its monofunctional analogues, namely simple aliphatic monoketones and fatty acid esters, are accordingly omitted in this discussion.

[5]) Similar losses of $RCOCH_2$ in general, and of CH_3COCH_2 in particular, have been observed in related classes of compounds of the type R- or $CH_3COCH_2(CH_2)_n$—X [6]–[13], and also ascribed to functional group interaction [6] [12] [13].

secondary decomposition of the arising fragment, *i.e.* the elimination of MeOH/CO (**A** → **B** and **B** → **C**), can be probed for evidence in favour of hidden rearrangement and thus against the unlikely operation of unassisted cleavage:



The results of this analysis, to be discussed in the following section, seem to be, to some degree, more inclined to discredit two simple mechanistic models of interaction entertained earlier [6], than to establish beyond all doubt one single and more complicated route compatible with the results. Deuterium labelling, being extensive, proves useful in this connection, but not quite sufficient to provide positive proof or disproof of the adopted more complex mechanistic rationale owing to the inherent uncertainties of isotope effect operation and hydrogen scrambling.

Results and Discussion. – In the subsequent study of the positional origin of the atoms lost in the formation of the ions **A**, **B** and **C**, three deuterated analogues of I have been employed, carrying labels symmetrically placed with respect to the oxygenated sites, C(1) and C(10). The spectra of these compounds, methyl 10-oxoundecanoate-3,3,8,8-d_4 (Ia), -4,4,7,7-d_4 (Ib) and -5,5,6,6-d_4 (Ic), which provide complete β-, γ- and δ-labelling as to either functionality and α-labelling *per exclusionem*, are reproduced in Fig. 2, 3 and 4, respectively:

$$CH_3OOC\text{–}CH_2\text{–}CD_2\text{–}(CH_2)_4\text{–}CD_2\text{–}CH_2\text{–}COCH_3 \quad \text{(Ia)}$$

$$CH_3OOC\text{–}(CH_2)_2\text{–}CD_2\text{–}(CH_2)_2\text{–}CD_2\text{–}(CH_2)_2\text{–}COCH_3 \quad \text{(Ib)}$$

$$CH_3OOC\text{–}(CH_2)_3\text{–}CD_2\text{–}CD_2\text{–}(CH_2)_3\text{–}COCH_3 \quad \text{(Ic)}$$

The spectra show for ion **A**, the (M – 57) fragment of I, full retention of label without exception. The corresponding shifts of **A** from *m/e* 157 to 161 in all three instances, together with pertinent high-resolution data[6]), clearly establish its $C_9H_{17}O_2$ (M – CH_3COCH_2) composition and rule out operation of reciprocal hydrogen transfer and

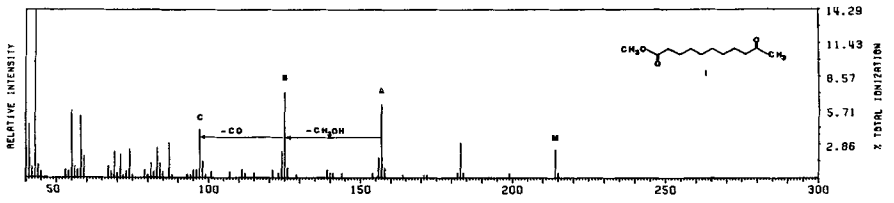


Fig. 1. *Mass Spectrum of Methyl 10-oxoundecanoate (I)*

[6]) The authors wish to thank Dr. *A. L. Burlingame* of the Space Sciences Laboratory of the University of California, Berkeley, for access to modern facilities.

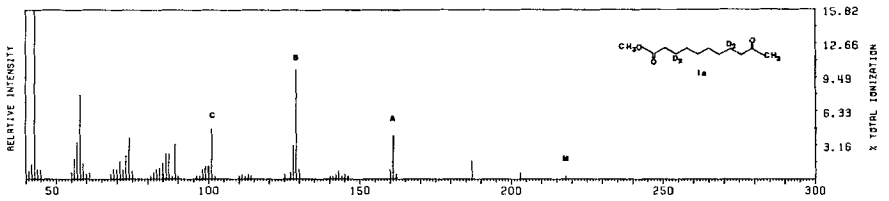


Fig. 2. *Mass Spectrum of Methyl 10-oxoundecanoate-3,3,8,8-d_4 (Ia)*

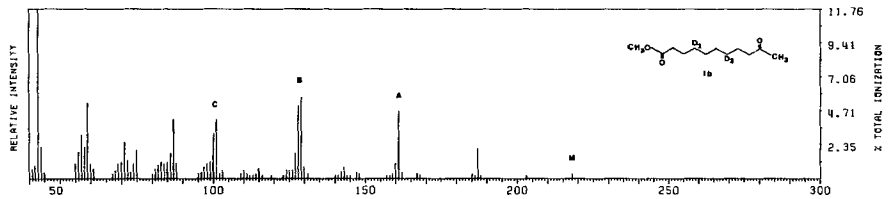


Fig. 3. *Mass Spectrum of Methyl 10-oxoundecanoate-4,4,7,7-d_4 (Ib)*

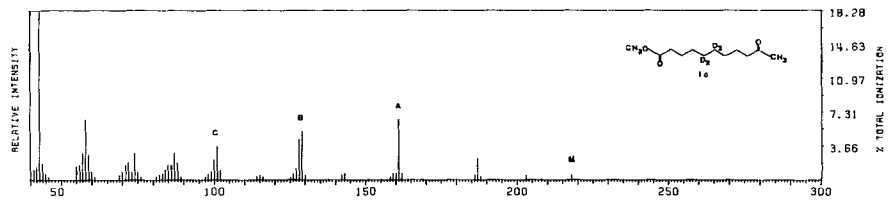
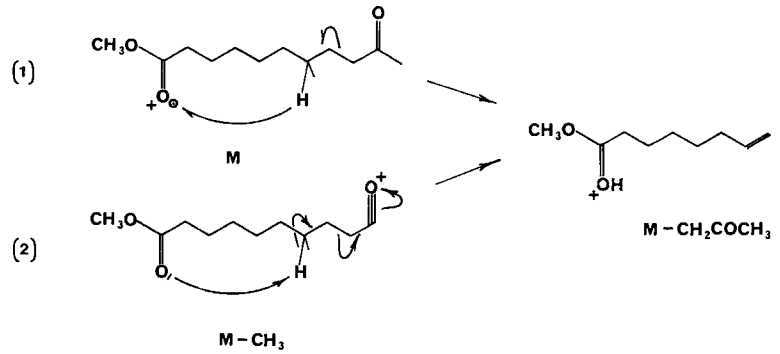


Fig. 4. *Mass Spectrum of Methyl 10-oxoundecanoate-5,5,6,6-d_4 (Ic)*

even hydrogen scrambling with respect to α-positions adjacent to the keto function (C(9) and C(11)).

Two alternative routes other than unaccountable direct cleavage of the C(8)–C(9) bond suggest themselves readily, both characterized by hidden long-range transfer of a hydrogen atom from C(7) to the participating ester function. Operation of hydrogen transfer as the triggering event of this unusual cleavage is likely to be borne out by the observed secondary loss of methanol from the latter site (**A** → **B**)[7]. As denoted in the scheme below, loss of a CH_3COCH_2 moiety from the molecular ion can be envisaged (in analogy to processes proposed for long-chain diketones: [6]) as loss of a single intact unit in a concerted process (route *1*), but also as a two-step sequence of losses of a methyl radical and a ketene molecule (route *2*). Confirming evidence from metastable peaks is lacking for either alternative:

[7] A direct, S_Ni-like attack of the ester function at the C(8)-C(9) bond seems, in principle, also conceivable and has, in fact, been suggested after completion of this work as an alternative rationale of functional group interaction in methylketo esters of varying chain-length [14]. However, such a mechanism – while being attractive for lower members of the homologous series in which ROH/CO elimination appears to be of lesser importance – would give rise to cyclic structures of **A** non-conductive to subsequent CH_3OH/CO elimination as such, *i.e.* without reopening. Hydrogen abstraction, though in a different timing, would still be required to secure elimination.



Direct loss of a CH_3COCH_2 radical (route *1*) as a consequence of hydrogen abstraction from C(7) could, *e.g.*, be enhanced by favourable product development control, inasmuch as conjugation of the new radical site with the carbonyl π-system is provided for the departing species[8]). Specific abstraction from this particular position (γ- with respect to the oxo-function) could thus be preferred to possible abstraction from all other sites within the saturated chain, lacking such special activation.

In the two-step version of this process (route *2*) an even-electron ($M - CH_3$) ion, observed as such in minor abundance, would serve as a genuine intermediate. The subsequent step, in contrast to the radical-type process *1* essentially ionic, would then make use of the basicity of the remote carboxyl group and trigger ejection of a neutral ketene molecule by abstraction of hydrogen as a proton from the same position as in route *1*. Indeed, this latter step would resemble an internal *Hofmann* elimination of solution chemistry, in which the acylium moiety $-CH_2-C\equiv O^+$ represents the leaving group, and C(7) with 'acidic' hydrogen atoms an activited site.

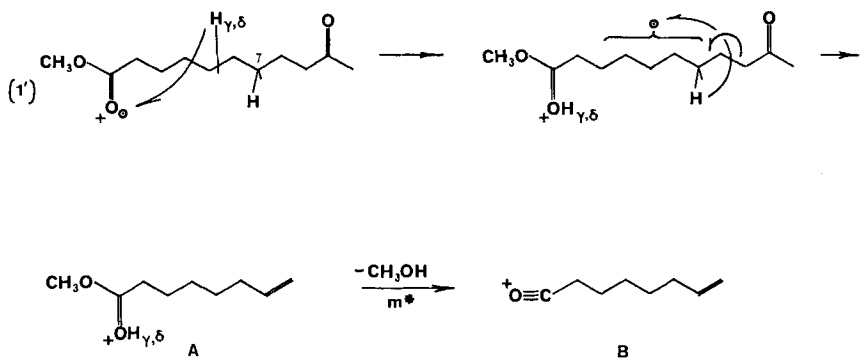
This premise of direct, selective hydrogen abstraction from C(7), as required by either alternative, and its reflection in methanol elimination with exclusive incorporation of the transferred hydrogen proves, however, untenable upon inspection of the γ- and δ-d_4 derivatives (Ib and Ic, Fig. 3 and 4, respectively): γ- as well as δ-positions are found to contribute, both to roughly equal extents (approximately 45% each), to elimination. Even in absence of isotopic discrimination against loss of CH_3OD, this result (accounting for about 90% of the hydrogen lost) limits contributions from the remaining α- and β-positions to rather small values. For the case of β-abstraction this is directly observed in the spectrum of the 3,3,8,8-d_4 compound (Ia, Fig. 2), which shows retention of all four labels in the genesis of **B** to a very high degree. These data would therefore, at best, accommodate only a partial operation (namely about 50%) either of both processes *1* and *2* together, or of only one of the alternative routes, which would still require the operation of an additional process to account for the remainder.

However, consideration of the spectral details of the further decomposition of ion **B** to **C** by loss of a carbon monoxide molecule renders these possibilities highly unlikely. Loss of CO from **B** (*m/e* 125) to a hydrocarbon fragment $C_7H_{13}^+$ (ion **C**, *m/e* 97) is confirmed by high-resolution measurements and by a proper metastable peak at

[8]) It has been estimated, though, that resonance energies of α-keto radicals are of only moderate magnitude [15].

m/e 75.3. Whereas both **B** and **C**, and the metastable peak, are clearly shifted to *m/e* 129, 101 and 79.1, respectively, in the β-labelled ester I a (Fig. 2), the same three peaks are each split into two components in the γ- and also the δ-labelled derivatives: *m/e* 128/129, *m/e* 100/101 and $m^* = 78.1/79.1$. In these cases, the relative contributions of the respective two components of **B**, **C** and m^* are all quite similar; in other words, the label distribution in ion **B** (ca. 4:5) is twice reproduced by that of its products, **C** and m^*. The plausible conclusion that comparable ease of loss of CO from each component of the split ion current of **B** (*m/e* 128/129) is indicated suggests the existance of one common precursor rather than two different ones, arising in the course of one single rather than two independent processes.

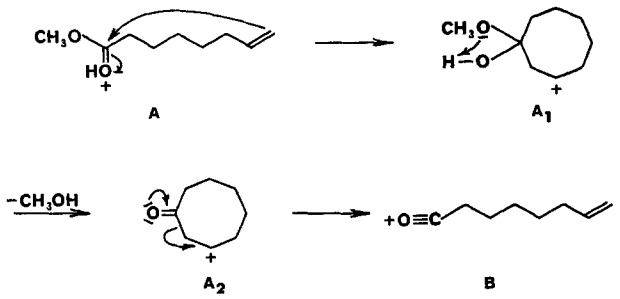
By assuming secondary, in contrast to direct, γ'-abstraction (*i.e.* C(7)) for process $M \rightarrow$ **A** as a more complex version of route *1* (subsequently denoted as route *1'*), a mechanistic rationale is obtained which is in much better agreement with these findings. Rapid migration of the radical site after nonspecific, instead of specific, primary hydrogen abstraction from the central portion of the chain (γ- and δ-positions) by additional secondary transfer steps should eventually reach the 'critical' γ'-position liable to facilitate C–C bond rupture (C(8)–C(9)) exactly as in route *1*:



If so, loss of methanol to **B** would reflect only the first, but not the 'last' hydrogen transfer, and therein lack final conclusiveness as to the operation of this mechnism by leaving γ'-abstraction, the decisive event of the genesis of **A**, obscured. α-positions have to be assumed to be excluded from primary and also secondary hydrogen abstraction (fragmentation along different paths might be induced), since loss of label is observed neither for C(9) nor C(11). The same would apply for primary abstraction of hydrogen from both β-positions.

Hydrogen abstraction from an alkyl chain by an ester function, such as is suggested in this formation of **A**, is likely to lead, with preference, to protonation of its carbonyl rather than of the methoxyl oxygen due to the probably higher basicity of the former site. However, it is not known with certainty whether elimination of methanol *via* a simple 4-center mechanism, such as depicted in the above scheme, can proceed from such a species with great ease. On the contrary, the tendency of (supposedly carbonyl-) protonated ester functions to undergo ROH elimination seems to depend, at least to some degree, on the presence of additional functional groups with donor qualities,

which would indicate participation of the latter in the reaction by ring formation[9]). Cyclization would indeed lead from an sp^2 to an sp^3 hybridization and thereby lower the distance between the methoxyl oxygen and the carbonyl-bonded hydrogen, favouring a fast process similar to an internal catalysis[10]:)



Reopening of structure $\mathbf{B}_1$ could then furnish the proper 'open' structure **B**, required for ejection of CO to ion **C**. Comparable heterolysis of oxonium ions generated from ketonic precursors is, of course, an amply documented incidence.

In view of the strict evidence against operation of mechanisms *1* and *2* in their simple specific versions, route *1'* obviously represents the interpretation of choice by providing satisfactory agreement with the data derived from symmetrical deuterium labelling of the molecule under study. At this point, *i.e.* in absence of unsymmetrical labelling, the possibility cannot be totally excluded that, as an additional complication, the radical sites generated by hydrogen abstraction from within the central chain undergo bonding reactions[11]) to one of the carbonyl functions prior to final cleavage of the C(8)–C(9) bond. It is known that such new-bond formation can proceed with greater ease than otherwise unfavoured C–C bond rupture being, of necessity, endothermic. Despite this uncertainty, the loss of the terminal CH_3COCH_2 moiety from the molecular ion of I, as described by process *1'*, is nonetheless likely to represent at least an approximation or simplified version of the true mechanistic course by which

[9]) Ions of analogous structure are likely to be encountered in the products of formal α-cleavage, *e.g.* of methyl hydroxyalkanoates, $\overset{+}{HO}{=}C(OCH_3)(CH_2)_nCH{=}O$ [3] [8]. These, as well as corresponding α-cleavage products of methoxy [8] [16] and oxo [8] [17] esters and the like, exhibit ROH elimination whenever functional group separation exceeds a certain minimum. Accordingly, only little loss of MeOH is observed for the prominent $\overset{+}{HO}{=}C(OCH_3)CH{=}CH_2$ ions (*m/e* 87) of simple methyl alkanoates, in which the very small ring-size of the required intermediate should impede cyclization and participation of the vinyl group in elimination.

[10]) It should not be ignored, however, that the very structure of **A**, $\overset{+}{HO}{=}C(OCH_3)(CH_2)_{n-2}CH{=}CH_2$, *i.e.* a protonated ester structure with terminal unsaturation, has been proposed (though not rigidly established) for a series of ions of the general composition $CH_3O_2C(CH_2)_n^+$ (maximizing at n = 2, 6, 10 etc.) [8] [17], believed to be formed from simple methyl alkanoates in a quite similar fashion [19]. Yet exactly these ions fail to eliminate CH_3OH to any larger extent, whereas ions **A** formed from I exhibit such elimination even at low ionizing voltages to a remarkable extent.

[11]) Implication of such new-bond formation has to be suspected, *e.g.*, in the genesis of the probably cyclic $C_6H_{10}O^+$ ions (*m/e* 98) and their lower and higher homologues, being relatively unimportant in I, yet quite prominent in related dicarboxylic esters [8].

interference of the fragmentation behaviour of the two similar functional groups is enacted over a relatively large molecular distance. This course would not suggest this interaction to be 'direct' and 'long-range' in a spatial sense, but rather to be 'indirect', *i.e.* transmitted through the intermediate chain, in several steps, by the medium of mobile tranferable hydrogen.

Experimental Part

Compounds I, Ia, Ib and *Ic*[12]) were prepared from sebacic acid labelled at the required positions, by successive conversion to the dichloride ($SOCl_2$), ester-chloride (1 mole CH_3OH), and reaction with $CH_3MgBr/CdCl_2$ according to known procedures [20]:

$$HOOC(CH_2)_8COOH \rightarrow ClCO(CH_2)_8COCl \rightarrow CH_3OOC(CH_2)_8COCl \rightarrow CH_3OOC(CH_2)_8COCH_3$$

Samples of I, or of its labelled analogues, were purified by GLC, which allows separation from concomitantly formed dimethyl sebacoate (due to use of excess CH_3OH). In a few instances, larger amounts of dodecanedione ($CH_3COC_8H_{16}COCH_3$) resulted from too low MeOH/dichloride ratios, and had to be removed by wet-chemical methods because of very similar retention behaviour with that of I under a variety of conditions. In these cases, saponification of the crude product (aqueous NaOH), removal of the neutral dione by ether extraction of the alkaline solution, isolation of the free oxo acid at pH = 1 and subsequent re-esterification yielded I.

Sebacic Acid-3,3,8,8-d_4, furnishing Ia, was obtained by $LiAlD_4$ reduction of adipic acid, conversion of the resulting hexanediol-1,1,6,6-d_4 into the dibromide (HBr/H_2SO_4) [21], and reaction with dimethyl malonate followed by the customary saponification/decarboxylation procedure of malonic ester synthesis.

Sebacic Acid-4,4,7,7-d_4, furnishing Ib, was obtained the same way except that adipic acid-2,2,5,5-d_4 (adipic acid twice exchanged in $D_2O/NaOD$ at 180° in a *Parr*-bomb) and $LiAlH_4$ was employed.

Sebacic Acid-5,5,6,6-d_4, furnishing Ic, had to be prepared by *ab initio* labelling using $BrCD_2$-CD_2Br (available from *Merck, Sharp & Dohme*, Canada) and twice employing the malonate procedure.

High- and low-resolution mass spectra were obtained on a modified *AEI* MS-902 mass spectrometer equipped with an all-glass inlet system (ion source and inlet system temperatures 250 and 200°, respectively, ionizing voltage 70 V).

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241. Geijerone (3-Isopropenyl-4-methyl-4-vinylcyclohexanone), a New, Naturally Occurring C_{12} Terpenoid

by **Alan F. Thomas**

Firmenich & Cie, Research Laboratory, Geneva

(28. VIII. 72)

Summary. In the essential oil of *Juniperus communis* L. (fruit), the title compound (*trans*-isomer) has been identified; its structure being confirmed by synthesis from elemol. The optical rotation of the natural compound was nearly the same as the synthetic sample, suggesting that it is not an artefact formed from a ten-membered ring precursor during the isolation.

In the course of an analysis of the essential oil of *Juniperus communis* L.[1]), a ketone, $C_{12}H_{18}O$, was isolated from the fraction with bp 81–86°/0.1 mm Torr, by combined chromatography on silica gel and gas chromatography (glpc.). The NMR.-spectrum of this ketone showed the typical signals for the *trans*-1-vinyl-2-isopropenyl-2-methyl structure associated with the elemenes and elemol[2]) and treatment with deuterium oxide under basic conditions [3] revealed the presence of four protons adjacent to the carbonyl group. There were thus two structures possible (not considering the stereochemistry), one of which (**1**) has already been described [4] [5]. Direct comparison of **1**, prepared from germacrone (**2**) [4], with the natural ketone showed them to be different, so there was a strong presumption that the new compound was represented by **3**.

It was found that elemol (**4**) is cleanly dehydrated to a mixture of β- (**5**) and γ-elemene (**6**) by phosphorus oxychloride in pyridine (pyrolysis of various esters is known to give complex mixtures [5]), and the two hydrocarbons can be separated by careful distillation. Epoxidation of γ-elemene (**6**) gave a mixture of two epoxides (**7a**, **7b**) which were separately characterized, but not separated for the next step. Treatment of the epoxides with dilute sulfuric acid in dioxan led to a mixture of glycols (**8**) that was converted to the desired ketone (**3**) with periodic acid. Treatment of the epoxide mixture (**7**) with periodic acid in aqueous dioxan also led directly to the ketone (**3**), for which the name *'geijerone'* is proposed.

[1]) Other compounds recently isolated from the same sample of oil have been described [1].
[2]) *cf. e.g.* [2].