portions of ether, which were combined, dried  $(Na_2SO_4)$ , and evaporated, gave 0.51 g (92%) of the unstable tosylate 10: NMR  $(CDCl_3) \delta 4.85 \text{ (dd, 1, } J = 6.4, 7.0 \text{ Hz}); \text{ IR (neat) } 1741 \text{ cm}^{-1}.$ Addition of 0.415 g of crude 10 to a solution of hexadecyltributylphosphonium bromide (0.067 g, 0.1 equiv) and sodium azide (0.173 g, 2 equiv) in 0.7 mL of water followed by stirring for 18 h at 25 °C and a normal workup gave 230 mg of crude 11 which was used immediately for the next step.

Methyl (2R\*,4R\*)-2-Amino-4-methylhexanoate (12). Crude azido ester 11 (150 mg) was hydrogenated over W-2 Raney nickel (50 mg) as previously described to give 159 mg of crude amino ester 12 which was used immediately: NMR (CCl<sub>4</sub>)  $\delta$  3.76 (m, 1); IR (CCl<sub>4</sub>) 3390, 3330, 1741 cm<sup>-1</sup>.

Methyl (2R\*,4R\*)-2-Phthalimido-4-methylhexanoate (13). Crude amino ester 12 (0.053 g) was converted to 0.113 g of crude phthalimide as previously described. Chromatography on silica gel (1:1 petroleum ether-ether) gave 17.3 mg (24% from 1) of pure phthalimide 13 whose NMR was identical with that of an authentic sample of the 2S,4S isomer:<sup>7</sup> NMR (CDCl<sub>3</sub>)  $\delta$  4.95 (dd, 1, J = 7, 8 Hz; IR (CDCl<sub>3</sub>) 1780, 1745, 1719 cm<sup>-1</sup>.

Anal. Calcd for C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub>: C, 66.42; H, 6.62. Found: C, 66.53; H, 6.71.

(2R\*,4R\*)-2-Amino-4-methylhexanoic Acid (14). Crude amino ester 12 (92 mg) was hydrolyzed as previously described to give 30 mg of a 1:1 mixture of amino acid 14 and NaCl (30% from 1): NMR (D<sub>2</sub>O)  $\delta$  3.78 (dd, 1, J = 6.9, 6.9 Hz), 2.10–1.20 (m, 5), 1.0–0.70 (m, 3), 0.93 (d, 3, J = 5.9 Hz); <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  38.6, 31.3, 29.0, 19.4, 11.1 (the C=O and  $\alpha$ -carbons were not observed); IR (KBr) 3460, 2970, 2930, 1610, 1495, 1455, 1425, 1385, 1340, 1315, 1225, 1115, 700 cm<sup>-1</sup>.

Methyl  $(2R^*, 4S^*)$ -2-Amino-4-methyl-5-hexenoate (15). Crude 11 (71.0 mg) was reduced with CrCl<sub>2</sub> as previously described to give 57.3 mg of crude amino ester 15 which was used immediately: NMR (CCl<sub>4</sub>) & 3.73 (m, 1); IR (CCl<sub>4</sub>) 3390, 3330, 1740 cm<sup>-1</sup>.

(2R\*,4S\*)-2-Amino-4-methyl-5-hexenoic Acid (16). Hydrolysis of crude 15 (57.3 mg) as previously described gave 20.2 mg of a 1:1 mixture of amino acid 16 and NaCl (26% from 1): NMR (D<sub>2</sub>O)  $\delta$  5.80 (ddd, 1, J = 7.7, 9.8, 17.7 Hz), 5.15 (dd, 1, J = 17.7, 2 Hz, 5.12 (dd, 1, J = 9.8, 2 Hz), 3.70 (dd, 1, J = 5.2, 8.0Hz), 2.34 (apparent heptuplet, 1, J = 7 Hz), 1.7-1.97 (m, 2), 1.07(d, 3, J = 6.6 Hz); <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  175.9, 143.7, 115.8, 54.4, 38.1, 35.3, 21.0; IR (KBr) 3425, 2950, 1590, 1522, 1402, 1361, 1337, 1308, 1188, 1136, 1061, 990, 912, 855, 830, 770, 692 cm<sup>-1</sup>. The NMR spectrum was superimposable with that of a sample of natural amino acid isolated by Rudzats et al. from Boletus.<sup>5</sup>

Acknowledgment. The authors are grateful to the National Institutes of Health (Grant No. GM-23159) for financial support.

**Registry No.**  $(\pm)$ - $(R^*, S^*)$ -1, 78019-18-8;  $(\pm)$ - $(R^*, R^*)$ -1, 78019-19-9; (±)-2, 78019-20-2; (±)-3, 78019-21-3; (±)-4, 78086-84-7; (±)-5,  $78086-85-8; (\pm)-6, 78019-22-4; (\pm)-7, 78086-86-9; (\pm)-8, 78019-23-5;$ (±)-9, 78019-24-6; (±)-10, 78019-25-7; (±)-11, 78019-26-8; (±)-12, 78019-27-9; (±)-13, 78086-87-0; (±)-14, 78019-28-0; (±)-15, 78019-29-1; (±)-16, 78086-88-1; methyl  $\alpha$ -bromoacrylate, 4519-46-4; trans-2-butene, 624-64-6.

## Synthesis of Electrophilic Allyl Dichlorides

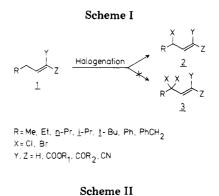
Dirk Courtheyn,\*<sup>1</sup> Roland Verhé, Norbert De Kimpe,<sup>2</sup> Laurent De Buyck, and Niceas Schamp

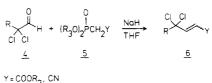
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Received September 16, 1980

Electrophilic allyl dichlorides have been prepared by starting from 2.2-dichloro aldehydes by various condensation reactions forming carbon-carbon double bonds. The Emmons-Wadsworth reaction gave rise to  $\gamma$ ,  $\gamma$ -dichloro- $\alpha,\beta$ -unsaturated esters and nitriles, while  $\gamma,\gamma$ -dichloro- $\alpha,\beta$ -unsaturated ketones were produced on condensation with 1,3-diketones. Allyl dichlorides geminally substituted with two electron-withdrawing groups in the  $\gamma$ -position were obtained by a Knoevenagel condensation with titanium tetrachloride-pyridine.

In the course of our studies toward the reactivity of geminally activated allyl halides<sup>3</sup> 2, we wanted to investigate the chemistry of mono- and diactivated alkenes 3 bearing two halogen atoms in the  $\gamma$ -position. The synthesis of the monohalogen alkenes did not give major problems as allylic halogenation of electrophilic alkenes gave rise to monohalogenation.<sup>3</sup> Chlorination of  $\alpha,\beta$ -unsaturated esters and cyanides with tert-butyl hypochlorite led to monochloro compounds,<sup>4</sup> while bromination of  $\alpha,\beta$ -unsaturated esters,<sup>5</sup> cyanides,<sup>6</sup> ketones,<sup>7</sup> and alkylidene malonates<sup>8</sup>





never afforded geminal dibromo electrophilic alkenes 3 (Scheme I). Consequently, we sought an efficient and

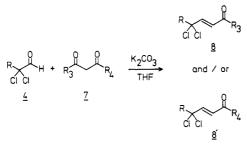
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<sup>(1) &</sup>quot;Aspirant" of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek"

<sup>(2) &</sup>quot;Bevoegdverklaard Navorser" of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek".
(3) (a) R. Verhé, N. De Kimpe, L. De Buyck, D. Courtheyn, and N. Schamp, Bull. Soc. Chim. Belg., 86, 55 (1977); 87, 215 (1978); Synthesis, 530 (1978); (b) R. Verhé, D. Courtheyn, N. De Kimpe, L. De Buyck, R. Thierie, L. Van Caenegem, and N. Schamp, Org. Prep. Proced. Int., 13, 10 (198). 13 (1981).

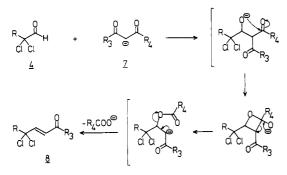
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R3, R2 = Me, Et, n-Pr, i-Pr, t - Bu, Ph

Scheme IV



viable synthetic alternative for the preparation of compounds 3.

The objective of the work reported here was to find a practical method for the synthesis of activated geminal allyl dichlorides. The introduction of a carbon-carbon double bond carrying one or two electron-withdrawing groups is a cornerstone of synthetic organic chemistry in the form of numerous reactions including Perkin,<sup>9</sup> Knoevenagel,<sup>10</sup> Stobbe,<sup>11</sup> Claisen,<sup>12</sup> and Wittig<sup>13</sup> condensations and dehydration products of Reformatsky<sup>14</sup> and aldol reactions.15

With this in mind we have examined several of these chain elongation reactions starting from 2,2-dichloro aldehydes 4, readily available by chlorination of aldehydes or alcohols in dimethylformamide.<sup>16</sup> The Emmons-Wadsworth modification of the Wittig reaction with dialkyl [(carboalkoxy)methyl]phosphonates<sup>17</sup> (5, Y =  $COOR_2$ ) exclusively afforded (E)- $\gamma$ , $\gamma$ -dichloro- $\alpha$ , $\beta$ -unsaturated esters 6 ( $Y = COOR_2$ ; Table I). The reaction with dialkyl (cyanomethyl)phosphonates<sup>18</sup> (5, Y = CN) always gave rise to a stereoisomeric mixture of the corresponding unsaturated nitriles 6 (Y = CN; Table I, Scheme II).

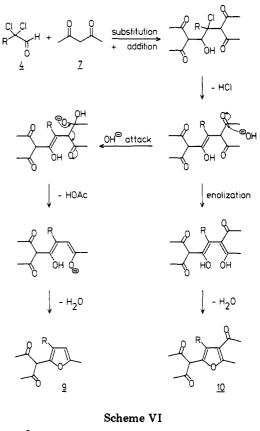
Only few reactions of  $\alpha$ -halo aldehydes with Wittig reagents have been reported. From  $\alpha$ -chloro aldehydes a

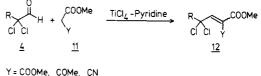
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mixture of E and Z unsaturated esters<sup>19</sup> and ketones<sup>20</sup> could be synthesized, while  $\gamma, \gamma$ -dibromo- $\alpha, \beta$ -unsaturated ketones<sup>21</sup> and aldehydes<sup>22</sup> have been obtained by reaction of 2,2-dibromo aldehydes with respectively (2-oxopropylidene)- and (2-oxoethylidene)triphenylphosphorane.

During our studies concerning the reactivity of 2,2-dihalo aldehydes we have recently developed a stereospecific synthesis of (E)- $\alpha,\beta$ -unsaturated ketones 8 involving a reaction with 1,3-diketones in THF in the presence of potassium carbonate.<sup>23</sup> At nearly the same time, Takeda and co-workers reported the same condensation of aldehydes with 1,3-dicarbonyl compounds.<sup>24</sup> Extension of our method to several 1,3-diones was proven to be successful and resulted in good isolated yields of compounds 8 and 8' (Table I, Scheme III).

The reaction mechanism involved addition of the enolate anion at the carbonyl function followed by an intramolecular nucleophilic addition furnishing an oxetane derivative. Ring opening and expulsion of a carboxylate anion gave 8 (Scheme IV). It is worthwhile to point out

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## Table I. Synthesis of Electrophilic Allyl Dichlorides



compd <sup>a,d</sup>	R	Y	Z	yield, %	bp (mm) or [mp], °C	E/Z ratio
6a	Me	COOMe	H	87	85 (11)	100/0
6b	$\mathbf{Me}$	COOEt	Н	84	100 (12)	100/0
6c	Et	$\mathbf{COOMe}$	Н	86	101 (12)	100/0
6d	<i>n-</i> <b>P</b> r	COOMe	Н	84	111 (11)	100/0
6e	<i>i-</i> Pr	COOMe	Н	87	106 (10)	100/0
<b>6</b> f	t-Bu	COOMe	Н	89	66 (0.015) [49]	100/0
6g	Ph	COOMe	Н	82	104-106 (0.05)	45/55 <sup>b</sup>
6ĥ	Me	CN	Н	91	77 (12)	50/50
6i	$\mathbf{Et}$	CN	Н	88	96-98 (12)	50/50
<b>6</b> j	i-Pr	CN	Н	87	107-110 (12)	50/50
6k	t-Bu	CN	Н	89	60-65 (0.01)	50/50
61	Ph	CN	Н	83	95-97 (0.02)	50/50
8a <sup>c</sup>	${ m Me}$	COMe	Н	77	54 (0.07)	100/0
8b	$\mathbf{Et}$	$\mathbf{COMe}$	Н	76	48 (0.015)	100/0
8c	<i>n-</i> Pr	COMe	Н	73	59 (0.015)	100/0
8d	i-Pr	COMe	н	74	54 (0.04)	100/0
8e	t-Bu	$\mathbf{COMe}$	Н	82	65 (0.09)	100/0
8f	$\mathbf{Bz}$	$\mathbf{COMe}$	н	68	122 (0.008)	100/0
8g	Me	COEt	H	72	54 (0.04)	100/0
8h	Me	CO-n-Pr	Н		66 (0.03)	100/0
8i	Me	CO- <i>i</i> -Pr	Н		58 (0.04)	100/0
<b>8</b> j	Me	CO-sec-Bu	Н	69	59 (0.01)	100/0
8k	Me	CO-t-Bu	Н	79	52 (0.02) [25.5]	100/0
81	Me	Ph	Н	70	111 (0.03)	100/0
12a	${ m Me}$	COOMe	COOMe	96	80.5 (0.01)	
12b	$\mathbf{Et}$	COOMe	COOMe	95	88 (0.15)	
12c	n-Pr	COOMe	COOMe	92	98 (0.4)	
12d	<i>i-</i> Pr	COOMe	COOMe	93	95 (0.2)	
12e	t-Bu	COOMe	COOMe	95	106 (0.3) [43]	
<b>12</b> f	$\mathbf{Et}$	COMe	COOMe	86	93 (0.15)	50/50
12g	Et	CN	COOMe	83	119 (0.18)	100/0

<sup>a</sup> The substitution pattern in the activated allyl dichlorides presented in this table is indicated by a generalized formula, RCCl<sub>2</sub>CH=CYZ. <sup>b</sup> Compound **6**g, after distillation, consisted of a mixture of 55% Z isomer and 45% E isomer. The total isolated yield was 82%. <sup>c</sup> Lit.<sup>21</sup> bp 77-80 °C (6 torr). <sup>d</sup> Satisfactory halogen analyses were reported for all compounds; in addition, satisfactory analytical data (±0.3% for C, H, and N when included) were reported for compounds **6a,b,f,h,i**, **8a,b,g,k**, and **12a,e,f,g**.

that in cases of unsymmetrical 1,3-diketones  $(R_3 \neq R_4)$  the less sterically hindered carboxylate is expelled. Thus, compound 8, with the bulkiest  $R_3$  or  $R_4$  group, was produced. When there is no significant difference in steric hindrance of both  $R_3$  and  $R_4$ , mixtures of the two possible  $\alpha,\beta$ -unsaturated ketones were isolated. This phenomenon was also observed by using 3,5-octanedione ( $R_3 = \text{Et}, R_4 =$ n-Pr) and 6-methyl-3,5-heptanedione ( $R_3 = \text{Et}, R_4 =$ i-Pr) where the formation of the compound with the larger  $R_3$  or  $R_4$  group was favored [72% 8' ( $R_4 = n$ -Pr), 28% 8 ( $R_3 = \text{Et}$ ), 61% 8' ( $R_4 = i$ -Pr), 39% 8 ( $R_3 = \text{Et}$ ), respectively].

The same condensation with water as solvent took a completely different course, and a mixture of two furan derivatives 9 and 10 was isolated. Besides a nucleophilic addition at the aldehyde function, a nucleophilic substitution took place. Compound 10 was formed via dehydrochlorination and ring closure of a 1,4-diketone derivative; while addition of a hydroxide anion, abstraction of an acetate anion, and subsequent ring closure provided 9 (Scheme V).

The method of choice for preparing allyl dihalides geminally substituted with two electron-withdrawing groups is undoubtedly a Knoevenagel condensation. The classical method of Cope using piperidine acetate failed to give any reaction.<sup>25</sup> However, condensation of 2,2-dichloro alde-

(25) A. Cope, C. Hofman, G. Wychoff, and E. Hardenbergh, J. Am. Chem. Soc., 63, 3452 (1941).

hydes with active methylene functions 11 in the presence of titanium tetrachloride-pyridine<sup>26</sup> gave  $\gamma,\gamma$ -dichloro- $\alpha,\beta$ -unsaturated esters 12 in 83-96% yields (Table I, Scheme VI).

When Y was CN the *E* isomer was exclusively formed while a stereoisomeric mixture  $(E/Z \text{ ratio} \approx 1)$  was obtained when Y = COCH<sub>3</sub>. Under the same circumstances no reaction occurred with 2,4-pentanedione, while reaction with malononitrile afforded only nondistillable products, which were not further investigated.

## **Experimental Section**

IR spectra were obtained with a Perkin-Elmer 257 spectrometer. NMR spectra were recorded on a Varian T60 apparatus. Mass spectra were determined on an AEI-MS20 instrument coupled with a Pye Unicam 104 gas chromatograph (Se-30, 5%, 1.5 m) at an ionizing voltage of 70 eV.

**Preparation of**  $\alpha_{,\beta}$ -**Unsaturated Esters 6 (Y = COOR<sub>2</sub>).** Triethyl phosphonoacetate (0.1 mol) was added dropwise to a slurry of 0.11 mol of sodium hydride (washed free from oil with hexane) in 100 mL of tetrahydrofuran, and the mixture was stirred for 1 h at room temperature. Then a solution of 0.1 mol of dichloro aldehyde in 50 mL of tetrahydrofuran was added, and the mixture was heated at reflux for 3 h. Water (50 mL) was added, followed by extraction with ether (3 × 50 mL). The combined extracts were dried (MgSO<sub>4</sub>), and the solvent was removed in vacuo. Fractional distillation gave pure esters 6. The spectral data of 6a are representative for all other compounds 6. Full spectral

<sup>(26)</sup> W. Lehnert, Tetrahedron, 29, 635 (1973).

data of compounds 6 are included in the supplementary material section (Table II).

Methyl 4,4-Dichloro-2-pentenoate (6a): IR (NaCl) 1730 (COOMe), 1660 cm<sup>-1</sup> (C=C); NMR (CCl<sub>4</sub>)  $\delta$  2.30 (s, 3 H, CH<sub>3</sub>), 3.77 (s, 3 H, COOCH<sub>3</sub>), 6.20 (d,  $J_{AB}$  = 15.3 Hz, 1 H, CH= CHCOOMe), 7.10 (d,  $J_{AB}$  = 15.3 Hz, 1 H, CCl<sub>2</sub>CH=CH); mass spectrum, m/e 151/153/155 (M<sup>+</sup> – OMe, 16), 147/149 (100), 123/125/127 (21), 119 (20), 87 (21), 59 (21), 53 (21), 36 (33).

Anal. Calcd for  $C_6H_8Cl_2O_2$ : C, 39.37; H, 4.41; Cl, 38.74. Found: C, 39.52; H, 4.39; Cl, 38.88.

**Preparation of**  $\alpha_{\beta}$ **-Unsaturated Cyanides 6 (Y = CN).** The cyanides were synthesized by the same procedure as above by using diethyl phosphonoacetonitrile. Full spectral data of compounds 6 (Y = CN) are included in the supplementary material (Table III).

Reaction of Dichloro Aldehydes with 1,3-Diketones: Preparation of  $\gamma,\gamma$ -Dichloro- $\alpha,\beta$ -unsaturated Ketones 8. A solution of 0.1 mol of dichloro aldehyde in 100 mL of tetrahydrofuran was treated with 15 g of potassium carbonate, immediately followed by addition of a solution of 0.1 mol of aldehyde in 50 mL of tetrahydrofuran. The reaction mixture was refluxed for 3 h. Filtration, evaporation of the solvent, and distillation afforded  $\gamma,\gamma$ -dichloro- $\alpha,\beta$ -unsaturated ketones 8. The spectral data of 8a are representative for all other compounds 8. Full spectral data of compounds 8 are included in the supplementary material (Table IV).

**5,5-Dichloro-3-hexen-2-one (8a):** IR (NaCl); 1710, 1685 (C=O); 1635 cm<sup>-1</sup> (C=C); NMR (CCl<sub>4</sub>)  $\delta$  2.29 (s, 3 H, CH<sub>3</sub>), 2.29 (s, 3 H, COCH<sub>3</sub>), 6.37 (d,  $J_{AB}$  = 15.5 Hz, 1 H, CH=CHCO), 6.90 (d,  $J_{AB}$  = 15.5 Hz, 1 H, CCl<sub>2</sub>CH=CH); mass spectrum, m/e 151/153/155 (M<sup>+</sup> – Me, 1.5), 131/133 (22), 123/125/127 (7), 103 (7), 87 (9), 67 (15), 53 (13), 51 (11), 43 (100).

Anal. Calcd for  $C_6H_8Cl_2O$ : C, 43.14; H, 4.83; Cl, 42.45. Found: C, 43.28; H, 4.85; Cl, 42.59.

Reaction of 2,2-Dichlorobutanal with 2,4-Pentanedione in Aqueous Medium: Preparation of Functionalized Furans 9 and 10. A suspension of 5 g of 2,4-pentanedione, 7.0 g of 2,2-dichlorobutanal, and 7.5 g of potassium carbonate in 50 mL of water was heated under reflux for 8 h. After being cooled and acidified with dilute hydrochloric acid, the reaction mixture was extracted with dichloromethane, dried (MgSO<sub>4</sub>), and evaporated in vacuo. The residual oil was found to consist of two components (54:46 ratio) by GLC analysis. These two components, furans 9 and 10, respectively, were isolated by preparative GLC on a 1.5-m, 10% SE-30, Chromosorb W column at 140-200 °C (8 °C/min) with respective retention times of 2.8 and 7.3 min.

**3-(3-Éthyl-5-methyl-2-furanyl)-2,4-pentanedione (9, R = Et):** IR (NaCl) 1720 (C=O), 1565 cm<sup>-1</sup> (C=C); NMR (CCl<sub>4</sub>)  $\delta$ 1.07 (t, J = 7.5 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>), 1.88 (s, 6 H, 2 CH<sub>3</sub>CO), 2.21 (q, J = 7.5 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>), 2.23 (s, 3 H, CH<sub>3</sub>C=C), 5.80 (s, 1 H, ==CH); mass spectrum, m/e 208 (M<sup>+</sup>, 37), 166 (7), 165 (37), 151 (7), 147 (13), 123 (18), 43 (100).

Anal. Calcd for  $C_{12}H_{16}O_3$ : C, 69.21; H, 7.74. Found: C, 69.34; H, 7.71.

**3-(4-Acetyl-3-ethyl-5-methyl-2-furanyl)-2,4-pentanedione** (10, R = Et): IR (NaCl) 1720 (C=O), 1675 (C=O), 1565 cm<sup>-1</sup> (C=C); NMR (CCl<sub>4</sub>)  $\delta$  1.03 (t, J = 7.4 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>), 1.88 (s, 6 H, 2 CH<sub>3</sub>CO), 2.37 (q, J = 7.4 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>), 2.38 (s, 3 H, CH<sub>3</sub>C=C), 2.56 (s, 3 H, 4-CH<sub>3</sub>CO); mass spectrum, m/e 250 (M<sup>+</sup>, 21), 208 (7), 190 (7), 165 (28), 151 (5), 147 (5), 123 (5), 43 (100).

Anal. Calcd for  $C_{14}H_{18}O_4$ : C, 67.18; H, 7.25. Found: C, 67.37; H, 7.27.

Knoevenagel Condensation of 2,2-Dichloro Aldehydes: Preparation of  $\gamma, \gamma$ -Dichloro- $\alpha, \beta$ -unsaturated Esters 12. A solution of 0.1 mol of titanium tetrachloride in 25 mL of carbon tetrachloride was slowly added to 200 mL of tetrahydrofuran (at 0 °C), followed by addition of 0.05 mol of the  $\alpha, \alpha$ -dichloro aldehyde 4 and 0.05 mol of the active methylene compounds. Afterward, a solution of 0.2 mol of pyridine in 35 mL of tetrahydrofuran was added during a period of 30-60 min at 0 °C. The reaction mixture was stirred for 1 h at room temperature and boiled for 10 h. The mixture was poured onto ice and extracted with ether. The combined extracts were successively washed with brine, saturated sodium hydrogen carbonate, and brine and were dried (MgSO<sub>4</sub>). Concentration and distillation gave Knoevenagel condensation products 12. The spectral data of 12a are representative for all other compounds 12. Full spectral data of compounds 12 are included in the supplementary material (Table V).

**Dimethyl (2,2-Dichloropropylidene)malonate (12a):** IR (NaCl) 1740 (COOMe), 1655 cm<sup>-1</sup> (C=C); NMR (CCl<sub>4</sub>)  $\delta$  2.32 (s, 3 H, CH<sub>3</sub>CCl<sub>2</sub>), 3.79 (s, 3 H, COOCH<sub>3</sub>), 3.82 (s, 3 H, COOCH<sub>3</sub>), 7.07 (s, 1 H, CCl<sub>2</sub>CH=); mass spectrum, m/e 209/211/213 (M<sup>+</sup> – OMe, 16), 205/207 (60), 173/175 (100), 169 (17), 145 (17), 59 (40), 51 (30), 36 (31).

Anal. Calcd for  $C_8H_{10}Cl_2O_4$ : C, 39.86; H, 4.18; Cl, 29.41. Found: C, 39.71; H, 4.21; Cl, 29.53.

Acknowledgment. The authors are indebted to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" for financial support to the laboratory.

**Registry No.** 4 (R = Me), 27313-32-2; 4 (R = Et), 23454-01-5; 4 (R = Pr), 41718-50-7; 4 (R = *i*-Pr), 76043-68-0; 4 (R = *t*-Bu), 1937-09-3; 4 (R = Ph), 50735-77-8; 4 (R = Bz), 76043-69-1; (E)-6a, 77572-21-5; (E)-6b, 77572-22-6; (E)-6c, 77572-23-7; (E)-6d, 77572-24-8; (E)-6e, 77572-25-9; (E)-6f, 77572-26-0; (E)-6g, 77572-37-1; (Z)-6g, 77572-38-2; (E)-6h, 77572-39-3; (Z)-6h, 77572-30-6; (E)-6i, 77572-31-7; (Z)-6i, 77572-32-8; (E)-6j, 77572-33-9; (Z)-6j, 77572-34-0; (E)-6k, 77572-35-1; (Z)-6k, 77572-36-2; (E)-6l, 77572-37-3; (Z)-6l, 77572-38-4; 7, 123-54-6; (E)-8a, 53779-77-4; (E)-8b, 65785-81-1; (E)-8c, 77572-39-5; (E)-8d, 77572-40-8; (E)-8e, 77572-41-9; (E)-8f, 77572-45-3; (E)-8k, 77572-44-2; (E)-8i, 77572-45-3; (E)-8k, 77572-50-0; 12a, 77572-48-6; 9 (R = Et), 77572-52-2; 12c, 77572-53-3; 12d, 77572-54-4; 12e, 77572-55-5; (E)-12f, 77572-56-6; (E)-12g, 77572-57-7.

Supplementary Material Available: Tables of spectrometric data for  $\gamma, \gamma$ -dichloro- $\alpha, \beta$ -unsaturated esters 6 (Table II) and nitriles 6 (Table III),  $\gamma, \gamma$ -dichloro- $\alpha, \beta$ -unsaturated ketones 8 (Table IV) and esters 12 (Table V) (9 pages). Ordering information is given on any current masthead page.