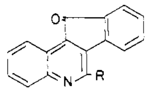
obtained 0.6 gram of 6-pentyl-11-indeno[1,2-*c*]quinolin-11-one (m.p. 146–47°). An oxime derivative of this ketone was prepared by the method of Shriner *et al.* (*6*) (m.p. 226–28°).

Table II. 6-Alkyl-11-indeno[1,2-c]quinolin-11-ones[a]



R	% Yield	M.P., ° C.	Oxime, M.P., ° C.
n-C_3H_7	40	150–51	255–56
Iso-C_3H_7	30	185–86[c]	265–66
n-C_4H_9	60	142–43	242–43
Iso-C_4H_9	50	131–32	264–65
sec-C_4H_9	30	122–23	197–99
n-C_5H_{11}	60	146–47	226–28
Iso-C_5H_{11}	60	146–47	236–38
n-C_6H_{13}	30	135–36	235–36

[a] Elemental analyses for N have been reviewed and agree within required limits for the assigned structures. [b] Elemental analyses for C and H have been reviewed and agree within required limits. [c] Reported m.p. 184° (*1*).

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Synthesis and NMR Data for Dialkyl and Diaryl Trichloromethylphosphonates

K. DARRELL BERLIN and N. K. ROY

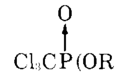
Department of Chemistry, Oklahoma State University, Stillwater, Okla. 74074

The NMR spectra of dialkyl and diaryl trichloromethylphosphonates were recorded. Diaryl trichloromethylphosphonates, a new family of trichloromethylphosphonates, were synthesized by reacting trichloromethylphosphonic dichloride with phenols.

Many organic phosphorus insecticides have been demonstrated to be exceptionally active inhibitors of cholinesterase enzymes and other enzymes with esterase action in mammals and in insects in both *in vivo* and *in vitro* studies (*9, 10*). Trichloromethyl substituted phosphorus compounds are not common but Dipterex, $(CH_3O)_2P(O)CH(OH)CCl_3$, has been reported as a toxicant for baits (*9*). For the most part, structure proof for a very few dialkyl trichloromethylphosphonates rests only on elemental analyses, and diaryl derivatives are unknown. For these reasons, we decided to develop a general synthesis for diaryl trichloromethylphosphonates and to examine the NMR spectra of these compounds and several dialkyl esters.

Although the reaction between carbon tetrachloride and trialkylphosphites has been observed (*5, 6, 8*), compounds containing trichloromethyl groups are not well characterized. Few properties of the dialkyl trichloromethylphosphonates, except melting points or boiling points, are recorded. We have investigated the dialkyl trichloromethylphosphonates by NMR spectroscopy and recorded the coupling constants J_{POCH} in Table I. Values for J_{POCH} for the alkyl derivatives were 6.9 to 11.5 cps, in the normal range for many phosphonates (*3, 4*). The broadness of several group resonances suggests magnetic nonequivalence, a phenomenon not uncommon in phosphorus esters (*1*). We have found a most convenient route to diaryl trichloromethylphosphonates (in high yields) by reacting trichloromethylphosphonic dichloride (*7*) with phenols at room temperature (Table II). The melting points and boiling points and ^{31}P shifts (Table III) for the diaryl trichloromethylphosphonates are positive relative to 85% H_3PO_4. This is surprising in view of the negative shifts for several related phosphonates such as $Cl_3CP(O)(OC_2H_5)_2$ (−6.5 ppm);

Table I. ^1H Data for Dialkyl Trichloromethylphosphonates (CCl_4, TMS)



$Cl_3C\overset{\overset{O}{\uparrow}}{P}(OR)_2$

R	δ Values, J_{POCH}-Hz
—CH_3	4.03(12)-d
—CH_2	4.38(7)-q(b)
CH_3	1.43(7)-t
—CH_2	4.26(~7)-q(bs)[a]
CH_2	1.72(~7)-h(bs)
CH_3	1.00(7.1)-t(bs)
—CH	4.80-m
H_3C CH_3	1.41(~7.1)-d(bs)
—CH_2	4.06-t(bs)[a]
CH	2.02-m
H_3C CH_3	0.98-d(bs)

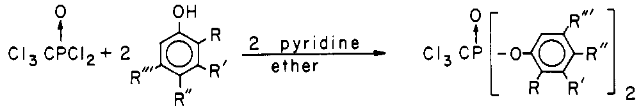
d = doublet; h = hextet; m = multiplet; q = quintet; t = triplet; b = broad; bs = broad with additional splitting suggesting non-equivalence of the two groups.

[a] The broadness in these two cases is most likely due to small differences in J_{POCH} and J_{HH}.

Table II. Diaryl Trichloromethylphosphonates

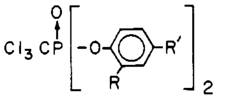
Compound[a]	M.P., ° C, or B.P., ° C/mm	Yield, %
1a	66	73
b	165/0.0005	78
c	170/0.002	77
d	57	77
e	48	78
f	48	78
g[b]	116	80
h	92.5	77
i	89	78
j	48.5	80
k	53.5	90
l	115	85
m	72	90
n	78	90

[a] All compounds gave satisfactory elemental analyses. [b] Recrystallized from benzene.



1a $R = R'' = R''' = H$
b $R = CH_3, R' = R'' = R''' = H$
c $R' = CH_3, R = R'' = R''' = H$
d $R'' = CH_3, R = R' = R''' = H$
e $R'' = Cl, R = R' = R''' = H$
f $R'' = Br, R = R' = R''' = H$
g $R = NO_2, R' = R'' = R''' = H$
h $R' = R'' = Cl, R = R''' = H$
i $R' = R''' = Cl, R = R'' = H$
j $R'' = OCH_3, R = R' = R''' = H$
k $R'' = OC_2H_5, R = R' \ R''' = H$
l $R' = R'' = R''' = CH_3, R = H$
m $R'' = SCH_3, R = R' = R''' = H$
n $R' = CH_3, R'' = SCH_3, R = R''' = H$

Table III. ^{31}P Data for Diaryl Trichloromethylphosphonates

	Chemical Shift, PPM Relative to 85% H_3PO_4
$R = R' = H$	+4.54
$R = H, R' = CH_3$	+3.70
$R = H, R' = Cl$	+3.82
$R = H, R' = OCH_3$	+2.96
$R = H, R' = SCH_3$	+3.62
$R = NO_2, R' = H$	+4.89

$C_6H_5P(O)(OC_6H_5)_2$ (−11.8 ppm); and $CH_3P(O)(OC_6H_5)_2$ (−22.0 ppm) (*2*). However, many phosphates and some disubstituted hydrogen phosphonates appear to give positive chemical shifts relative to H_3PO_4. Unfortunately, none of the materials have shown much insecticidal activity.

EXPERIMENTAL

Preparation of Diaryl Trichloromethylphosphonates. A general procedure is given. A solution of 1 mole equivalent of the trichloromethylphosphonic dichloride in dry benzene was added to a solution of 2 mole equivalents of a phenol in dry benzene or a mixture of benzene and ether, mixed with 2 mole equivalents of triethylamine with vigorous stirring under nitrogen. The reaction was exothermic and there was immediate separation of amine hydrochloride. The reaction mixture was then allowed to stir for 6 hours at room temperature. The precipitated hydrochloride was removed by filtration. Solvent was stripped off and the solid residue was then collected and recrystallized from hexane. NMR measurements were made on Varian A-60 and Varian HA-100 MHz units.

Preparation of Dialkyl Trichloromethylphosphonates. The same procedure was used as reported (*5*, *6*).

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