67. Potassium Carboxylates by Direct Carbonylation of Potassium Alkoxides

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(28.I.87)

Reaction of the K^+ alkoxide of linalool (**1**) in benzene with CO at 425-440 bar and 120–130° for 12–30 h gave the K^+ salt of 2,6-dimethyl-2-vinyl-5-heptenoic acid (**4a**) in a *ca.* 25% yield based on *ca.* 65% converted alkoxide. Reaction of the $[K^+ \subset 18\text{-crown-6}]$ alkoxide of **1** with CO at 50–55 bar and 40° for 90–140 h gave a mixture containing mainly the $[K^+ \subset 18\text{-c-6}]$ salts of **4a** (*ca.* 62%) and of the homogeranic acids **3a** and **6a** (together *ca.* 27% of the mixture) in a *ca.* 35% combined yield based on 50–60% converted alkoxide. The uncomplexed or complexed K^+ alkoxide of (*S*)-**1** gave, with *ca.* 85% net retention, the K^+ salt of (*S*)-**4a**. Reaction of the $[K^+ \subset 18\text{-c-6}]$ alkoxide of geraniol (**2**) with CO at 50 bar and 40° for 65–70 h gave myrcene (**10**) and geranyl formate (**11**) in a *ca.* 40–50% yield each based on *ca.* 85% converted alkoxide. Reaction of the $[K^+ \subset 18\text{-c-6}]$ alkoxide of 3-pentyl-1,4-pentadien-3-ol (**14**) at 50 bar and r.t. for 70 h gave a mixture of the $[K^+ \subset 18\text{-c-6}]$ salts of 2-pentyl-2-vinyl-3-butenoic acid (**15a**) (67%) and the 4-pentyl-2,4-hexadienoic acids **18a** and **19a** (together 23% of the mixture) in a *ca.* 90% combined yield based on *ca.* 65% converted alkoxide.

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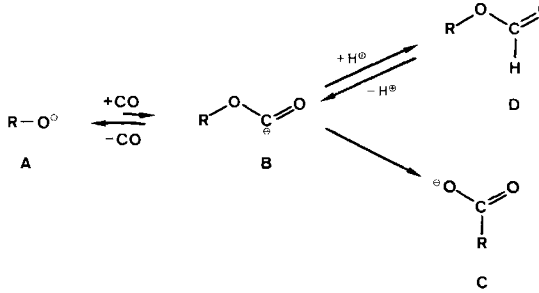
1. Introduction. – We have been seeking an efficient way of converting an allyl alcohol into the homologous acid or ester, for example, linalool (**1**) or geraniol (**2**) into homogeranic acid (**3a**). Following a suggestion by *A. Eschenmoser*[1]), we treated various alkoxides with CO, and this indeed gave carboxylates. This paper describes these carbonylations, which are mechanistically intriguing and may have synthetic potential. The scope is not fully delineated; we have mainly worked with the alkoxides of **1** and **2**.

We reasoned that an alkoxycarbonyl anion **B**, formed by addition of an alkoxide **A** to CO, might rearrange to a carboxylate **C** (*Scheme 1*). Although the present carbonylations are almost certainly without precedent, this *Scheme* can be traced far back in time. Related are: *1) Berthelot*'s synthesis of formate salts (1855) by addition of hydroxide to CO [1], **A**→**B**→**C**, R = H. *2)* The synthesis of alkyl formates (1914) *via* addition of alkoxides to CO [2][2]), **A**→**B**→**D**; the reaction is run in excess alcohol which traps **B** by protonation. *3)* The deprotonation of alkyl

Scheme 1



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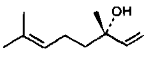
[1]) Research seminars at *Firmenich*, January 1980 and 1985.

[2]) For the addition of Li^+ amides to CO at atmospheric pressure in an aprotic medium to give aminocarbonyl anion-Li^+ salts (carbamoyllithiums), see [3].

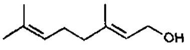
formates to give alkoxycarbonyl anions which decarbonylate at atmospheric pressure [4], **D**→**B**→**A**, the reverse of *2*. Reactions *1–3* are well understood, and *1* and especially *2* are carried out industrially. The alkoxycarbonyl anions **B** are best viewed as short-lived intermediates[3]). Apart from the trapping by protonation in *2*, this is suggested by the observation of $^1H/^2H$ exchange which is thought to proceed *via 3* [5][3]); attempts to alkylate **B** *via 3* have failed [4a]. The concept of a possible carbonylation **A**→**C** can also be traced back to *Berthelot* (1861) [6] and then to *Geuther* (1880), who actually reported that exposure of solid Na$^+$ methoxide and ethoxide to CO at atmospheric pressure and 160° gave Na$^+$ acetate and propionate, respectively, in low yield [7]. However, this could not be reproduced, and the synthesis of alkyl formates (*2*) was discovered instead [2a][4])[4a]).

From the above, we concluded that in order to favor **A**→**B**→**C**, we should use strongly nucleophilic alkoxides and high CO pressure to favor the formation of **B**, a non-acidic medium to block **B**→**D**, and R with high migratory aptitude to facilitate **B**→**C** (see *Section 6*)[5]).

2. Experiments with Linalool (1). – We have found that the K$^+$ alkoxide of **1** reacts in benzene[6]), at elevated temperature and pressure, with CO to give the K$^+$ salt of the tertiary acid **4a**, and that the [K$^+$ $\subset$ 18-crown-6] alkoxide of **1** [12][6])[7]) already reacts slowly near r.t. and at low CO pressure to afford mainly the [K$^+$ $\subset$ 18-c-6] salt of **4a** accompanied by the salts of its allylic isomers **3a** and **6a**.



(+)-(*S*)-**1**



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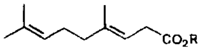
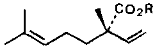
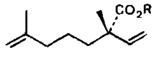


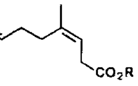
3a,b



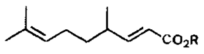
(+)-(*S*)-**4a**
(+)-(*S*)-**4b**



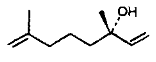
(*S*)-**5a**
(*S*)-**5b**



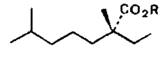
6a,b



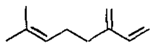
7a,b



(*S*)-**8**



(+)-(*R*)-**9a**
(+)-(*R*)-**9b**



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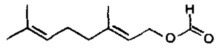

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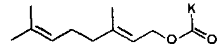

12

a R = H **b** R = Me

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[3]) For another interpretation, see [4a].

[4]) For the pre-*Reppe* patent literature on the synthesis of acetic acid from methanol and CO, see [8].

[4a]) **Added in Proof.** A patent (1933) also describes the carbonylations EtONa + CO→EtCO$_2$Na and BuONa + CO→BuCO$_2$Na in Et$_2$O at 70–140 bar and 20–60° [27].

[5]) We thought that [2,3] sigmatropic rearrangements might occur for R = allyl; for related [2,3] rearrangements, see [9], and for related rearrangements *via* a radical pair, see [10].

[6]) Benzene is a weak acid (pK_a 43), is resistant to nucleophilic reagents, and dissolves K$^+$ alkoxides. Our K$^+$ alkoxides should be more soluble in benzene than K$^+$ *tert*-butoxide whose solubility is *ca.* 0.18M at r.t. [11]. We worked with formally *ca.* 1.6M solutions. Whether our K$^+$ alkoxides were indeed in solution at r.t. could not be discerned because an excess of KH was used (a total of *ca.* 1.6 equiv. because dosage is difficult), which remained suspended. Addition of 18-c-6 (*ca.* 1.2 mol/mol KH) to these light-brown suspensions gave brown, opaque 'solutions'. What happened when the suspensions and 'solutions' were heated in the autoclave under CO pressure is unknown. After cooling and degassing, black suspensions were obtained from both the suspensions and the 'solutions'.

[7]) We have no direct evidence that we have the [K$^+$ $\subset$ 18-c-6] alkoxides in hand, but the effects that we see are good indirect evidence. We also do not know whether the [K$^+$ $\subset$ 18-c-6] alkoxides are stable throughout the experiments.

In typical experiments, the K^+ alkoxide of racemic **1** generated from **1** and KH[8]) in benzene was exposed to CO at 425–440 bar and 120–130° for 12–30 h in an autoclave fitted with a glass insert[8]). The autoclave was allowed to cool to r.t. and degassed. Hydrolytic workup, esterification with CH_2N_2, and distillation gave a 97:3 mixture of ester **4b** and its double-bond-shifted α-isomer **5b**. Recovered **1** also had its α-isomer **8** admixed in a 99:1 ratio. The yields fluctuated, with our best combined yield of **4b** and **5b** being *ca.* 50% based on *ca.* 65% converted **1**, but combined yields of *ca.* 25% for similar conversions are more representative.

In typical experiments with the [$K^+ \subset$ 18-c-6] alkoxide of **1**, carbonylation at 50–55 bar and 40° for 90–140 h[8]) followed by the operations indicated above gave mixtures of *ca.* 62% **4b**, *ca.* 5% **5b**, *ca.* 17% **3b**, *ca.* 10% **6b**, and *ca.* 6% **7b**. The combined yields of these were 35–40% based on 50–60% converted **1** and somewhat more reproducible than in the experiments with the uncomplexed alkoxide. Recovered **1** had **8** admixed in a 91:9 ratio. Long reaction times at relatively low temperature were indicated because the [$K^+ \subset$ 18-c-6] alkoxides are thermally fragile.

The fluctuations in yield could be due to inefficient mass transport in our three-phase systems[6]). The alkoxide of **8** and the salt of **5a** are undoubtedly formed by equilibration involving deprotonation and reprotonation of allylic sites[9]).

Analogous carbonylation of the uncomplexed K^+ alkoxide (360 bar, 120°, 12 h), the [$K^+ \subset$ 18-c-6] alkoxide, and also the [$K^+ \subset$ [2.2.2]cryptand] alkoxide [12] (55 bar, 40°, 120 h) derived from (+)-(*S*)-**1** [14], 65% ee[10]), led to (+)-(*S*)-**4a**[11]) and thence to (+)-(*S*)-**4b**[11]), 53–57% ee. The spread of the ee values for (*S*)-**4a** and (*S*)-**4b** is close to the analytical error (NMR[11]), and the ee correspond to 82–88% net retention of configuration in the carbonylations. The absolute configuration of (+)-**4a** was unknown but readily established to be (*S*) by hydrogenation, which gave the known tetrahydro derivative (+)-(*R*)-**9a** [16] [17][12]).

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[8]) KH from *Aldrich*, 35 wt.-% in mineral oil, or *Fluka, pract.*, *ca.* 20% in mineral oil. The reaction between substrate alcohol and KH was carried out in the septum-sealed glass insert under Ar. A brief contact with air occurred when the septum was removed to introduce the insert into the autoclave. Once charged with the insert, the autoclave was purged with Ar, then sealed, and finally pressurized with CO (purity ≥ 99.97%). In the runs at high pressure and temperature (with the uncomplexed K^+ alkoxides), the autoclave was shaken (no stirring). In the runs at low pressure and temperature (with the complexed K^+ alkoxides), the reaction mixtures were stirred with a magnetic stirring bar. Excess KH survived the reaction conditions with all substrates except **2**, as evidenced by the evolution of H_2 on treatment of the reaction mixture with H_2O in the workup. The carbonylations may be sensitive to the purity of KH; for a discussion of this problem and a method for purification, see [13].

[9]) We only detected the α-isomers of the major components **1** and **4a, b**; the α-isomers of the minor components were undoubtedly also present, but in too low concentrations.

[10]) (+)-(*S*)-**1** was isolated from coriander oil, $[\alpha]_D^{20} = +14.0 \pm 0.2°$ (c = 0.573, $CHCl_3$), 65% optically pure with respect to the largest reported optical rotation ($[\alpha]_D^{20} = +21.62°$ (neat) [15]), *ca.* 65% ee by NMR analysis using $Eu(hfbc)_3$ (tris-[3-(heptafluoropropylthydroxymethylidene)-*d*-camphorato]europium). The ee of recovered (+)-(*S*)-**1** was unchanged.

[11]) It was difficult to separate (GC) **4a** from **5a** and **4b** from **5b**. From the same sample (*S*)-**4a**+(*S*)-**5a** (ratio 93:7) was isolated (GC) a 97:3 mixture of (*S*)-**4a** and (*S*)-**5a** of $[\alpha]_D^{20} = +2.1 \pm 0.1°$ (c = 0.760, $CHCl_3$), and, after esterification, a 99:1 mixture of (*S*)-**4b** and (*S*)-**5b** of $[\alpha]_D^{20} = +2.1 \pm 0.1°$ (c = 1.290, $CHCl_3$). The ee of this (*S*)-**4a** and (*S*)-**4b** was 53–55% as determined by NMR analysis of (*S*)-**4b** using $Eu(hfbc)_3$.

[12]) A fraction of the sample (*S*)-**4a**+(*S*)-**5a** (93:7) used in the characterization above[11]) was hydrogenated to give (*R*)-**9a** of $[\alpha]_D^{20} = +4.1 \pm 0.2°$ (c = 0.450, $CHCl_3$). This (+)-(*R*)-**9a** was formed from both (*S*)-**4a** and (*S*)-**5a**, but the ee of both these can be assumed to be the same, 53–55%[11]). Neither an $[\alpha]_D$ of (*R*)-**9a** nor its sign is given in [16], but Professor *Dev* informed us that [17] reports $[\alpha]_D = +5.64°$ (c = 2.8%, $CHCl_3$); this (+)-(*R*)-**9a** was of high optical purity. Our 53–55% ee and $[\alpha]_D^{20} = +4.1 \pm 0.2°$ suggest an $[\alpha]_D^{20} = +7.6 \pm 0.5°$ ($CHCl_3$) for optically pure (*R*)-**9a**.

A substantial part of **1** is lost in an unknown manner in these experiments. Non-volatile, uncharacterized material was formed. Elimination of KOH and [K$^+$ ⊂ 18-c-6]OH$^-$ to give myrcene (**10**)13) was only a very minor side reaction, and we have no evidence for β-cleavage [18]13).

The carbonylations proceed only with the extremely nucleophilic K$^+$ and complexed K$^+$ alkoxides. Attempts to carbonylate Li$^+$, Na$^+$, Cu$^+$, and Mg^{2+} alkoxides, uncomplexed or complexed, were unsuccessful; Cs$^+$ alkoxides have not yet been tried.

3. Experiments with Geraniol (2). – Attempts to carbonylate the [K$^+$ ⊂ 18-c-6] alkoxide of **2** failed. Instead, myrcene (**10**) and geranyl formate (**11**) were obtained. The elimination of KOH from the K$^+$ alkoxide of **2** to give **10** *via* allylic deprotonation of the CH_3 group is well known [19], and this is probably what happens in our case14). If so, the [K$^+$ ⊂ 18-c-6]OH$^-$ so formed14) must be acidic enough to protonate the geranyloxycarbonyl anion-[K$^+$ ⊂ 18-c-6] salt (**12**), which is concurrently formed but thus trapped to give **11**. The [K$^+$ ⊂ 18-c-6]OH$^-$ would also react with the CO to give [K$^+$ ⊂ 18-c-6] formate [1], which indeed we found.

In typical experiments, the [K$^+$ ⊂ 18-c-6] alkoxide of **2** was treated with CO at 50 bar and 40° for 65–70 h. After workup, **10** and **11** were each obtained in, roughly estimated, 40–50% yield based on *ca.* 85% converted **2**. In three experiments, we also obtained mixtures of **3a, b** (major component), **6a, b,** and **4a, b** in low yield, but this could not be reproduced.

A carbonylation experiment with the uncomplexed K$^+$ alkoxide of **2** at 80 bar and 200° showed that the *Dumas-Stas* reaction [20]15) combined with net mono-hydrogenation intervened, and this experimental variant was therefore not pursued.

4. Experiments with 3-Pentyl-1,4-pentadien-3-ol (14). – With the tertiary, bis-allylic alcohol **14** designed to 'fit' our carbonylation, carbonylation indeed proceeded remarkably well. Thus, treatment of the [K$^+$ ⊂ 18-c-6] alkoxide of **14** with CO at 50 bar and r.t. for 70 h followed by the operations indicated previously led to a mixture of 67% of the tertiary ester **15b** and 11 and 22% of the isomeric esters **18b, 19b**16)**,** in a *ca.* 90% combined yield based on *ca.* 65% converted **14**. The [K$^+$ ⊂ 18-c-6] salts of **18a** and **19a** are evidently formed *in situ* from those of the allylic isomers **16a** and **17a** of that of **15a** by prototropic isomerisation. Similar results were also obtained with the uncomplexed K$^+$ alkoxide of **14** (45 bar, 120°, 12 h).

5. Experiments with Non-allylic, Tertiary Alcohols. – Non-allylic, tertiary alkoxides barely reacted with CO, and only as the uncomplexed K$^+$ alkoxides at elevated tempera-

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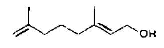
13) For the elimination of [K$^+$ ⊂ 18-c-6]OH$^-$ and the β-cleavage of C–H bonds (*Dumas-Stas* reaction), see *Section 3.*

14) In the absence of CO, the [K$^+$ ⊂ 18-c-6] alkoxide of **2** in benzene did eliminate to give **10** and, presumably, [K$^+$ ⊂ 18-c-6]OH$^-$. We again7) have no direct evidence for the presence of this species and do not know whether it would be stable under the conditions of the experiment. As stated above8), the excess of KH did not survive in these runs. Recovered **2** had none of the α-isomer **13** admixed which indicates that this system quickly loses its initially high basicity. Treatment of the reaction mixture with ^2H_2O under CO pressure after 17 h at 50 bar and 40° gave unlabeled **11**.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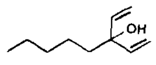
15) The textbook stoichiometry of the *Dumas-Stas* reaction is $RCH_2OH + KOH \rightarrow RCO_2K + 2\ H_2$. Its mechanism is unknown, but its basis is undoubtedly β-cleavage of a C–H bond in the *Meerwein-Ponndorf-Verley* manner, *cf.* [18b].

16) Which of the isomers **18b** and **19b** was the major and which the minor component was not determined.



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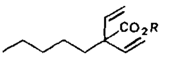
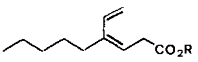
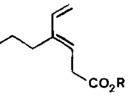


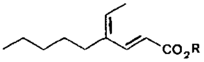
15a,b



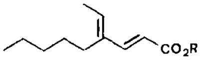
16a,b



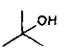
17a,b



18a,b



19a,b



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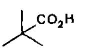
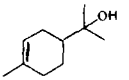


21a



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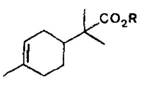
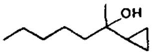


23a,b



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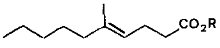
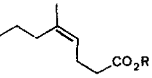
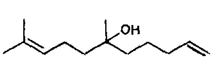


28a,b



29a,b



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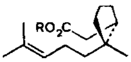
31a,b



32a,b

a R = H **b** R = Me

ture. Thus, the K^+ alkoxide of *tert*-butyl alcohol (**20**) reacted with CO at 70 bar and 160° for 12 h to give the K^+ salt of pivalic acid (**21a**) in a 4% yield based on the total of **20** started with, and the K^+ alkoxide of α-terpineol (**22**) reacted (210 bar, 200°, 15 h) to give the K^+ salt of the acid **23a** in a *ca.* 1% yield based on the total of **22** used[17]).

Nevertheless, two mechanistic tests were made. The K^+ alkoxide of the tertiary cyclopropylmethanol **27** gave (350 bar, 120°, 12 h) a 67:33 mixture of the K^+ salts of the ring-opened acids **28a, 29a**[18]), and the K^+ alkoxide of the tertiary alcohol **30** containing a 5-hexen-1-ol unit (380 bar, 160°, 12 h) a 82:18 mixture of the K^+ salts of the ring-closed acids **31a, 32a**[18]) in low yield.

6. Mechanism. – The common rationale for the present results is clearly a dissociation/recombination mechanism following the addition of the K^+ alkoxides **E** to CO to give the alkoxycarbonyl anion-K^+ salts **F** *(Scheme 2)*. Dissociation of **F** to give the alkyl or allyl radical/$CO_2^{-\cdot}/K^+$ triplets **G**[19]) seems more likely (despite one inconsistency, see below) than dissociation leading to carbanion/CO_2/K^+ triplets **G'**. Recombination starting from **G** or **G'** would give the carboxylates **H**. Analogous mechanisms can be written with [$K^+ \subset$ 18-c-6] replacing K^+. Parenthetically, we note that all these mechanisms embody new evidence for the intermediacy of **F**.

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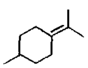
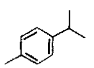
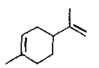
[17]) The main component of the acid/ester fraction was **23a, b** and the main component of the neutral fraction recovered **22** (*ca.* 80% conversion), but both fractions contained a host of other, minor components which were not identified. The neutral fraction in addition contained 4(8)-*p*-menthene (**24**) and *p*-cymene (**25**) as major components, each being formed in a *ca.* 10% yield based on the total of **22** started with. These are undoubtedly formed from limonene (**26**) by isomerization [21] and disproportionation, **26** in turn being formed by elimination of KOH from the K^+ alkoxide of **22**.



24



25

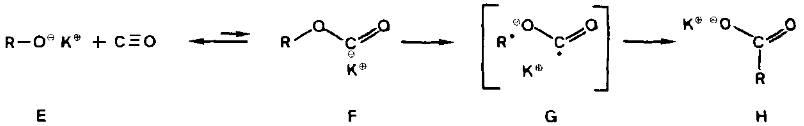


26

[18]) Which of the isomers **28a, b** and **29a, b** or **31a, b** and **32a, b** was the major and which the minor isomer was not determined. Compounds **31a, b** and **32a, b** were accompanied by the corresponding α-isomers, *cf.* **5a, b** and **8**.

[19]) For a review on $CO_2^{-\cdot}$, see [22].

Scheme 2



That we find only the salts of the cyclic acids **31a** and **32a** is puzzling. Since geminate recombination within **G** would be faster than ring closure in solution [23] and in the solid state[6]), this would mean that these are formed from R˙ that escape their partners (**G**) and encounter other $CO_2^{-\cdot}$ which seems unlikely. The R˙ that escape would probably not react with the CO that is present in high concentration. It has recently become clear that the cyclizations could in principle also involve carbanions (**G'**) [24], but the cyclization and recombination rates for **G'** are unknown. The R^- that escape would react with the CO.

A comparison of the present reactions with three known ones is indicated, but it must be stressed that all four are really very different so that one can expect only the broadest of resemblances. The first is the rearrangement of alkoxycarbenes RO–C–R to give ketones [25] and the second the rearrangement of the dialkoxycarbene allylO–C–OMe to give esters [10]. Both of these uncharged systems rearrange *via* dissociation to radicals. The third and most closely related is the *Wittig* rearrangement [26]. But not only are the nature and origin of the migration termini different, but also the cations, solvents, and temperatures. The dissociation/recombination mechanism **F**→**G**→**H** is essentially the same as that by which alkyl groups appear to migrate in *Wittig* rearrangements, but in our case, allyl groups seem to migrate by that same mechanism, while [2,3] sigmatropy[5]) predominates in the *Wittig* rearrangement.

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