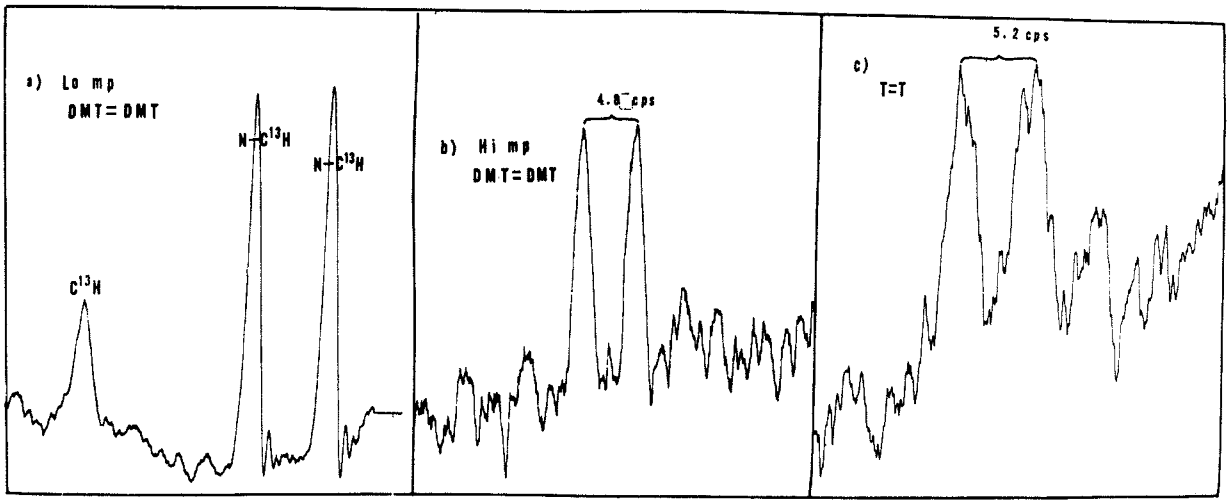

Figure 3.—Low-field C^{13}–H satellite spectra: (a) low-melting DMT=DMT, 10% (w/w) in $CDCl_3$, 300 runs; (b) high-melting DMT=DMT, 10% (w/w) in $CDCl_3$, 50 runs; (c) T=T, 3% (w/w) in CF_3COOD, 64 runs.

peaks (J = 5.2 ± 0.5 cps), T=T must also have the *syn* or head-to-head arrangement. The several coupling constants measured for the three dimers are given in Table I. The C^{13}–H coupling constants are accurate to ±2 cps. The coupling constants for I agree, within the range of experimental error, with those reported by Anet.[10]

TABLE I

COUPLING CONSTANTS OF THE THREE DIMERS

Dimer		$J_{C^{13}H}$, cps	$J_{NC^{13}H}$, cps	J_{HH} (cyclobutane), cps
Low-melting	DMT=DMT	155	148, 150	0
High-melting	DMT=DMT	151	140, 142	4.8 ± 0.5
T=T		158	...	5.2 ± 0.5

Experimental Section

T=T and Mixture of DMT=DMT Isomers.—Dimers from frozen, aqueous solutions and T=T from solid films were prepared as previously described.[11]

Separation of DMT=DMT Isomers.—The residue from the irradiated frozen solutions of 3 l. of 0.1 M DMT was dissolved in chloroform and mixed with 1 g of acid-washed alumina. After removal of the excess chloroform, the mixture was placed on the top of a 19 cm × 1.8 cm^2 column of acid-washed alumina and eluted with ether (1.4 l.), 0.2% ethanol-ether (1.6 l.), and chloroform. About 40% of the starting material was recovered from the ether fraction. The 0.2% ethanol-ether fraction yielded a product with mp 225-226° (low-melting DMT=DMT) after crystallization from chloroform-petroleum ether (bp 30-60°). From the chloroform fraction, an isomer with mp 258-259° (high-melting DMT=DMT) was obtained. The two isomers were present in equal amounts and the total yield was 50-60%.

Nmr Spectra.—These spectra were obtained on the Varian HA-100 spectrometer operating in the field-sweep mode. Chemical shifts were measured directly from the precalibrated charts. Naturally abundant C^{13}–H satellites were observed by time averaging a 50-cps region beginning 100 cps to low field of the cyclobutane CH peaks using the Varian C-1024 time-averaging computer. Fifty runs were sufficient to give acceptable spectra for the 3-10% concentrations employed.

Registry No.—Thymine homodimer, 7721-75-7; I (R = CH_3), 7721-76-8; II (R = CH_3), 7721-77-9.

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The Reaction of Trifluoromethyl Ketones with Resonance-Stabilized Alkylidene Phosphoranes[1]

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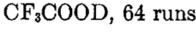
We wish to report a convenient and general synthesis of trifluoromethyl-containing α,β-unsaturated carbonyl compounds of type I. Certain compounds of this type



$$CF_3\overset{R}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-R'$$

I

where R′ is OH or OC_2H_5 have been reported.[2-6] The Knovenagel condensation with trifluoromethyl ketones leads to β-hydroxy acids instead of α,β-unsaturated acids. Some of these β-trifluoromethyl-β-hydroxy acids and esters have proven very resistant to dehydration and we therefore were forced to find another general route to such compounds.

It was found that trifluoromethyl ketones readily react with resonance-stabilized alkylidene phosphoranes. To the best of our knowledge only one Wittig reaction of this type has been reported, namely the reaction of hexafluoroacetone with acetylmethylenetri-

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[1] We gratefully acknowledge support for these studies by the U. S. Public Health Service (GM-05248) and the National Science Foundation (GP 3888).

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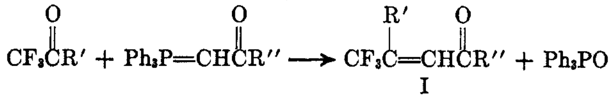
[4] H. M. Walborsky, M. Baum, and D. F. Loncrini, *ibid.*, **77**, 3637 (1955).

[5] H. M. Walborsky and M. Schwarz, *ibid.*, **75**, 3241 (1953).

[6] R. N. Hazeldine, *J. Chem. Soc.*, 3495 (1952).

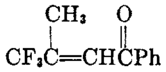
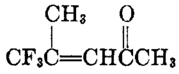
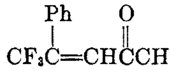
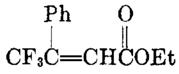
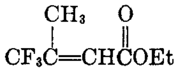
TABLE I

TRIFLUOROMETHYL KETONE REACTIONS WITH PHOSPHORANES



$$CF_3\overset{O}{C}R' + Ph_3P{=}CH\overset{O}{C}R'' \longrightarrow CF_3\overset{R'}{C}{=}CH\overset{O}{C}R'' + Ph_3PO$$

I

R'	R''	Product[a]	Yield, %	Bp (mm), °C	n_D (°C)	Calcd, % C	Calcd, % H	Found, % C	Found, % H
CH_3	Ph[b]	 $CF_3\overset{CH_3}{C}{=}CH\overset{O}{C}Ph$	70	76–77 (2.5)	1.4883 (21)	61.68	4.23	61.38	4.10
CH_3	CH_3[c]	 $CF_3\overset{CH_3}{C}{=}CH\overset{O}{C}CH_3$	58	109–112 (760)	1.3726 (21)	47.47	4.63	47.17	4.56
Ph	CH_3	 $CF_3\overset{Ph}{C}{=}CH\overset{O}{C}CH_3$	77	71–73 (1.0)	1.4760 (22)	61.78	4.23	61.61	4.13
Ph	OEt[d]	 $CF_3\overset{Ph}{C}{=}CH\overset{O}{C}OEt$	78	75–82 (1.5)	1.4660 (22)	59.01	4.54	59.42	4.53
CH_3	OEt	 $CF_3\overset{CH_3}{C}{=}CH\overset{O}{C}OEt$	70	131–133 (760)	1.3750 (22)	[e]	[e]	[e]	[e]

[a] Products purified and analyzed by gas chromatography, Carbowax 20 M, 20 ft × 0.25 in., 60-ml/min helium flow, 135–195°. Representative reaction conditions are given in the Experimental Section. [b] See D. B. Denney and S. T. Ross [*J. Org. Chem.*, **27**, 998 (1962)] for the preparation of benzoylmethylenetriphenylphosphorane. [c] See F. Raminez and S. Dershowitz [*ibid.*, **22**, 41 (1957)] for preparation of acetylmethylenetriphenylphosphorane. [d] See O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller [*Helv. Chim. Acta*, **40**, 1242 (1957)] for the preparation of carbomethoxymethylenetriphenylphosphorane. [e] Reference 2.

phenylphosphorane.[7] Very recently there has been a communication[8] of the reaction of trifluoromethyl ketones with trialkylphosphines to give olefins, which has in part prompted the report of our work at this time.

Although acetone and acetophenone react only under forcing conditions with resonance-stabilized ylides,[9] we find that 1,1,1-trifluoroacetone and 2,2,2-trifluoroacetophenone react rapidly with such reagents, the former reacting even at room temperature in ether solvent. The results of these reactions are summarized in Table I.

Gas chromatographic analysis of these products indicates in each case that one geometrical isomer has been formed to the virtual exclusion of the other. This is in accord with the general observation already noted for reactions of resonance-stabilized ylides.[9]

This ease of reaction is to be expected based on the greatly enhanced electrophilicity of the carbonyl group in trifluoromethyl aldehydes and ketones. This procedure promises to be a useful method for the synthesis of many compounds of this general type. The following experimental results are representative of those reported in Table I.

Experimental Section

1,1,1-Trifluoro-2-phenyl-2-penten-4-one.—In a dry, 250-ml, three-necked flask fitted with a reflux condenser was placed 12.8 g (0.04 mole) of acetylmethylenetriphenylphosphorane,[10] 7.0 g (0.04 mole) of 2,2,2-trifluoroacetophenone (Columbia Organic Chemicals), and 60 ml of dry benzene. Upon heating to reflux, solution occurred; refluxing was then continued for 3 hr. After cooling, the benzene was removed under reduced pressure, the residue was mixed with hexane, and the mixture was filtered. Distillation of the filtrate gave 6.6 g (77% yield) of a yellow liquid, bp 71–73° (1.0 mm), (C=O) 1700 cm^{-1}. See Table I for analysis and properties.

Ethyl β-Trifluoromethylcrotonate.[2,4]—In a dry, 250-ml, three-necked flask fitted with a Dry Ice condenser were placed 34.8 g (0.10 mole) of carboethoxymethylenetriphenylphosphorane,[11] 75-ml of dry ether, and 12.8 g (0.11 mole) of 1,1,1-trifluoroacetone (Columbia Organic Chemicals). Reaction occurred immediately with formation of a thick paste. An additional 50-ml of ether was added and the mixture was stirred at room temperature for 16 hr. The reaction mixture was filtered, the ether was removed by distillation, and the residue was mixed with pentane. Distillation of the filtrate gave 12.7 g (70% yield) of ethyl β-trifluoromethylcrotonate. See Table I for properties.

Registry No.—I (R' = Ph; R'' = CH_3), 10075-04-4; (R' = CH_3; R'' = OEt), 691-77-0; (R' = CH_3; R'' = Ph), 10102-92-8; (R' = CH_3; R'' = CH_3), 10075-05-5; (R' = Ph; R'' = OEt), 10075-06-6.

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[7] V. F. Plakhova and N. P. Gamburgan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **681** (1962); *Chem. Abstr.*, **57**, 13596e (1962).

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[9] A. Maercher, *Org. Reactions*, **14**, 277 (1965).

[10] See Table I, footnote *c*.

[11] See Table I, footnote *d*.

Synthesis of Acetal Choline Phosphatide[1]

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Received July 22, 1966

Plasmalogens are a group of aldehydogenic lipids, widely distributed in both animal and plant kingdoms.[3] Natural plasmalogen isolated from beef muscle[4] was at first believed to have the structure 1,2-O-alkylidine-glycerol-3-phosphorylethanolamine, the synthesis of which has been reported.[5,6] However, recent work has shown that the cyclic acetal structure may have been produced as an artifact during the isolation procedure after the alkaline hydrolysis of the natural plasmalogen.

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[1] Abstracted from a part of the dissertation submitted by G. K. Chacko to the University of Illinois Graduate College, March 1966, in partial fulfillment of the requirements of the Ph.D. degree.

[2] Author to whom inquiries should be addressed.

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[5] Th. Bersin, H. G. Moldtman, H. Nafziger, B. Marchand, and W. Leopold, *ibid.*, **269**, 241 (1941).

[6] M. J. Egerton and T. Malkin, *J. Chem. Soc.*, 2800 (1953).