the residue was transferred to a small distillation flask, and fresh Amberlyst was added. The residue was heated for 3–4 hr at 135° and the material which distilled was collected. To the residue, fresh dimethoxymethane (20 ml) and Amberlyst was added, the solution was boiled for 3 hr, and the above procedure was repeated. At the end, the bath temperature was increased to 150°. The combined distillates were purified by glpc on the column mentioned above at 110°, with 330-ml/min He flow, retention time 6 min: yield 0.52 g (23%); mp 19°; n^{20}D 1.3752.

Anal. Calcd for $C_4H_6F_2O_2$: C, 38.71; H, 4.87. Found: C, 38.78; H, 4.88.

^{19}F nmr spectrum (−124°): ϕ_a 113.2, ϕ_e 115.2, ϕ_{av} (room temperature) 114.7 ppm; $J_{F_eF_e} = 253$, $J_{F_aH_{4(6)a}} = 25$, $J_{F_4H_{4(6)e}} = 10.9$ Hz. ^{1}H nmr spectrum (−112°): $\delta_{H_{2e}}$ 5.11, $\delta_{H_{2a}}$ 4.77 ppm, $J_{H_{2e}H_{2a}} = -5.75$ Hz; (room temperature) 3.92 (t, J = 11 Hz, 4 H), 4.89 ppm (d, J = 1.2 Hz, 2 H).

When the original residue after distillation of excess dimethoxymethane and **4** was subjected to gas chromatography in the above column at 190° with a 310-ml/min He flow, two compounds were obtained, **8**, retention time 6 min, and **9**, retention time 11 min. Proton nmr spectra and elemental analyses were in accord with the structures assigned. *Anal.* Calcd for $C_5H_{10}F_2O_3$ (**8**): C, 38.46; H, 6.45. Found: C, 38.88; H, 6.56. *Anal.* Calcd for $C_7H_{14}F_2O_4$ (**9**): C, 42.00; H, 7.05. Found: C, 42.55; H, 7.25.

When **9** was heated over Amberlyst in a distilling flask, it was converted entirely into **4** and dimethoxymethane, as evidenced by gas chromatographic analysis of both the distillate and the residue. In contrast, similar treatment of **8**, while giving the same distillate (**4** and dimethoxymethane), left a residue containing some unchanged **8** as well as $HOCH_2CF_2CH_2OH$ (**7**).

Barrier Measurement.—The nmr spectrum of **4** was measured in a solvent mixture of 80% acetone-d_6 and 20% trichlorofluoromethane with some TMS.[27] For the low-temperature runs, the temperature was measured by letting the probe, refrigerated by a stream of precooled nitrogen, come to equilibrium and replacing the sample with a copper–constantan thermocouple located inside an nmr tube. A period of 10 min was allowed to allow either the sample tube or the thermocouple tube come to temperature equilibrium with the probe. Temperature readings were reproducible to ±2°. The proton signals (AB pattern for the H-2's) were located at 283 (ν_1), 289 (ν_2), 304.5 (ν_3), and 310 Hz (ν_4), indicating a coupling constant of −5.75 ± 0.25 Hz, and the chemical shifts reported above were calculated by the usual equation, $\Delta\nu_{AB} = (\nu_4 - \nu_1)^{1/2}(\nu_3 - \nu_2)^{1/2} = 20.46$ Hz. The coalescence temperature was found to be −96° by varying the temperature first in intervals of 5° and then, near the coalescence temperature, in intervals of 2°. The rate constant was calculated from the computed chemical shifts and the coalescence temperature by the equation given in the discussion and was found to be 55.2 sec^{-1} at −96°. The activation energy $\Delta G^{\ddagger}$ was calculated to be 8.8 kcal/mol by application of the Eyring equation, $k = \mathbf{k}T/h)e^{-\Delta G^{\ddagger}/RT}$ or $\Delta G^{\ddagger} = -RT \ln hk/\mathbf{k}T$. To simulate the spectrum in the vicinity of the coalescence point we used the program QUABEX,[15] which in addition to ν_A, ν_B, and J_{AB} requires the relaxation time T_2 as input; T_2 was taken at $1/\pi W$ where W is the width (in hertz) at half height of the peak. Spectra were calculated by a Univac 1107 computer and plotted by a Calcomp 750 plotter.

The fluorine data were handled similarly. Chemical shifts and coupling constants have been reported above at low temperature. Coalescence to a very broad spectrum occurred at approximately −84°, at which temperature the rate constant was calculated to be 1437 sec^{-1} and the activation energy 8.2 kcal/mol.

Rate constants and activation energies for **5** and **6** were determined similarly from the H-2 proton spectra.

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Registry No.—**4**, 36301-44-7; **5**, 505-22-6; **6**, 766-15-4; **7**, 428-63-7; **8**, 42116-92-7; **9**, 42116-93-8.

(27) We used the most polar solvent available which would not freeze at the low temperature required in the nmr experiment, since, as indicated in Scheme I, the axial preference of fluorine is greatest in the most polar solvents. From results on 5-methoxy-1,3-dioxane [O. Hofer in E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **11**, 739 (1972), Table VIII] acetone should favor the axial isomer **2** more than ether and benzene but less than acetonitrile.

An Exceptionally Facile Reaction of α,α-Dichloro-β-keto Esters with Bases

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α,α-Dichloro-β-keto esters react rapidly with even relatively weak nucleophiles such as sodium bicarbonate, potassium acetate, and diethylamine to give products according to eq 1.

$$MeCOCCl_2COOEt + MeCOONa \xrightarrow{EtOH} MeCOOEt + CHCl_2COOEt \quad (1)$$

To our knowledge, such a facile fragmentation of an α,α-disubstituted β-keto ester derivative with a base (eq 1) is unprecedented.[1] This reaction proceeds under extremely mild conditions. For example, when a solution of ethyl α,α-dichloroacetoacetate in ethanol is stirred at 25° for 30 min in the presence of a catalytic quantity of sodium acetate, ethyl acetate and ethyl dichloroacetate are produced in nearly quantitative yield. The results on other representative reactions are summarized in Table I.

The present reaction appears to be an example of retro acetoacetic ester consensation.[2] The characteristics noteworthy of this novel fragmentation process are (1) there is no reaction between the dichloro compound and the alcohol in the absence of required base; (2) when ethyl α,α-dichloroacetoacetate and sodium acetate are stirred together in a solvent such as benzene, chloroform, or dimethyl sulfoxide, the formation of acetic anhydride is not detected (ir, glpc) (however, upon the addition of an alcohol to this reaction mixture, the expected products are produced rapidly); and (3) when ethyl α,α-dichloroacetoacetate is stirred with potassium benzoate or ethyl α,α-dichlorobenzoylacetate is stirred with potassium acetate in a solvent such as chloroform or dimethyl sulfoxide in order to achieve a redistribution according to eq 2, the starting materials are recovered unchanged in both cases.

$$C_6H_5COCCl_2COOEt + KOCOCH_3 \rightleftharpoons H_3CCOCCl_2COOEt + C_6H_5COOK \quad (2)$$

Although a study of the precise mechanism of this reaction has not been undertaken, it would appear likely that the present fragmentation proceeds *via* an attack of the nucleophile on the reactive carbonyl moiety of the dichloro compound.[3]

(1) For a recent report on a related reaction which results in the ring opening of certain α,α-dihalospirocyclobutanones with bases, see B. M. Trost and M. J. Bodganowicz, *J. Amer. Chem. Soc.*, **95**, 2038 (1973).

(2) For a discussion of the principles involved in the acetoacetic ester condensation, see H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, Chapter 11.

(3) For a discussion of the reactivity of α- and β-keto halides, see (a) E. W. Trachtenberg and T. J. Whall, *J. Org. Chem.*, **37**, 1494 (1972), and references cited therein; (b) R. G. Pews and R. A. Davis, *J. Chem. Soc., Chem. Commun.*, 269 (1973).

TABLE I

REACTION OF α,α-DICHLORO-β-KETO ESTERS WITH REPRESENTATIVE BASES[a]

Registry no. (ester)	α,α-Dichloro-β-keto ester	Registry no. (base)	Base	Reaction time, min	Products identified (mmol)
6134-66-3	$MeCOCCl_2COOEt$	7542-12-3	$NaHCO_3$	30	MeCOONa (8)[b]
					$HCCl_2COOEt$ (10)
		127-08-2	$KOCOCH_3$	15	MeCOOEt (10)
					$HCCl_2COOEt$ (10)
		532-32-1	$NaOCOC_6H_5$	15	C_6H_5COOEt (8)
					MeCOOEt (1)
		141-52-6	NaOEt	1	MeCOOEt (9)
					$HCCl_2COOEt$ (10)
		109-89-7	Et_2NH	1	$MeCONEt_2$ (8)
					$HCCl_2COOEt$ (9)
42071-71-6	$C_6H_5COCCl_2COOEt$		$KOCOCH_3$	15	C_6H_5COOEt (8)
					MeCOOEt (1)
					$HCCl_2COOEt$ (9.5)
			NaOEt	1	C_6H_5COOEt (8)
					$HCCl_2COOEt$ (9)
			Et_2NH	1	$C_6H_5CONEt_2$ (8.5)
					$HCCl_2COOEt$ (9.5)

[a] A mixture of α,α-dichloro-β-keto ester (10 mmol), ethanol (10 ml), and the appropriate base (10 mmol) was stirred at 25°. The reaction mixture was then analyzed by glpc (5% DC 550 on Chromosorb W) using an internal standard. [b] Yield by isolation.

The α,α-dichloro-β-keto esters required in the present study were synthesized by the chlorination of the corresponding β-keto esters with sulfuryl chloride.[4] Our improved procedure, described herein, now provides these dichloro keto esters in virtually quantitative yields. The formation of any side products in these chlorinations is negligible (glpc, nmr), thus permitting the direct use of these powerful lacrymators without further purification.

The novel fragmentation reaction reported here demonstrates the potential of readily available α,α-dichloro-β-keto esters as acyl transferring agents. Also, this reaction could be useful in organic structural elucidation where the degradation of a β-keto acid (ester) moiety can now be achieved under very mild conditions to give readily identified fragments of defined functionality.[5]

Experimental Section[6]

Preparation of α,α-Dichloro-β-keto esters.—*Caution:* α,α-Dichloro-β-keto esters are powerful lacrymators. The preparation of these compounds should be conducted in a well-ventilated hood.

The synthesis of ethyl α,α-dichloroacetoacetate is representative of this procedure. Ethyl acetoacetate (6.5 g, 50 mmol) was placed in a round-bottom flask and sulfuryl chloride (14.9 g, 110 mmol) was added to it in 0.5 hr keeping the reaction temperature below 35° with occasional cooling. After the reaction mixture was stirred for an additional 0.5 hr at 25°, glpc analysis showed a quantitative yield of the desired product. The residual sulfuryl chloride was removed under vacuum, and the crude compound thus obtained (98% pure) was used in the subsequent reactions: nmr ($CDCl_3$, TMS) δ 1.33 (t, 3 H, J = 7 Hz), 2.80 (s, 3 H), and 4.39 (q, 2 H, J = 7 Hz).

Ethyl α,α-dichlorobenzoylacetate was prepared by a similar procedure in 98% yield: nmr ($CDCl_3$, TMS) δ 1.15 (t, 3 H, J = 7 Hz), 4.31 (q, 2 H, J = 7 Hz), 7.56, and 7.96 (m, 5 H).

Reaction of α,α-Dichloro-β-keto Esters with Bases.—A typical reaction is described here. To a stirred mixture of potassium acetate (22.1 g, 225 mmol) and ethanol (90 ml), ethyl α,α-dichloroacetoacetate (43.0 g, 225 mmol) was added in 0.5 hr. The reaction was slightly exothermic (25° → 35°), and, after an additional 15 min, glpc analysis showed it to be complete. The composition of the reaction mixture was determined (Table I), and then water (400 ml) was added to it. After extraction with methylene chloride and drying, distillation gave 32.6 g (92%) of ethyl dichloroacetate: bp 152–156°; nmr ($CDCl_3$, TMS) δ 1.33 (t, 3 H, J = 7 Hz), 4.32 (q, 2 H, J = 7 Hz), and 5.95 (s, 1 H).

The reactions with other bases were performed in an identical manner.

Reaction of Ethyl α,α-Dichloroacetoacetate with a Catalytic Quantity of Potassium Acetate.—This experiment was performed according to the general procedure described above, except that only 5 mol % of potassium acetate per mole of dichloro ester was used. The reaction required 30 min for completion at 35°.

Reaction of Ethyl α,α-Dichloroacetoacetate with Potassium Acetate in Benzene.—A mixture of ethyl α,α-dichloroacetoacetate (4.98 g, 25 mmol), potassium acetate (2.45 g, 25 mmol), and benzene (25 ml) was stirred at 25° for 12 hr. Ir and glpc analysis of the benzene solution revealed the absence of any acetic anhydride. Upon the addition of ethanol (5 ml) to this reaction mixture, a rapid reaction occurred giving ethyl acetate (24 mmol) and ethyl dichloroacetate (24 mmol).

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(4) D. P. Wyman, P. R. Kaufman, and W. R. Freeman, *J. Org. Chem.*, **29**, 2706 (1964). For a recent discussion on the mechanism of ketone halogenation, see K. E. Teo and W. W. Warnhoff, *J. Amer. Chem. Soc.*, **95**, 2728 (1973).

(5) For a recent application of this concept in the structural determination of certain α,α-dihalocyclobutanones, see L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

(6) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Glpc analyses were performed on a DC-550, 5% on Chromosorb W, 5 ft × 0.25 in. column. Nmr spectra were recorded on a Varian A-60 instrument.

Lithiotriphenylphosphinioacetonide as a Convenient Reagent for the Introduction of the Acetonyl Synthon

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We wish to report that lithiotriphenylphosphinioacetonide (2) prepared from readily available acetyl-