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## ✿ A Comparison of Conventional and in situ Methods of Transesterification of Seed Oil from a Series of Sunflower Cultivars

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### ABSTRACT

The cost of vegetable oil monoesters represents one of the major restrictions on their use as an alternative fuel for diesel engines. This cost can be reduced by increasing the yield of esters produced from a given quantity of oilseed.

Transesterification of sunflowerseed oil in situ with acidified methanol has been shown to produce fatty acid methyl esters in yields significantly greater than those obtained from conventional reaction with pre-extracted seed oil. Yield improvements of over 20% were achieved and could be related to the moisture content of the seed. Fatty ester compositions and cloud points of the products from the in situ reactions were virtually identical to those of esters produced using conventional techniques.

### INTRODUCTION

In many parts of the world considerable interest has been focused over recent years on the possibility of using vegetable seed oils and their derivatives as extenders of, or replacements for, conventional distillate as a fuel for diesel engines. The Australian position has been described by Stewart et al. (1). From the numerous reports which have appeared, it has become apparent that most seed oils and their monoesters, formed by transesterification with simple aliphatic alcohols, are capable of performing very satisfactorily in a diesel engine, particularly over the short to medium term. Some problems associated with longer term running have been identified with and attributed to the high viscosity of the vegetable oils (typically 10 times that of distillate) and to the high degree of unsaturation of the fatty acids of some candidate oils (e.g. linseed).

However, it is perhaps not in the area of performance, but in that of economics, where the widespread use of such an alternative fuel has its greatest impediment. Consequently, it is of the utmost importance that seeds of high oil content are considered and that processing efficiencies are maximized. It is to the improvement of processing efficiency that the present paper is addressed.

Bruwer and his colleagues (2) suspected that the high viscosity of sunflowerseed oil detracted from its effectiveness as a diesel fuel substitute; they introduced the practice of converting the raw oil to its methyl or ethyl monoesters by the relatively simple process of alkali-catalyzed transesterification. These simple esters of sunflower oil were of

a viscosity approaching that of conventional distillate and performed well in dynamometer tests with tractor engines.

Transesterification of vegetable seed oil is conventionally carried out by subjecting the pre-extracted oil to treatment with the appropriate alcohol, in the presence of an acid or alkaline catalyst.

The concept of transesterification of sunflowerseed oil in situ was described in an earlier report (3), and it was demonstrated there that significant increases in ester yields could be achieved by such a method. At that time, little data were presented concerning the qualitative nature of the esterified products. It is of obvious importance that the products obtained by in situ reaction be at least as suitable as a diesel fuel substitute as those derived from the conventional treatment of the oil and do not detract from this suitability by, for example, introducing more oxygenated species, increasing viscosity or raising the fuel cloud point.

This paper describes results obtained from the transesterification in situ of seed oil from a series of sunflower cultivars grown under the influence of different temperature regimes, and compares these results with those obtained from conventional transesterification of the pre-extracted oil.

### EXPERIMENTAL

#### Sunflower Seeds

Seeds were from sunflower cultivars Suncross 150 and Hysun 31, grown in an artificially controlled environment under the influence of a range of temperature regimes. Seed moisture and oil contents were evaluated and are tabulated in the next section.

#### Thin Layer Chromatography (TLC)

Thin layer chromatography was performed on glass plates coated with silica gel HF254 (Merck). The developing solvent was petroleum ether, diethyl ether and acetic acid (85:15:1, v/v/v). Iodine vapor was used for visualization.

#### Gas Liquid Chromatography (GLC)

Gas liquid chromatography was carried out on a Pye Series 104 Gas Chromatograph equipped with a flame ionization detector, using nitrogen as carrier gas. Separation of the fatty acid methyl esters was accomplished using a glass

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column (2m × 5mm) packed with diethyleneglycol succinate (25%) on Chromasorb W. Calibration of the chromatograph was carried out by direct injection of pure methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. Detector response was linear for each of the esters studied.

### Conventional Transesterification

Transesterification of the pre-extracted oils was carried out according to the following example: Sunflower oil (Hysun 31, 27/22 C [see Table I], 177.8 g) and anhydrous methanol (1 liter) were heated together at reflux for 5 hr in the presence of concentrated sulphuric acid (30 ml). The products were transferred to a separatory funnel with petroleum ether (300 ml) and washed with water until the washings were neutral (3 × 500 ml). Emulsions which formed during the washing stage were readily broken by the addition of sodium chloride. The organic layer was dried over sodium sulfate and the solvent removed under vacuum. The esterified product (169.2 g, 95.2%) was obtained as a pale, amber-colored mobile liquid. Thin layer chromatography indicated the presence of a small amount of unreacted oil. Distillation under reduced pressure (150 C, 0.1 mm) gave the pure methyl esters (144 g, 81% on original oil basis).

### Transesterification in Situ

Transesterification of sunflower oil was carried out in situ using whole seeds according to the following example: Whole seeds (Hysun 31, 21/16 C, 20.6 g) were macerated in methanol (50 ml) in a laboratory homogenizer to give a product with the particle size of coarse sand. The slurry was transferred quantitatively to a round bottom flask (500 ml), and methanol was added to a total volume of 150 ml. The mixture was heated at reflux for 4 hr with a catalyst of concentrated sulfuric acid (6 ml). The reaction mixture was filtered through sintered glass, and petroleum ether (150 ml) was added to the filtrate. The petroleum ether solution was washed with water (4 × 150 ml) until the washings were neutral. The organic layer was dried over sodium sulfate, filtered and evaporated to give the esterified product (7.7 g, 37.5% on air-dried whole seed basis). TLC showed the product to contain only small traces of unreacted oil.

The seed residue from the above filtration felt oily to the touch and was re-extracted in a Soxhlet apparatus for 5 hr with n-hexane to yield a further quantity (0.6 g) of esterified product, giving a total yield of 8.3 g (40.4% on air-dry seed basis). Distillation under reduced pressure (0.1 mm, 160 C) gave the pure methyl esters (8.0 g, 38.9% on air-dry seed basis).

## RESULTS AND DISCUSSION

The sunflower cultivars used in these experiments provided a convenient selection of seeds with different moisture and oil contents and with fatty acid compositions varying over a wide range.

The processes of conventional and in situ transesterification are summarized schematically in Figure 1.

### Maceration and Oil Extraction (A-B)

Maceration of the whole seeds, as described in the Experimental Section, followed by hexane extraction for 9 hr, should remove all of the accessible oil and any other materials (e.g. waxes) which are soluble in the hydrocarbon. In the present work, oil extraction was carried out on a small scale (ca. 20 g seeds) to evaluate seed oil content and on a larger scale (ca. 200 g seeds) to provide sufficient material for further studies. Oil contents measured on the small scale were consistently higher than those obtained from the larger scale extractions. Since the seeds were prepared and treated

TABLE I

Oil Contents (%) of Sunflower Cultivars

Sample	Small-scale		Large-scale	
	Air-dry basis	Moisture-free basis <sup>b</sup>	Air-dry basis	Moisture-free basis
Suncross 150				
15/10 C <sup>a</sup>	34.5	36.0	32.2	33.6
21/16 C	42.8	45.1	34.5	36.3
24/19 C	44.0	46.1	36.8	38.5
27/22 C	39.7	42.1	38.2	40.5
30/25 C	42.8	44.6	39.8	41.5
Hysun 31				
15/10 C	33.7	35.0	36.5	37.8
21/16 C	40.6	42.7	34.7	36.4
24/19 C	48.8	51.4	42.9	45.2
27/22 C	43.5	—	35.4	—

<sup>a</sup>Figures denote "day" temperatures (8 hr) and "night" temperatures (16 hr) of the artificially controlled environment.

<sup>b</sup>The moisture referred to here is that removed from a macerated sample by treatment for 3 hr with toluene in a Dean and Stark apparatus.

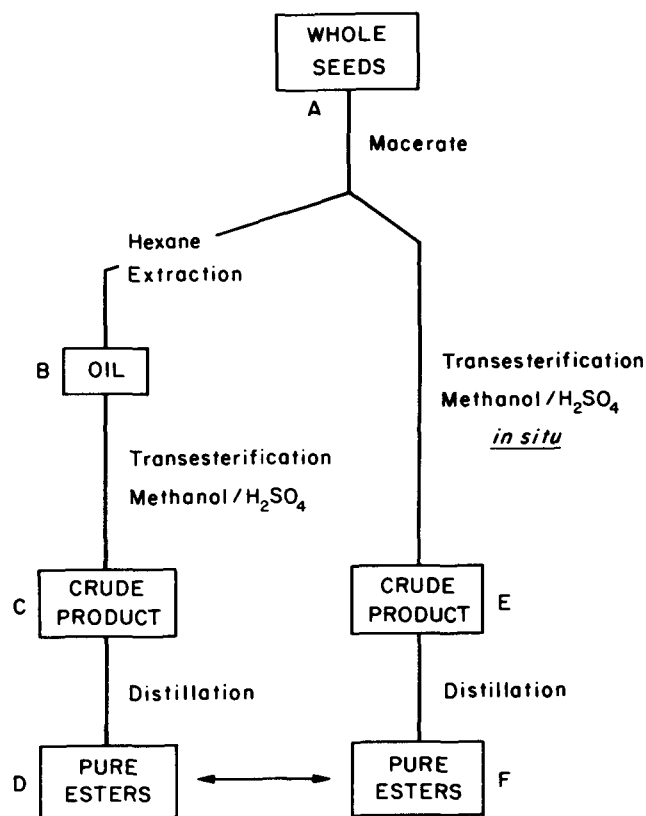


FIG. 1. Schematic summary of conventional and in situ transesterification processes.

identically in all cases, it appears that the Soxhlet extraction was more efficient on the smaller scale than it was on the larger, perhaps due to solvent channeling in the latter case. Oil contents are shown in Table I. Examination of these oils by TLC failed to detect any qualitative differences.

### Conventional Oil Transesterification (B-C-D)

Transesterification of the extracted oil in boiling methanol with a sulphuric acid catalyst gave, after water washing,

## IN SITU ESTERIFICATION OF SEED OIL

TABLE II

Yields of Crude and Purified Esters from Conventional Transesterification

Sample	Yield of crude esters (%)		Yield of purified esters (%)	
	Oil basis	Seed basis	Oil basis	Seed basis
<b>Suncross 150</b>				
15/10 C	96.3	33.2 (34.6) <sup>a</sup>	92.7	32.0 (33.4)
21/16 C	93.5	40.0 (42.1)	87.3	37.4 (39.4)
24/19 C	97.9	43.1 (45.2)	85.5	37.6 (39.4)
27/22 C	92.0	36.5 (38.7)	89.2	35.4 (37.6)
30/25 C	96.2	41.2 (42.9)	88.4	37.8 (39.4)
<b>Hysun 31</b>				
15/10 C	95.8	32.3 (33.5)	89.6	30.2 (31.3)
21/16 C	96.0	39.0 (40.9)	92.3	37.5 (39.4)
24/19 C	94.9	46.3 (48.7)	94.0	41.0 (43.2)
27/22 C	95.2	41.4 ( - )	80.4	35.0 ( - )

<sup>a</sup>Figures in parentheses are for yields calculated on a solvent-dried basis. All other yields are on the basis of air-dried seeds.

TABLE III

Yields of Crude and Purified Esters from Transesterification in Situ

	Yield of esters (% seed basis)			
	Crude		Purified	
<b>Suncross 150</b>				
15/10 C	38.9	(40.5) <sup>a</sup>	33.9	(35.3)
21/16 C	43.6	(45.9)	38.7	(40.7)
24/19 C	43.5	(45.6)	42.9	(44.9)
27/22 C	38.3	(40.6)	36.7	(39.0)
30/25 C	41.1	(42.8)	39.8	(41.4)
<b>Hysun 31</b>				
15/10 C	41.3	(42.8)	36.8	(38.1)
21/16 C	40.4	(42.4)	39.0	(40.9)
24/19 C	47.9	(50.4)	45.5	(47.9)
27/22 C	42.0	( - )	41.1	( - )

<sup>a</sup>Figures in parentheses are for yields calculated on a solvent-dried basis.

TABLE IV

Effect of Transesterification in Situ on Ester Yields<sup>a</sup>

	Crude	Purified
<b>Suncross 150</b>		
15/10 C	117.1	105.7
21/16 C	109.0	108.8
24/19 C	100.9	114.0
27/22 C	104.9	103.7
30/25 C	100.0	105.1
<b>Hysun 31</b>		
15/10 C	127.8	121.7
21/16 C	103.7	103.8
24/19 C	103.5	110.9
27/22 C	101.4	117.4

<sup>a</sup>Relative to conventional yield = 100.

## Transesterification in Situ (A-E-F)

Acid-catalyzed transesterification in situ with boiling methanol gave a crude product of composition similar to that from the conventional reaction with pre-extracted oil. Vacuum distillation gave the purified product. Figure 2 compares the thin layer chromatograms of the products from conventional and in situ reactions. The yields of crude and purified esters from the in situ reaction are listed in Table III.

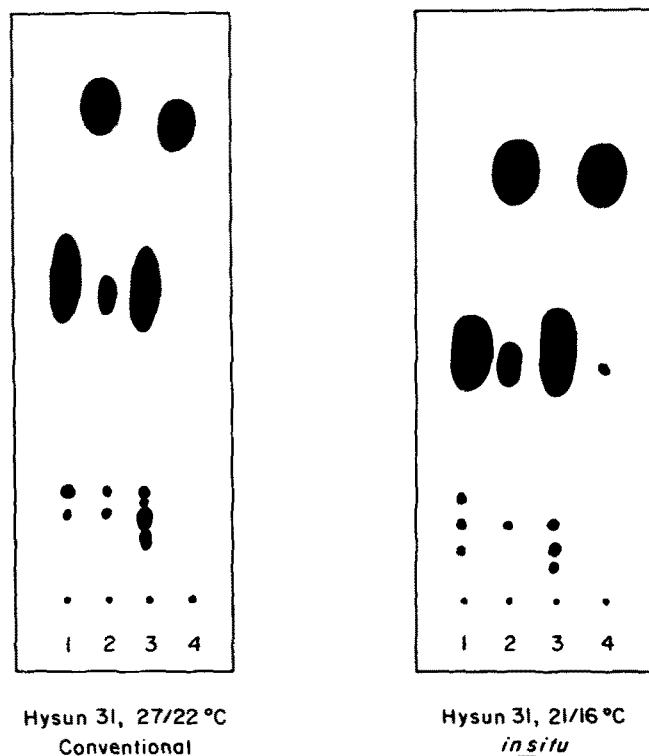
Inspection of Tables II and III shows that in all cases, the yields of methyl esters obtained from in situ reactions were greater than those from the conventional treatments.

Table IV summarizes these results and expressed the increases relative to yields obtained from conventional methods.

Although the crude esterified product from the in situ reaction might be expected to contain a range of compounds arising from the treatment with acidified methanol and soluble in methanol and/or n-hexane, TLC analysis indicated that the non-ester components closely correspond to those contained in the seed oil, extracted with n-hexane in the normal manner. Similarly, the distilled product was shown to contain nearly pure fatty acid methyl esters.

## Effect of Moisture on Reaction in Situ

Since water is a competing reagent, the efficiency of the transesterification reaction should be highest when conducted under anhydrous conditions. In the cases where pre-extracted seed oil is transesterified with methanol, this



1. Extracted oil
2. Crude transesterification products
3. Distillation residue
4. Pure methyl esters

FIG. 2. Thin layer chromatography of products from conventional and in situ transesterification.

a crude product containing the fatty acid monoesters, unreacted oil and other substances in small amounts. Vacuum distillation of the crude product gave the methyl esters in purified form. Table II lists the yields of both crude and purified products.

TABLE V

Effect of Seed Moisture on Ester Yields from in Situ Reaction<sup>a</sup>

	Crude yield (%)		Purified yield (%)	
	Moist	Dry	Moist	Dry
<b>Suncross 150</b>				
15/10 C	40.5	41.5	35.3	38.8
24/19 C	45.6	48.8	44.9	42.0
<b>Hysun 31</b>				
15/10 C	42.8	45.5	38.1	40.8
21/16 C	42.4	44.9	40.9	42.6

<sup>a</sup>Yields calculated on solvent-dried basis.

TABLE VI

Moisture Contents of Oilseeds (%)

	Air dried basis	Solvent dried basis	Oven-dried basis
			(130 C)
<b>Suncross 150</b>			
15/10 C	4.05	4.22	
21/16 C	5.00	5.26	
24/19 C	4.55	4.77	5.09
27/22 C	5.73	6.08	
30/25 C	3.99	4.16	
<b>Hysun 31</b>			
15/10 C	3.53	3.66	
21/16 C	4.73	4.96	5.21
24/19 C	4.99	5.25	
27/22 C	—	—	

condition is closely approached, because the moisture content of the extracted oil is virtually zero. However, when the esterification reaction is carried out on the seed oil in situ, the air-dried seed moisture content (ca. 5%) can be expected to give rise to a lower ester yield.

To examine this possibility, seed samples from four cultivars were macerated and solvent-dried with toluene in a Dean and Stark apparatus. The dried residue was then transesterified in situ in the usual way. Ester yields are shown in Table V and are compared with corresponding yields from esterification of the air-dried or "moist" seeds.

It can be seen from Table V that ester yields are generally improved as water is excluded from the transesterification reaction. It should be noted that solvent drying did not produce a completely dry seed. On heating the solvent-dried, macerated oilseed at 130 C for 3 hr, a small amount of water could be driven off, together with other volatiles. Moisture contents of the oilseeds used in these investigations are listed in Table VI.

### Fatty Acid Composition of Esters

The esterified products obtained from both conventional and in situ reactions were analyzed by GLC, and the fatty acid compositions were evaluated. Table VII lists the weight percentages of each of the four principal methyl esters.

### Physical Properties of the Esters

Reactions carried out in situ using the whole seed introduce the possibility that chemical substances other than the methyl esters from triglycerides may find their way through the process to contaminate the final esterified product. Compounds such as high molecular weight waxes could detract from the fuel value of the final product by changing the critical properties of viscosity and cloud point. Table

TABLE VII

Weight Percentages of Principal Fatty Esters in Products from Conventional and in Situ Transesterification

	Conventional		in Situ	
	Crude	Purified	Crude	Purified
<b>Suncross 150</b>				
15/10 C				
Methyl palmitate (P)	6.5	6.6	7.2	7.4
Methyl stearate (S)	11.8	11.9	12.6	12.7
Methyl oleate (O)	12.2	12.1	13.4	13.4
Methyl linoleate (L)	69.5	69.4	66.8	66.5
<b>Suncross 150</b>				
21/16 C				
P	5.9	5.8	6.2	6.2
S	9.1	9.3	7.6	7.6
O	25.8	25.9	24.0	24.0
L	59.3	59.0	62.2	62.2
<b>Suncross 150</b>				
24/19 C				
P	5.2	5.2	5.0	5.0
S	8.9	8.8	9.3	9.8
O	40.2	40.9	41.2	40.9
L	44.9	45.1	44.5	44.4
<b>Suncross 150</b>				
27/22 C				
P	5.2	5.3	5.6	5.4
S	9.2	9.4	9.4	9.6
O	47.3	47.5	48.3	48.1
L	38.4	37.8	36.7	36.9
<b>Suncross 150</b>				
30/25 C				
P	5.7	5.7	5.9	5.8
S	7.7	7.7	8.0	7.9
O	63.9	63.8	63.5	62.7
L	22.7	22.7	22.6	23.7
<b>Hysun 31</b>				
15/10 C				
P	6.5	6.5	6.7	6.8
S	10.0	10.0	10.6	10.4
O	14.0	14.1	14.1	14.2
L	69.5	69.5	68.6	68.5
<b>Hysun 31</b>				
22/16 C				
P	6.1	6.2	6.4	6.5
S	7.8	7.8	7.7	8.2
O	21.2	21.8	21.9	22.2
L	64.9	64.1	63.9	63.1
<b>Hysun 31</b>				
24/29 C				
P	5.5	5.4	5.7	5.6
S	7.8	7.4	7.5	7.6
O	38.9	40.2	40.1	39.7
L	47.8	47.0	46.7	47.1
<b>Hysun 31</b>				
27/22 C				
P	5.6	4.9	6.0	5.6
S	7.2	6.1	7.9	7.4
O	45.6	40.7	47.4	44.6
L	41.5	47.9	38.7	42.4

VIII compares the cloud points of products from in situ reaction with those of products from conventional reaction. It can be seen that the cloud point temperatures of the in situ products are generally lower than those of the esterified products of conventional methods. Density and viscosity values for the conventional products are included in the table, but insufficient material from the in situ reactions prevents a similar comparative examination.

From the data reported here, it can be concluded that:

- Methyl esters of sunflowerseed oil fatty acids can be produced satisfactorily by reaction with the oil in situ.
- Considerable increases in the yields of esters have been demonstrated by the use of in situ techniques.

TABLE VIII

Some Physical Properties of Esters Prepared by Conventional and *In Situ* Methods

	Cloud pt ( $^{\circ}$ C)		Viscosity (cP) <sup>a</sup>		Density (g/cc) <sup>a</sup>
	Conventional	<i>In Situ</i>	Conventional	Conventional	Conventional
Suncross 150					
15/10 C	3.0	3.0	5.9		0.88
21/16 C	-0.8	-5.5	5.8		0.88
24/19 C	-1.0	-0.8	6.8		0.88
27/22 C	-0.8	-1.3	5.6		0.87
30/25 C	-2.5	-2.0	6.2		0.87
Hysun 31					
15/10 C	1.5	2.0	5.8		0.88
21/16 C	-1.5	-3.5	5.4		0.88
24/19 C	-2.0	-2.0	6.7		0.88
27/22 C	-2.3	-2.5	6.5		0.87

<sup>a</sup>Dynamic viscosity and density measurements were taken at 25 C.

• Purification of the esterified crude product by distillation does not significantly change the fatty ester composition of the mixture.

- The presence of moisture in the oilseed reduces the yield of methyl esters obtained from reactions *in situ*.
- The fatty ester composition of the products derived from reactions *in situ* is essentially the same as that from conventional transesterification of the pre-extracted oil.
- The cloud points of the esters produced by *in situ* reactions appear slightly lower than those prepared by conventional methods.

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## Enolate Anions from Lipid Derivatives. Alkylation of Acylisopropylidene Glycerols

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## ABSTRACT

The enolate anions from isopropylidene protected monoacylglycerols have been successfully alkylated with alkyl iodides of various chain length. From these products the corresponding monoacylglycerols and triacylglycerols can be prepared. This is exemplified by the synthesis of 2-butyl-dodecanoyl-didodecanoyl glycerol, di-2-butyl-dodecanoyl-dodecanoyl glycerol and tri-2-butyl-dodecanoyl glycerol.

## INTRODUCTION

Branched mono- and triacylglycerols are potentially interesting for industrial use, because they have physical properties different from the corresponding straight chain analogues. For example, the 2-alkyl-branched monoacylglycerols have superior surface active properties compared to the straight chain compounds (2).

In a previous paper (1) we described the preparation of 2-alkyl-branched monoacylglycerols from the corresponding 2-alkyl-branched fatty acids. We now present the preparation of such monoacylglycerols directly from the acylisopropylidene glycerols through alkylation of their enolate anions. Cleavage of the isopropylidene group gives the monoacylglycerol, which can be acylated with acid chlorides to give branched triacylglycerols (Scheme 1). We have studied how different chain length of the monoglyceride and of the alkylating agent influence the product yields. We also have compared the efficiency of the direct alkylation method presented here, with the multistep route (1).

The preparation and alkylation of ester enolate anions has been well studied (3-14), and has been reviewed by Petragnani and Yonashiro (15). One problem with this type of reactions is the tendency of enolate anions to undergo self-condensation to form the corresponding  $\beta$ -ketoesters (3,7). This side reaction can, however, be suppressed by the

use of a low reaction temperature (-70 C) during anion preparation. Rathke and coworkers (3) have shown that even though the amount of self-condensation product is large when the anions are generated at 0 C, anions prepared at -70 C are stable even at room temperature. They also have shown that the alkylation of lithio-*t*-butylacetate is successful, while a mixture of condensation and alkylation products is obtained with lithio ethyl acetate. Furthermore, they found that lithio ethyl hexanoate could be alkylated in good yields. Thus, it seems that a long alkyl chain in the acid part and a bulky alcohol part favor alkylation compared to side reactions. If the  $\alpha$ -position is sterically hindered, for instance through alkyl groups in the  $\beta$ -position, it is even possible to prepare and alkylate the enolate anion at 0 C without condensation (6). The product yields also are dependent on the temperature and the solvent used in the alkylation step. Addition of the enolates to the alkylating agent in a mixture of tetrahydrofuran and dimethylsulfoxide at room temperature gives the best yields, according to Rathke (3), while Cregge and his coworkers (4) suggest that direct addition of the alkyl halide in THF/HMPA to the enolate at -70 C is better. On the other hand, MacPhee and Dubois (6) have found that alkylation is slow at -70 C, and that the reaction mixtures should reach room temperature before work-up. They also have reported that changing the alkylating agent from methyl to ethyl to isopropyl iodide has little effect on the yield, in the alkylation of an ester with a secondary  $\alpha$ -carbon.

## EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrometer. <sup>1</sup>H NMR