2,7 g (11,5 mMol) **15** wurde das Gemisch 30 Min. bei – 35° gerührt und anschliessend mit einer Lösung von 5,7 ml (92 mMol) Methyljodid in 25 ml abs. Äther versetzt. Man liess unter Rühren das Ammoniak verdampfen und verteilte nach Zersetzen mit Butanol-Eiswasser zwischen Natriumhydrogencarbonat-Lösung und Chloroform. Man erhielt 3 g kristallines Rohprodukt, das aus Isopropyläther 2,38 g (83%) **16** in hellgrauen Kristallen vom Smp. 141–142° lieferte. UV. λ_{max}: 288 (3,82); 300 (3,70) nm (log ε). NMR. ($CDCl_3$): *M*/1,6–2,4/2H; *M*/2,7–3,3/4H; *S*/3,72/3H; *S*/5,65/1H; *M*/7,1–7,4/4H; *M*/7,8–8,1/1H.

$C_{13}H_{15}NS_2$	Ber.	C 62,6	H 6,1	N 5,6	S 25,7%
(249,4)	Gef.	,, 62,9	,, 6,1	,, 5,5	,, 25,8%

1-Methyl-3-(2-methyl-1,3-dithian-2-yl)-indol (**17**): In eine bei – 20° gerührte Lösung von 250 mg (1 mMol) **16** in 30 ml abs. Tetrahydrofuran wurden unter Stickstoff 4 mMol n-Butyllithium in Hexan eingetragen. Nach 5 Std. Rühren bei – 20° versetzte man mit 1 ml Methyljodid und liess über Nacht bei Raumtemperatur stehen. Nach Aufarbeitung wie für **16** erhielt man 310 mg eines halbkristallinen Produktes, das aus Isopropyläther kristallisierte. Nach Umkristallisation aus Methylenchlorid/Isopropyläther unter Aktivkohlezusatz 140 mg (53%) **17** in farblosen Nadeln vom Smp. 159–160°. UV. λ_{max}: 289,5 (3,79); 300 (3,70) nm (log ε). NMR. ($CDCl_3$): *M*/1,8–2,2/2H; *S*/2,05/3H; *M*/2,7–3,1/4H; *S*/3,75/3H; *M*/7,0–7,4/4H; *M*/8,0–8,3/1H.

$C_{14}H_{17}NS_2$	Ber.	C 63,8	H 6,5	N 5,3	S 24,3%
(263,4)	Gef.	,, 63,9	,, 6,3	,, 5,5	,, 24,5%

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11. A Novel Synthesis of 2,6-Diolefinic Esters: Ethyl and Methyl *trans*-2,*cis*-6-Dodecadienoate, two Bartlett Pear Constituents

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(17. XI. 71)

Summary. Ethyl and methyl *trans*-2,*cis*-6-dodecadienoate, two Bartlett pear constituents, have been prepared by a novel two-step synthesis: 1,6-addition of lithium di-*cis*-1-heptenylcuprate to ethyl or methyl *trans*-2,4-pentadienoate gave exclusively the 3,6-diolefinic esters, which were isomerized to the desired 2,6-diolefinic esters. The double-bond geometry of the vinyl unit is retained during the addition step.

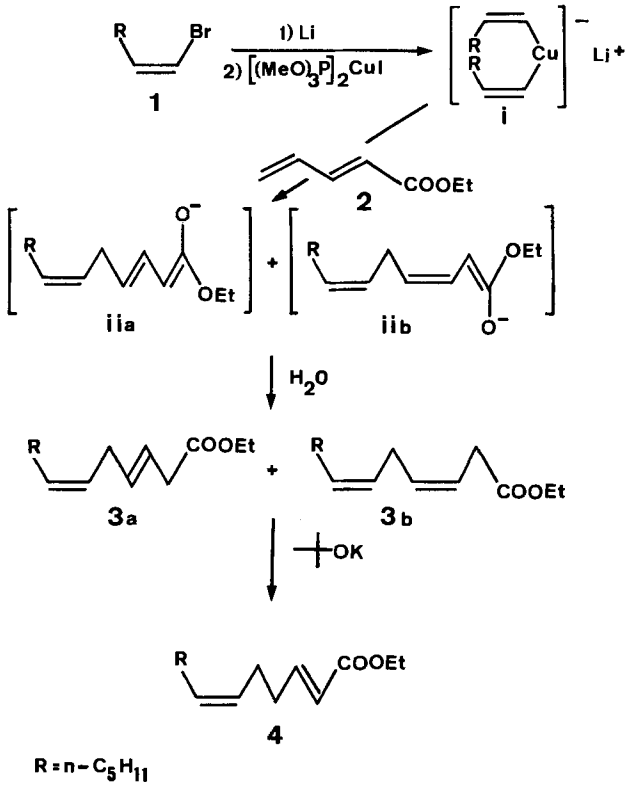
The volatile fraction of Bartlett pear contains a large number of esters of mono- and poly-unsaturated fatty acids [1–3]. With the exception of the Δ^2-monoethylenic esters, they are not readily accessible. Only the C-1 to C-6 *n*-alkyl *trans*-2,*cis*-4-deca-

dienoates [2] [4] have so far been synthesized. For the preparation of the latter, as well as for that of *cis*-4-decenoates, an efficient synthesis has been developed in our laboratory based on the stereospecific addition of vinyl-cuprolithium complexes to α,β-unsaturated carbonyl compounds [5].

In the present communication we report a facile synthesis of two further *Bartlett* pear constituents, ethyl and methyl *trans*-2,*cis*-6-dodecadienoate, (**4**) and (**5**). These esters, which have recently been isolated and characterized by *Jennings et al.* [3], have proved essential to the reconstruction of good pear flavour.

Ethyl trans-2,cis-*6-dodecadienoate* (**4**). The key step of our synthesis consists of a formal *1,6-addition* of lithium di-*cis*-1-heptenylcuprate (**i**)[1]) to ethyl *trans*-pentadienoate (**2**) [8] which gives a 1:1 mixture of ethyl *trans*-3,*cis*-6-dodecadienoate (**3a**) and the *cis*-3,*cis*-6-isomer **3b** in 55% yield. None of the *trans*-Δ^6-isomer has been found, showing that the *cis*-geometry of the vinylcuprate is retained in the addition step as in the analogous 1,4-addition to α,β-unsaturated carbonyl compounds [5].

Scheme



[1]) Prepared by reaction of *cis*-1-heptenyllithium with $[(CH_3O)_3P]_2CuI$ according to [5]; see also [6] [7].

The reaction of lithium organocuprate with a 2,4-dienoic ester has not yet been reported[2]; but it is related to the known Cu^I-catalysed conjugate addition of *Grignard* reagents to 2,4-dienoic esters [10] and ketones [11], which also produces 1,6-addition products only. We assume that in our reaction the intermediate dienolates **iia** and **iib** are formed, which, like other 1,3-dienolates [12], are exclusively protonated at C-2 to give the deconjugated 3,6-dienoic esters **3a** and **3b**. The desired 2,6-dienoic ester (**4**) is therefore not obtained directly from the 1,6-addition reaction. However, isomerization of the Δ^3-double bond in **3a** or **3b** is readily accomplished by potassium *t*-butoxide in *t*-butanol and gives isomerically pure ethyl *trans-2,cis*-6-dodecadienoate (**4**), along with some unchanged **3a** and **3b**.

Methyl trans-*2*,cis-*6-dodecadienoate* (**5**) has been prepared analogously.

The spectra (MS. and IR.) of the synthetic esters **4** and **5** are in good agreement with those reported by *Jennings et al.* [3].

Experimental[3]. – *Ethyl esters* **3a** *and* **3b**. A solution of 19 g (0.107 mol) of *cis*-1-heptenyl bromide [5] in 30 ml of anhydrous ether was reacted with 1.5 g (0.214 g-atom) of finely cut lithium (with 1.5% Na) in 30 ml of anhydrous ether at $-10°$. The resulting solution was added, dropwise and with stirring, to a suspension of 23.6 g (0.054 mol) of $[(CH_3O)_3P]_2CuI$ [7] in 150 ml of dry ether at $-30°$, and the red mixture was stirred an additional 15 min to complete solution. A solution of 6.75 g (0.054 mol) of ethyl *trans*-2,4-pentadienoate (**2**) [8] in 20 ml of ether was added at $-30°$. After stirring for 30 min at $-30°$, the mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with ether. The ethereal extract was washed, dried ($MgSO_4$), concentrated, and filtrated in hexane-ether 4:1 through a column of 100 g of silica gel to give 15 g of yellow oil. Chromatography on 300 g of silica gel with hexane-ether 95:5 afforded, after distillation at 80–82°/0.02 Torr, 6.57 g (55%) of a preparatively unseparable 1:1 mixture of **3a** and **3b**. – NMR. spectrum: δ = 0.89 (3H, CH_3); 1.2 (3H/*t*, J = 7 Hz, CH_3); 1.75–2.3 (2H/*m*, =C–CH_2); 2.6–3.1 (4H/2 *m*, =C–CH_2–C=, =C–CH_2–C=O); 4.05 (2H/*q*, J = 7 Hz, O–CH_2); 5.1–5.7 (4H/2 *m*, =CH) ppm. – IR. spectrum (neat): 1735 (C=O); 965 (C=C *trans*); 730 (C=C *cis*) cm^{-1}. – MS.: *m/e*: 224 (10), 195 (<0), 178 (18), 150 (22), 136 (54), 121 (17), 107 (14), 93 (45), 79 (100), 67 (84), 55 (55), 41 (57).

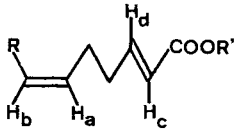
Ethyl ester **4**. To 20 mg of potassium dissolved in 10 ml of abs. *t*-butanol under argon 1 g (4,5 mmol) of a 1:1 mixture of **3a** and **3b** was added. After the yellow reaction mixture had been stirred 5 days at room temperature it was diluted with water, extracted twice with pentane, washed with H_2O and NaCl solution, dried ($MgSO_4$), and concentrated. Bulb distillation at 110° (external temp.)/0.1 Torr gave 750 mg of an oil, which, on separation by gas liquid phase chromatography (5% Carbowax, 200°), yielded 68% of ester **4** and 32% of esters **3a** and **3b**. – Ester **4**: NMR. spectrum[4]: δ = 0.89 (3H, CH_3); 1.23 (3H/*t*, J = 7 Hz, CH_3); 1.7–2.5 (6H/3 *m*, 3 = C–CH_2); 4.07 (2H/*q*, J = 7 Hz, O–CH_2); 5.3 (2H/*m*, C=CH_{a+b}); 5.7 (1H/*d*, J = 16 Hz, C=CH_c); 6.83 (1H/*d*, J = 16 Hz, C=CH_d) ppm. – IR. spectrum (neat): 1720 (C=O conj.); 1655 (C=C conj.); 972 (C=C *trans*, conj.); 720 (C=C *cis*) cm^{-1}. – MS.: *m/e*: 224 (<1), 179 (5), 114 (100), 95 (7), 86 (41), 69 (58), 55 (45), 41 (37).

Methyl ester **5**. This was prepared similarly from methyl *trans*-2,4-pentadienoate. – NMR. spectrum[4]: δ = 0.91 (3H, CH_3); 1.8–2.5 (6H, 3 = C–CH_2); 3.7 (3H/*s*, O–CH_3); 5.42 (2H/*m*,

[2] After completion of the present manuscript, *Marshall et al.* [9] published an interesting investigation on the regioselectivity in the conjugate addition of lithium dimethylcuprate to 2,4-dienones of the decalin type.

[3] For general remarks see experimental section of [5].

[4] Designation of olefinic protons:



$C=CH_{a+b}$); 5.83 (1H/broad *d*, J = 16 Hz, $C=CH_c$); 7.0 (1H/broad *d*, J = 16 Hz, $C=CH_d$) ppm. – IR. spectrum (neat): 1727 (C=O conj.); 1660 (C=C conj.); 970 (C=C *trans*, conj.); 720 (C=C *cis*) cm^{-1}. – MS.: *m/e*: 210 (<1), 179 (2), 100 (100), 81 (8), 69 (69), 55 (52), 41 (57).

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12. Quinacridones: Structure and Mechanism of Formation

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(16. VIII. 71)

Summary. The NMR. spectra of two acridones and twenty-two quinacridones in $(CD_3)_2SO$—NaOD are reported. A NMR. technique is described for determining the composition of mixtures of various substituted quinacridones. A general mechanism is proposed for quinacridone formation *via* cyclodehydration of 2,5-diarylamino-terephthalic and 2,5-diarylamino-1,4-benzoquinone-3,6-dicarboxylic acids/esters.

Introduction. – After the initial controversy over the structure of 5,7,12,14-tetrahydro-quino[2,3-*b*]acridine-7,14-diones[1]) (I) (linear *trans*-quinacridones) had been resolved in 1935 by *Liebermann* [1], research in the chemistry of these heterocycles remained quiescent for the next two decades. The utility of quinacridones as synthetic organic pigments was first recognized by *DuPont* chemists, and interest in their chemistry subsequently revived.

The most commonly used methods for the synthesis of quinacridones (I) are shown in Chart 1 [2]:

[1]) Chemical Alstracts name: quino[2,3-*b*]acridine-5, 12-dihydro-7, 14-diones (Editor).