Anionic Dimerization in Reductive Cleavage of an Allyl Ether with Sodium–Potassium Alloy

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The reaction of 9-methoxy-9-vinylfluorene (**2a**) with sodium–potassium alloy does not yield the expected 9-vinylfluorenylanion (**1**). The anions derived from the reaction were characterized by carbonation and subsequent methylation. Four esters (**5**, **6**, **7**, and **8**) accounting for about two-thirds of the starting material were isolated and characterized. Structures were assigned on the basis of mass spectra and n.m.r. spectra in particular using decoupling experiments. A brief mechanistic scheme is presented.

La réaction du méthoxy-9 vinyl-9 fluoréne (**2a**) avec un alliage sodium–potassium ne conduit pas à l'anion vinyl-9 fluorényle (**1**). On a caractérisé les anions dérivés de cette réaction en effectuant successivement une carbonatation et une méthylation. On a pu isoler et caractériser quatre esters (**5**, **6**, **7** et **8**) qui permettent de tenir compte d'environ les deux tiers du produit de départ. On a attribué des structures à ces composés en se basant principalement sur les spectres de masse et de r.m.n. en faisant appel aux techniques de découplage. On présente un bref mécanisme réactionnel.

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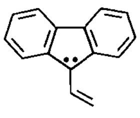
Introduction

Reductive cleavage of ethers by alkali metals has proved to be one of the more successful routes to organic derivatives of the alkali metals. The presence of a site of unsaturation in the ether, often a phenyl ring, facilitates the reaction and allyl- and benzyl-type carbanides have been prepared most commonly (1–6). In an attempt to prepare and study restricted rotation in the alkali metal derivatives of anion **1**, a sample of 9-methoxy-9-vinylfluorene **2a** was prepared and reacted. Unlike analogous 9-substituted-9-methoxy-fluorenes (**2b** (7), **2c** (8), and **2d** (8)), the expected anion was not observed (**1** in this case). Other analogous ethers which have been reacted successfully to produce their potassium salts are **3** and **4** (9).



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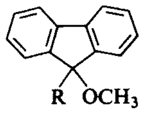

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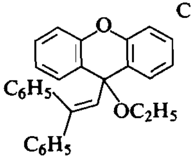
$a = CH_2{=}CH—$
$b = H$
$c = C_6H_5$
$d = OCH_3$



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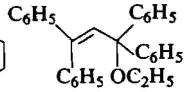

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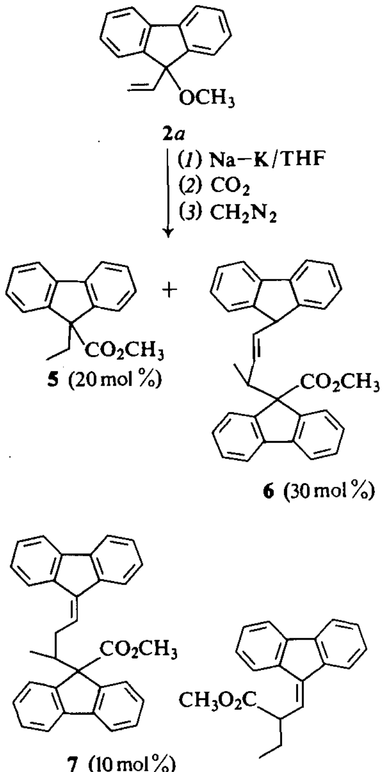
Results

A sample of 9-methoxy-9-vinylfluorene (**2a**) was prepared as described in the Experimental section. A dilute solution (*ca.* 0.1 *M*) of **2a** in freshly distilled tetrahydrofuran was stirred under an argon atmosphere for two days with a slight excess over the stoichiometric amount of sodium–potassium alloy. During the course of the reaction a dissolving deep-red coloration developed on the surface of the alloy and the final solution was deep red. In an attempt to characterize the organometallics present, this solution was passed into a room temperature solution of carbon dioxide in tetrahydrofuran. The acids accounted for 85 wt% of the total isolated materials and no **2a** could be detected in the neutral fraction.

Instead of a mixture of the two acids expected upon carbonation of the desired anion, thin layer chromatography indicated a mixture of at least nine components and n.m.r. suggested that neither of the predicted products was present. This result proved to be reproducible. The acids were converted to their methyl esters on treatment with diazomethane and again both thin layer chromatography and n.m.r. showed about nine components. By a combination of thick layer chromatography and vapor phase chromatography (v.p.c.), four components of the mixture were isolated and characterized as described in the Experimental section.

Structures **5**, **6**, **7**, and **8** have been assigned



2*a*

5 (20 mol %)

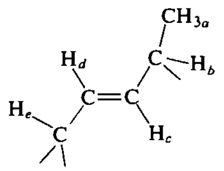
6 (30 mol %)

7 (10 mol %)

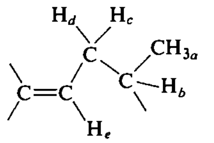
8 (10 mol %)

on the basis of their n.m.r. and mass spectra. The structure assigned to **5** has been verified by mixed melting point with an authentic sample.[1] All the esters proved to be crystalline solids except **8** which remained a viscous oil. Both the n.m.r. and analytical results for **8** suggest the presence of a small amount of impurities which, however, do not interfere with the structural assignment.

Integration of the 100 MHz n.m.r. spectrum of **6** (Fig. 1) indicated the presence of two fluorenyl groupings and this was substantiated by the mass spectrum parent peak at $m/e = 442$. A first order analysis of this and the decoupled n.m.r. spectra yielded $\delta a = 0.81$, $\delta b = 3.47$, $\delta c = 5.53$, $\delta d = 5.14$, $\delta e = 4.14$, and $J_{ab} = 6.8$ Hz, $J_{bc} = 8.0$ Hz, $J_{cd} = 15.0$ Hz, $J_{de} = 8.8$ Hz. The structure of the carbon chain was clarified by proton–proton decoupling experiments. The high field methyl doublet (protons *a*) collapsed to a singlet when proton *b* was irradiated. At the same time the low field quartet due to a vinyl proton (*c*) collapsed to a doublet. Irradiation of the doublet at $\delta = 4.14$ (proton *e*) collapsed the upfield vinyl proton (*d*) to a doublet. These results require a carbon chain of the following type. The large coupling ($J_{cd} = 15.0$ Hz) between the vinyl protons is consistent with a *trans* geometry. Introduction of two fluorenyl ring systems and a carbomethoxy group lead to structure **6**.



The n.m.r. spectrum of **7** is shown in Fig. 2 along with the results of integration. The mass spectrum (parent peak at $m/e = 442$) show that **6** and **7** are isomers. The n.m.r. again suggests the presence of two fluorenyl rings and a carbomethoxy grouping. Again homonuclear decoupling experiments proved very useful in the assignment of the structure of the carbon chain. The methyl doublet (protons *a*) collapsed to a singlet when the signal at $\delta = 3.14$ due to a single proton (*b*) was irradiated. Furthermore the multiplet due to two protons (*c* and *d*) at $\delta = 2.4$ simplified to an unsymmetrical triplet. Irradiation at $\delta = 2.4$ caused the triplet due to a single vinyl proton (*e*) to collapse to a singlet. These results are consistent with the following skeleton.



Further decoupling experiments showed that irradiation of the signal due to the vinyl proton *e* changed the character of the multiplet due to protons *c* and *d* so that it appeared as the AB part of an ABX. The multiplet at $\delta = 3.14$ (proton *b*) could be changed to a quartet by irradiation of either protons *a* or protons *c*

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[1] The authors wish to thank F. A. L. Anet for providing a sample of 9-ethyl-9-carbomethoxyfluorene for comparison.

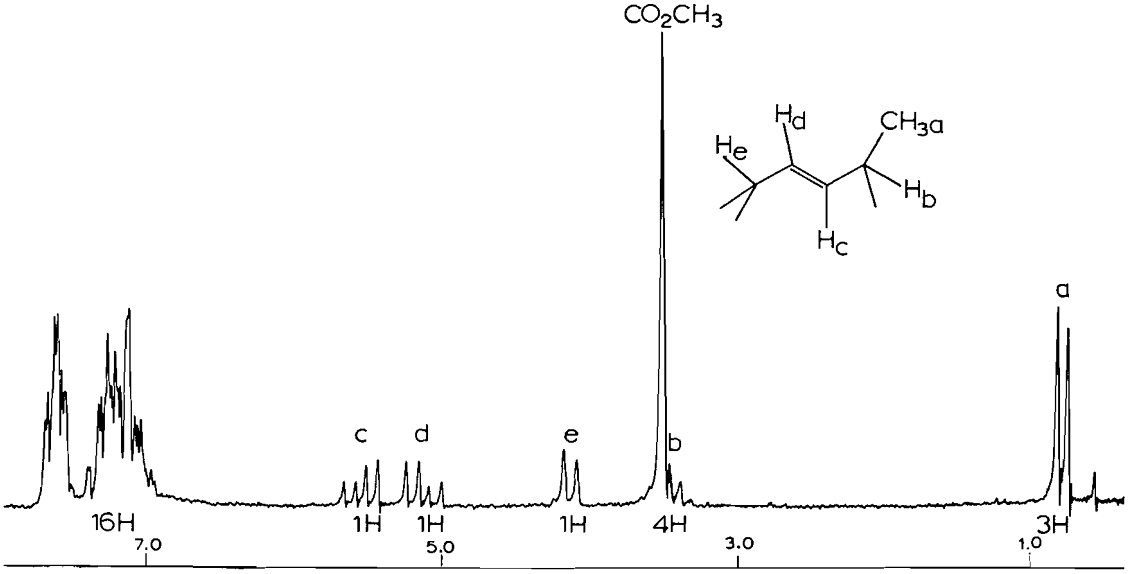


FIG. 1. The 100 MHz n.m.r. spectrum of ester **6**.

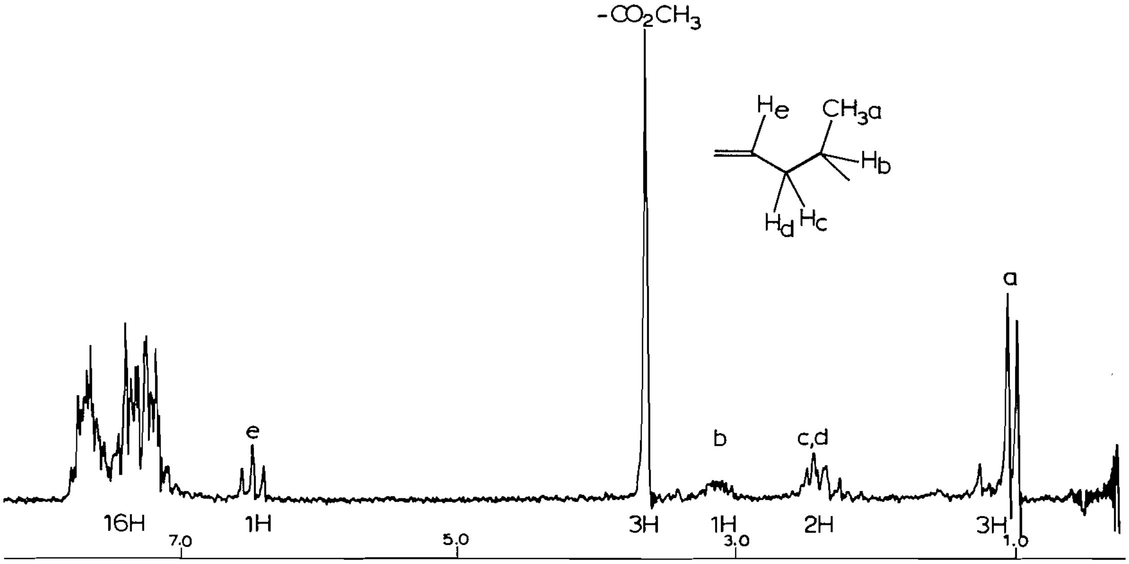


FIG. 2. The 100 MHz n.m.r. spectrum of ester **7**.

and *d*. This latter piece of evidence and the complex pattern due to protons *c* and *d* show that protons *c* and *d* are magnetically nonequivalent due to the asymmetric center. Inclusion of the fluorenyl rings and the carbomethoxy group leads to structure **7**. The signals formed by protons *b*, *c*, and *d* on successive irradiation of protons *a* and *e* were analyzed as an ABC pattern. The following parameters were obtained for the entire system: $\delta_a = 1.02$, $\delta_b = 3.16$, $\delta_c = 2.32$, $\delta_d = 2.50$, $\delta_e = 6.49$ and $J_{ab} = 6.9$, $J_{bc} = 10.3$, $J_{bd} = 4.1$, $J_{cd} = -14.8$, and J_{ce}, $J_{de} = 7.9$.

It can be seen that **6** and **7** are just double bond isomers. An attempt was made to determine which is the thermodynamically more stable

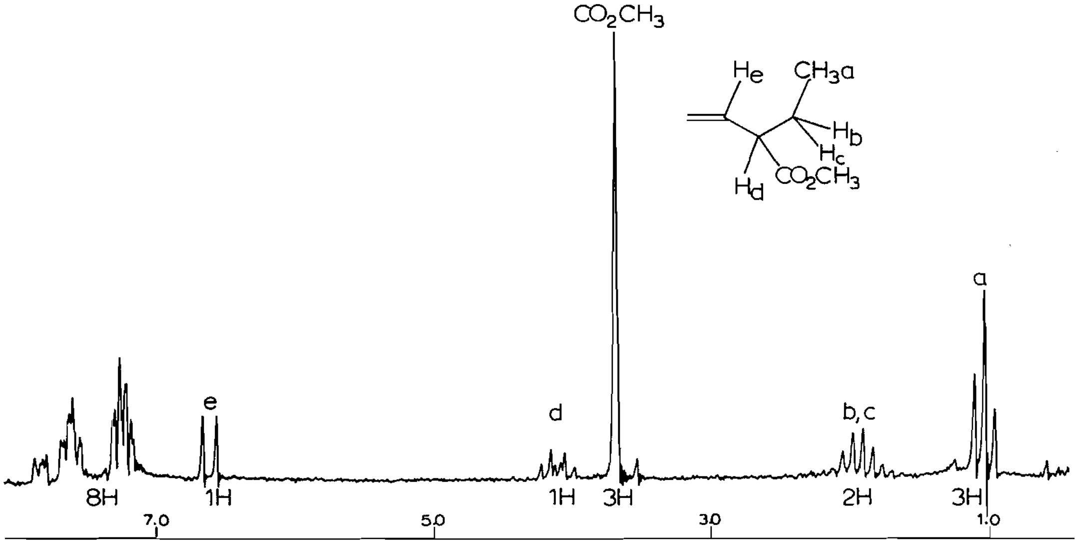
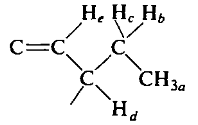


FIG. 3. The 100 MHz n.m.r. spectrum of ester **8**.

isomer and to provide further evidence on the interrelationship of the structures. Treatment of **6** in methanol with 0.4 *M* potassium methoxide at 60° led to nearly complete conversion of **6** to **7**. Further reaction led to the complete disappearance of **7** and the formation of new and unidentified products. This result requires that the isomer with the conjugated double bond (**7**) is the more stable of the two.

Unlike esters **6** and **7**, the mass spectrum (parent peak at $m/e = 278$) and the integrated n.m.r. spectrum (Fig. 3) of ester **8** are consistent with the presence of just one fluorenyl nucleus and one carbomethoxy group. The structure of the attached carbon chain for this compound also was elucidated with decoupling experiments.

Irradiation in the region of the signals due to the two protons labelled *b*, *c* resulted in the collapse of the perturbed methyl triplet (proton *a*) at high field to a singlet and the collapse of the one proton doublet of triplets (proton *d*) at $\delta = 4.13$ into a doublet. This same multiplet (*d*) at $\delta = 4.13$ changes to a triplet when irradiation is applied to the signal at $\delta = 6.62$ (proton *e*). Conversely irradiation of the signal at 4.13 p.p.m. collapses the doublet at 6.62 (proton *e*) to a singlet and the character of the two proton multiplet (proton *b*, *c*) at 1.96 p.p.m. alters but to more than four lines. The following carbon skeleton is suggested.



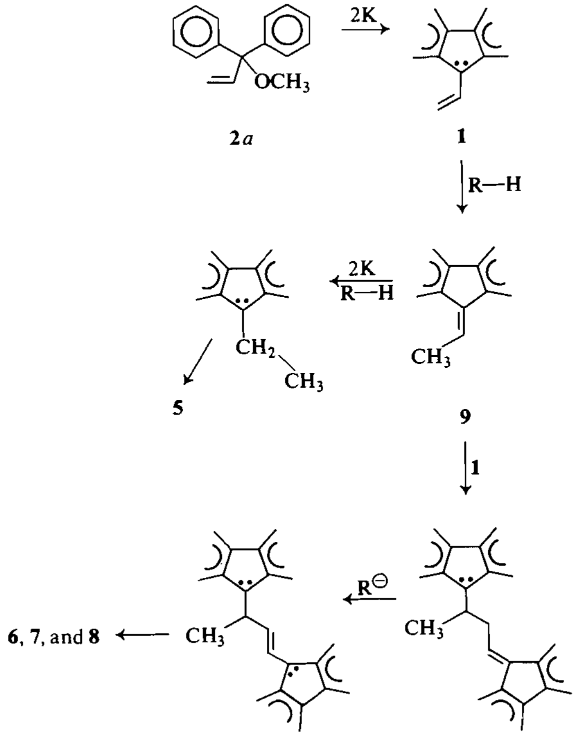
From the complexity of both the decoupled and undecoupled signal due to protons *b*, *c* it is apparent that the methylene protons are magnetically nonequivalent. On the basis of a first order analysis, the spectral parameters have been partially assigned: $\delta_a = 1.24$, $\delta_{b,c} \approx 1.96$, $\delta_d = 4.13$, $\delta_e = 6.62$, and $J_{ab} = 7.4$, $J_{bd} = 7.0$, and $J_{ed} = 9.8$ Hz. The structure of ester **8** is completed by attaching the fluorenyl ring and the carbomethoxy grouping.

The separation of these four esters (**5**, **6**, **7**, and **8**) was sufficiently involved that only low yields of purified materials were obtained. The yields of the various esters, indicated under their formulas, were estimated from the n.m.r. spectrum of the original ester mixture and account for about two-thirds of the original material.

Discussion

The unique feature of the reaction of **2a** is the apparent absence of the monomeric anion **1**, as judged by n.m.r. of the anions and of the CO_2 quenched material. Instead, significant amounts of dimeric products were produced. As was mentioned in the Introduction section, reductive cleavage of unsaturated ethers by alkali metals usually succeeds and has been applied fairly widely (1). Reagents commonly used are potassium, sodium, sodium–potassium alloy, lithium or magnesium in ether, tetrahydrofuran, or hexamethylphosphoramide (2). Thus allylmagnesium phenoxide (3), allyllithium (4), allylsodium (5), and allylpotassium (6) have all been prepared in reasonable yield from allylphenylether or diallylether.

Unlike ethers **2b–d**, **3**, and **4**, ether **2a** produces an anion which reacts further to eventually dimerize. Aside from ester **5**, the other isolated products, **6**, **7**, and **8**, seem to have arisen from an end to middle coupling of the original carbon skeleton. This structural feature can be accommodated if 9-ethylidenefluorene **9** is generated as an intermediate in the reaction (see Scheme 1).



This olefin **9** could arise by protonation of **1** (10) as the monoanion or in a more highly charged form (11–13). Reduction of **9** to the 9-ethylfluorenylanion with eventual production[2] of ester **5** and addition of **1** across the double bond (14) of **9** could follow. The polymerization reaction could terminate at the dimeric stage with formation of the dianion. Ester **8** apparently arises following carbon–carbon bond cleavage (1) of one of the dimeric species. Esters **6** and **7** arise upon carbonation and methylation of the dimeric anions. While a variety of ions and radicals can be involved as intermediates, the present results do not bear on this feature and only a simplified mechanism is included.

Polymerization has been reported for cinnamylethers and 2-phenylallylphenylether during reductive cleavage by alkali metals (2, 3). Unlike **2a**, these ethers could be viewed as substituted styrenes and thus are prone to polymerize in the presence of carbanions (15). Ether **2a** first required a double bond shift and then reaction in a manner similar to the styrenes.

Experimental

Infrared spectra were obtained of carbon tetrachloride solutions with a Beckman IR-10. The n.m.r. spectra (CCl_4 or $CDCl_3$) were run on a Varian HA-100 spectrometer using internal TMS. Mass spectra were obtained using a Varian M-66 mass spectrometer. Melting points and boiling points are uncorrected. Microanalyses were run by A. B. Gygli, Toronto.

The tetrahydrofuran used as solvent was freshly distilled from lithium hydride onto sodium–potassium alloy. The tetrahydrofuran-d_8 (Stohler Isotope Chemicals) was dried with sodium–potassium alloy before use.

9-Methoxy-9-vinylfluorene

Reaction of 90 g (0.5 mol) of 9-fluorenone with a 300 ml tetrahydrofuran solution of vinylmagnesium bromide prepared from 14.6 g (0.6 g-atoms) of magnesium turnings and 70 g (0.65 mol) of vinylbromide yielded 9-vinyl-9-fluorenol. Recrystallization from ether-ligroin gave 121 g (0.45 mol, 90%) of material (m.p. 89–90°, lit. (16) m.p. 91°).

The methyl ether was prepared (17) by stirring a mixture of 50 g (0.25 mol) of 9-vinyl-9-fluorenol, 60 ml (0.96 mol) of methyl iodide, 129 g of barium oxide and 0.8 g of water in 20 ml of dimethylformamide for 40 h at 20 °C. Water–methylene chloride extraction was followed by elution chromatography on alumina using 5% ether in pentane. Recrystallization from 2:1 methanol–water yielded 49 g (88%) of colorless crystals, m.p. 50–51°.

The infrared (i.r.) showed band at 1186 cm^{-1} attributable to the ether C—O stretch. The n.m.r. spectrum in CCl_4 appeared consistent with the expected structure. The aromatic protons appeared as a multiplet δ 7.04 to 7.52 (8H), the methoxy protons appeared as a singlet δ 2.75 (3H) and the vinyl protons (3H) appeared as a multiplet which was analyzed as an ABC pattern with $\delta_A = 5.83$, $\delta_B = 5.42$, $\delta_C = 5.04$, and $J_{AB} = 17.2$ Hz, $J_{BC} = 1.7$ Hz, and $J_{AC} = 10.6$ Hz.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.34. Found: C, 86.34; H, 6.41.

Reaction of 9-Methoxy-9-vinylfluorene

Sodium-potassium alloy (5.7 wt% sodium; 6 ml, 108 mmol) was added to a solution of 9-methoxy-9-

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[2] Treatment of a sample of **9** with sodium–potassium alloy under the reaction conditions followed by carbonation and methylation produced **5** in about 15% yield.

vinylfluorene (12 g, 54 mmol) in 450 ml of tetrahydrofuran. The tetrahydrofuran solution was degassed and the atmosphere exchanged for argon before addition of the alloy. The solution was stirred at room temperature for 48 h and acquired a deep red color.

The anions were carbonated by slow addition of the deep red solution to 100 ml of tetrahydrofuran saturated with dried carbon dioxide. The reaction mixture was stirred at room temperature and carbon dioxide was constantly bubbled into the solvent. The resulting pale green solution was stirred for another hour and the majority of the tetrahydrofuran removed with a rotary evaporator.

The reaction products were extracted with dilute sodium hydroxide – ether. The aqueous layer was acidified and extracted with ether to yield 10.2 g (85 wt%) of acids, and neutrals amounting to 1.2 g were obtained.

Thin layer chromatography of the neutral fraction indicated the absence of 9-methoxy-9-vinylfluorene while t.l.c. of the acid fraction using 3% acetic acid in chloroform on silica gel suggested at least 9 components.

The mixture of acids was methylated using both diazomethane and boron trifluoride etherate-methanol. The ester mixture prepared by either route appeared to be of the same composition as judged by t.l.c. on silica gel using 30% ether-pentane and contained about nine components. The conversion of acids to esters appeared to be complete on the basis of weight (103 wt.% yield) and n.m.r.

Separation of the Esters

A gross separation of the ester mixtures from the diazomethane reactions was obtained with elution column chromatography. The esters were chromatographed on silica gel eluting with 30% ether in pentane. Two major components, labelled esters **6** and 7, were collected in a purified state. Further purification with thick layer chromatography, eluting three times with 10% ether–pentane yielded nearly pure samples of both esters. Each ester was then recrystallized from methanol to yield sharp melting colorless crystals.

Ester **6**: m.p. 118–119°. The i.r. peak due to the ester carbonyl appeared at 1730 cm^{-1}.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.86; H, 5.93. Found: C, 86.76; H. 5.92.

Ester 7: m.p. 162–163°. The i.r. carbonyl peak appeared at 1730 cm^{-1}.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.86; H, 5.93. Found: C, 86.61; H, 5.90.

The less pure fractions containing ester **6** from the column chromatography showed three carbomethoxy signals in the n.m.r. spectrum. The remaining ester **6** was removed from this material by thick layer chromatography eluting three times with 10% ether–pentane. The remaining band was extracted and n.m.r. indicated a mixture of two esters. These were separated and collected using g.l.p.c. (¼ in. × 6 ft column of 10% SE-30 on 45-60 Chromosorb W) with a column temperature of 220 °C.

The two components were labelled esters **5** and **8.** Ester **8** was a liquid which was distilled using a molecular still (b.p. 60–63° @ 0.05 mm of Hg). The i.r. showed an ester carbonyl at 1727 cm^{-1}.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 80.42; H, 6.73.

Ester **5** was a solid which was sublimed under vacuum to yield material of m.p. 77–78°. Admixture with an authentic sample **1** of the methyl ester of fluorene-9-ethyl-9-carboxylic acid gave m.p. 77–78°.

A comparison of the n.m.r. spectra of the separated esters **5** and **8** with the mixture before g.l.p.c. indicated that no chemical changes had occurred during the separation.

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