The Self-Quaternization of Dialkyl-2-acetoxyethylphosphines

M. M. Rauhut, Grace B. Borowitz, and Helen Currier Gillham

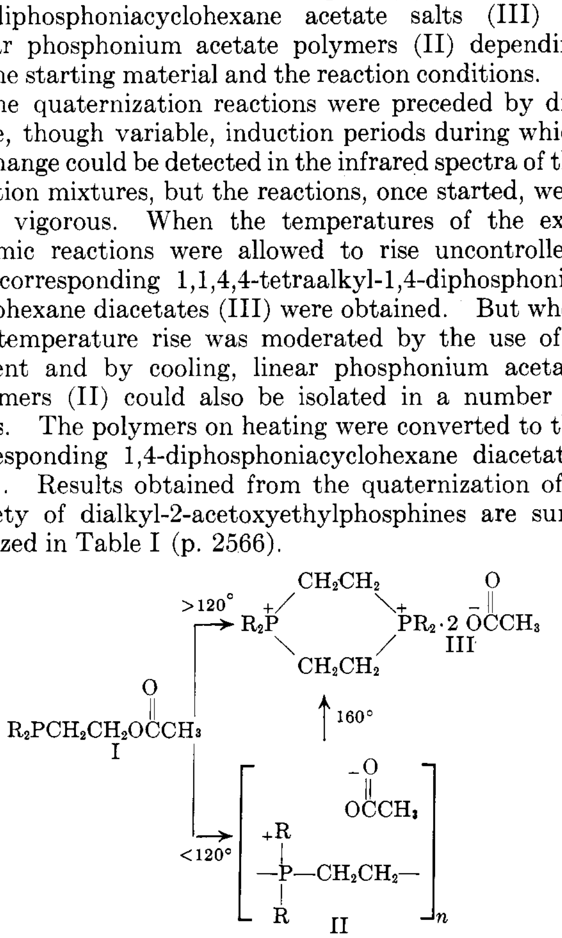
Chemical Research Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut

Received March 1, 1963

Dialkyl-2-acetoxyethylphosphines (I) quaternized exothermically following induction periods to give the corresponding 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane diacetate salts (III). Under controlled conditions poly(dialkyl)ethylenephosphonium acetates (II) also were isolated in several cases. The reactions were initiated by the polymeric phosphonium acetates (II) and inhibited by tributylphosphine. An ionic, autocatalytic mechanism is proposed.

Quaternary phosphonium salts are commonly prepared by the reaction of a tertiary phosphine with an alkyl halide. Alkyl acetates, on the other hand, would not be expected to react with tertiary phosphines under the relatively mild conditions customarily employed, and, indeed, such reactions have not been reported. However, we find that dialkyl-2-acetoxyethylphosphines (I) self-quaternize spontaneously at temperatures in excess of about 80° to give 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane acetate salts (III) or linear phosphonium acetate polymers (II) depending on the starting material and the reaction conditions.

The quaternization reactions were preceded by discrete, though variable, induction periods during which no change could be detected in the infrared spectra of the reaction mixtures, but the reactions, once started, were very vigorous. When the temperatures of the exothermic reactions were allowed to rise uncontrolled, the corresponding 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane diacetates (III) were obtained. But when the temperature rise was moderated by the use of a solvent and by cooling, linear phosphonium acetate polymers (II) could also be isolated in a number of cases. The polymers on heating were converted to the corresponding 1,4-diphosphoniacyclohexane diacetates (III). Results obtained from the quaternization of a variety of dialkyl-2-acetoxyethylphosphines are summarized in Table I (p. 2566).



a, $R = n\text{-}C_4H_9$
b, $R = i\text{-}C_4H_9$
c, $R = n\text{-}C_8H_{17}$
d, $R = C_6H_{11}$
e, $R = CH_2CH_2CN$

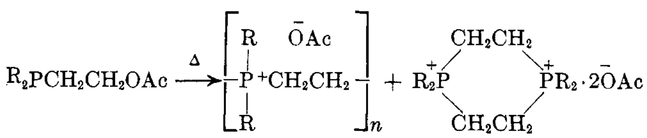
Bis(2-cyanoethyl)-2-acetoxyethylphosphine (Ie) was the most active of the 2-acetoxyethylphosphines studied, quaternizing suddenly and exothermically about five to ten minutes following its preparation at 80°. Attempts to isolate the intermediate polymeric phosphonium acetate IIe in this case were unsuccessful, presumably because of its rapid rearrangement to the cyclic dimer IIIe. Di-*n*-butyl-2-acetoxyethylphosphine (Ia) and di-*n*-octyl-2-acetoxyethylphosphine (Ic) were less reactive requiring variable periods in excess of one hour at 80° before the onset of quaternization. Diisobutyl-2-acetoxyethylphosphine (Ib), still less reactive, was stable at 80° but quaternized after a variable induction period at 120°. 2,4,6-Triisopropyl-5-(2-acetoxyethyl)-1,3-dioxa-5-phosphacyclohexane, probably for steric reasons, did not quaternize even when heated at 300° for three hours. The exceptional nature of the quaternization reaction was amplified by the evident stability of di-*n*-butyl-3-acetoxypropylphosphine which remained unchanged even at 300°. This result demonstrated that a phosphine substituent beta to the leaving group was essential for facile quaternization.

The induction periods preceding the onset of quaternization and the quaternization reactions themselves were not altered by the presence of excess bis(2-cyanoethyl)phosphine, vinyl acetate, or α,α'-azobisisobutyronitrile. Furthermore, the addition of ten mole per cent of triethylamine, acetic acid, or the corresponding 1,4-diphosphoniacyclohexane diacetate (III) prior to quaternization was without effect. However, the reactions were initiated by the polymeric phosphonium acetate products II. In the presence of a small amount of the polymer the induction periods were eliminated and smooth quaternizations were obtained at lower temperatures than were otherwise effective. Under these relatively mild conditions the polymeric phosphonium acetate II was generally the predominant product. Thus dibutyl-2-acetoxyethylphosphine (Ia) quaternized exothermically following a thirty-minute induction period at an initial temperature of 95° to give the cyclic dimer IIIa in 59% yield, while in the presence of added polymer in 2-propanol solution at 78°, infrared analysis demonstrated that a smooth reaction occurred without an induction period to give the polymer IIa in 72% yield. In the absence of added polymer under these latter conditions, no change was detected by infrared analyses during a four-hour period.

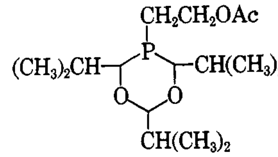
The quaternization reactions were strongly inhibited by trialkylphosphines. Thus, bis(2-cyanoethyl)-2-acetoxyethylphosphine (Ia) was unchanged in the presence of ten mole percent of tributylphosphine when heated two hours at 80° and then for thirty minutes at 100°, while in the absence of tributylphosphine it consistently quaternized exothermically within a few minutes at an initial temperature of 80°. Di-*n*-octyl-2-acetoxyethylphosphine (Ic) in the presence of trioctylphosphine and polymeric phosphonium acetate in 2-propanol solution was unchanged at 85° after six hours, while in the absence of trioctylphosphine under these

TABLE I

QUATERNIZATION OF DIALKYL-2-ACETOXYETHYLPHOSPHINES



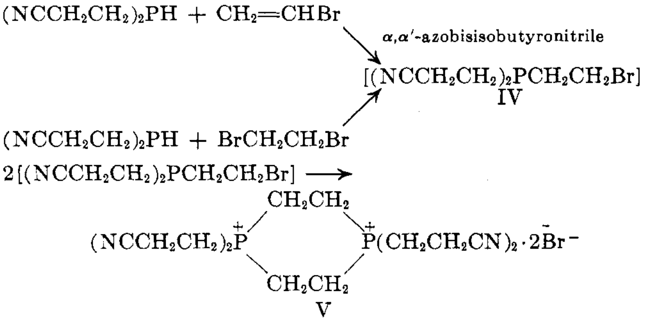
I II III

R	Moles	Solvent	Ml.	Temp., °C.	Time, min.	Yield, % II	Yield, % III
n-C_4H_9	0.50	None	...	95^a	30^b	0	59
n-C_4H_9	0.50	Heptane	50	105	15^b	46	26
n-$C_4H_9{}^c$	0.25	2-Propanol	250	78	480^d	72	0
i-C_4H_9	0.04	None	...	150	3^b	0	21
i-$C_4H_9{}^e$	0.30	2-Propanol	200	84	560^d	38^f	25
n-$C_8H_{17}{}^g$	0.20	None	...	120	120^d	0	33^f
n-$C_8H_{17}{}^e$	0.20	2-Propanol	200	82	330^d	84	0
C_6H_{11}	0.05	None	...	150	60	0	15^f
$C_6H_{11}{}^e$	0.18	2-Propanol	50	84	960	0	33
$NCCH_2CH_2{}^h$	0.20	Acetonitrile	20	80^a	5^b	0	50
$NCCH_2CH_2{}^e$	0.20	Acetonitrile	50	55	25	0	39
$NCCH_2CH_2{}^i$	0.05	Acetonitrile	5	100	30	0	0^j
	0.02	None	...	300	180	0	0^j

[a] Initial temperature, prior to the onset of reaction. [b] Length of induction period. The subsequent reaction was very rapid. [c] One-tenth gram of poly(di-n-butyl)ethylenephosphonium acetate was added initially. In the absence of added polymer under these conditions no change was detected by infrared analysis during four hours. The reaction was not initiated by 1,1,4,4-tetra-n-butyl-1,4-diphosphoniacyclohexane diacetate. [d] Total reaction time. The quaternization proceeded smoothly without an induction period. [e] One-half gram of poly(di-n-butyl)ethylenephosphonium acetate was added initially. [f] Isolated as iodide salt. [g] Poly(di-n-butyl)-ethylenephosphonium acetate (0.2 g.) and approximately one gram of trioctylphosphine were initially present. In an otherwise identical experiment carried out in 250 ml. of 2-propanol at 85°, no change was detected by infrared analysis during six hours. [h] Similar reaction mixtures which contained 10 mole % of bis(2-cyanoethyl)phosphine, vinyl acetate, α,α'-azobisisobutyronitrile, triethylamine, acetic acid, or 1,1,4,4-tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane diacetate gave essentially the same results. [i] One gram of tri-n-butylphosphine was present initially. [j] The starting material was essentially unchanged.

conditions a smooth quaternization occurred providing poly(di-n-octyl)ethylenephosphonium acetate (IIc) in 84% yield.

The quaternary phosphonium salts were identified by analyses, molecular weight determinations, and infrared spectra of the phosphonium acetates and their halide salts prepared by metathesis. For added structural confirmation 1,1,4,4-tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane dibromide (V) was prepared unambiguously by the reaction of 1,2-ethylenebis[bis-(2-cyanoethyl)phosphine][1] with ethylene bromide. 1,1,4,4 - Tetrakis(2 - cyanoethyl) - 1,4 - diphosphoniacyclohexane dibromide (V) was also prepared by reaction of bis(2-cyanoethyl)phosphine with vinyl bromide in the presence of α,α-azobisisobutyronitrile and by reaction of bis(2-cyanoethyl)phosphine with ethylene bromide.



V

In neither case was intermediate bis(2-cyanoethyl)-2-bromoethylphosphine (IV) isolated. Hydrolysis of 1,1,4,4 - tetrakis(2 - cyanoethyl) - 1,4 - diphosphoniacyclohexane diacetate (IIIe) with hydrochloric acid gave 1,1,4,4-tetrakis(2-carboxyethyl)-1,4-diphosphoniacyclohexane dichloride in 70% yield.

The required dialkyl-2-acetoxyethylphosphines (I) were prepared by the addition of the respective dialkylphosphines to vinyl acetate in the presence of α,α'-azobisisobutyronitrile.[2] The reactions proceeded smoothly at 80°, and the yields were substantially quantitative as indicated by infrared analyses of the crude reaction mixtures. Di-n butyl-3-acetoxypropylphosphine was prepared analogously from dibutylphosphine and allyl acetate. 2,4,6·Triisopropyl-5-(2·acetoxyethyl)-1,3 dioxa-5-phosphacyclohexane and di-n-butyl-3-acetoxypropylphosphine were stable and readily ditislled; di-n-butyl- and diisobutyl-2-acetoxyethylphosphines could be distilled satisfactorily at reduced pressures, but the di-n-octyl, the dicyclohexyl, and the bis(2-cyanoethyl) derivatives quaternized at temperatures below their boiling points.

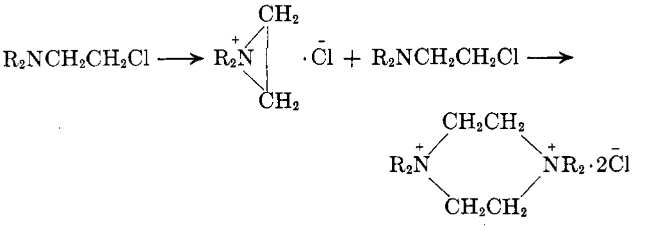
Discussion

The quaternization of dialkyl-2-acetoxyethylphosphines is formally analogous to the quaternization of dialkyl-2-haloethylamines. The latter reaction is be-

---

(1) M. Grayson, P. T. Keough, and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959).

(2) See A. R. Stiles, F. F. Rust, and W. E. Vaughan, *ibid.*, **74**, 3282 (1952); M. M. Rauhut, H. A. Currier, A. M. Semsel, and V. P. Wystrach, *J. Org. Chem.*, **26**, 5138 (1961).

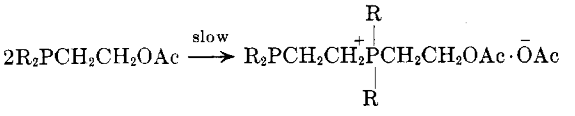


lieved to occur by way of a three-membered cyclic intermediate.[3]

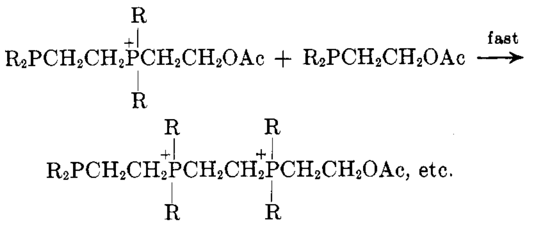
While participation of an analogous cyclic intermediate in the initial step of the quaternization of dialkyl-2-acetoxyethylphosphines has not been ruled out, it is evident from the experimental results that the over-all mechanism is more complex.

An acceptable mechanism must be consistent with the following facts: (a) in the absence of added catalysts or inhibitors, the reaction is preceded by a discrete induction period; (b) following the induction period the reaction rate accelerates rapidly; (c) the reaction is initiated by a poly(dialkyl)ethylene phosphonium acetate (II), but not by a 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane diacetate (III); (d) the polymeric phosphonium acetates (II) rearrange on heating to the cyclic dimers (III); (e) the reaction is inhibited by tributylphosphine but not by triethylamine.

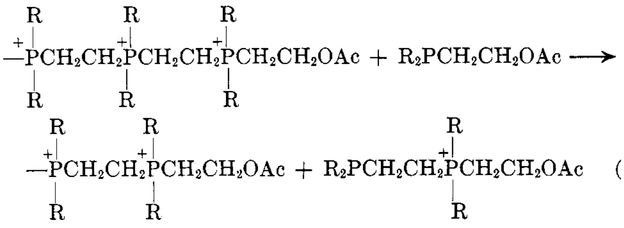
A mechanism consistent with these facts is presented in the following equations.



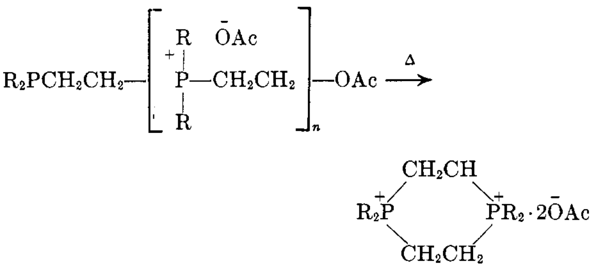
$$2R_2PCH_2CH_2OAc \xrightarrow{slow} R_2PCH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc\cdot\overset{-}{O}Ac \tag{1}$$



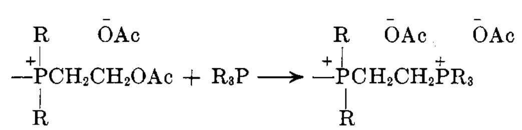
$$R_2PCH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc + R_2PCH_2CH_2OAc \xrightarrow{fast} R_2PCH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc, \text{ etc.} \tag{2}$$



$$-\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc + R_2PCH_2CH_2OAc \longrightarrow -\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc + R_2PCH_2CH_2\overset{R}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc \tag{3}$$



(4)



$$-\overset{R\ \ \overset{-}{O}Ac}{\underset{R}{\overset{+}{P}}}CH_2CH_2OAc + R_3P \longrightarrow -\overset{R\ \ \overset{-}{O}Ac}{\underset{R}{\overset{+}{P}}}CH_2CH_2\overset{\overset{-}{O}Ac}{\overset{+}{P}}R_3 \tag{5}$$

Step 1 is evidently required to initiate the uncatalyzed reaction but must be slow to account for the observed induction periods (fact a). Step 2 propagates the polymer and must be rapid to accommodate the observed autocatalysis (fact c). Step 3 provides for a branched-chain reaction and seems necessary to account for the rapid acceleration of the reaction following the induction period (fact b) as well as the apparently low molecular weights of the polymers obtained. Step 4 accommodates the conversion of polymer to cyclic dimer (fact d) and may be viewed tentatively as an intramolecular version of step 3. Except for the quaternization of bis(2-cyanoethyl)-2-acetoxyethylphosphine, steps 3 and 4 are evidently important only above about 120°. Equation 5, entirely analogous to step 2, accounts for the inhibition by tributylphosphine (fact e) by chain termination.

Steps 2 and 5 require that a tertiary phosphine readily displace an acetoxy group located β to a phosphonium group. This was confirmed by a model reaction of tributyl-2-acetoxyethylphosphonium bromide with tributylphosphine. The ethylenebis(tributylphosphonium salt) (isolated as the diiodide) was readily obtained under conditions used for the dialkyl-2-acetoxyethylphosphine quaternizations.

$$(C_4H_9)_3\overset{+}{P}CH_2CH_2OAc\cdot\overset{-}{Br} + (C_4H_9)_3P \longrightarrow (C_4H_9)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_4H_9)_3\cdot\overset{-}{Br},\ \overset{-}{O}Ac$$

The results of a detailed kinetic study of this model reaction will be presented in a subsequent communication.

Contrary to a recent report,[4] the reaction of triphenylphosphine with 2-chloroethyl acetate also follows the same pattern. The product isolated was ethylenebis(triphenylphosphonium chloride), identical to the product obtained by reaction of triphenylphosphine with ethylene dichloride. The intermediate triphenyl-2-acetoxyethylphosphonium chloride was not found under the conditions employed.

$$(C_6H_5)_3P + ClCH_2CH_2OAc \xrightarrow{slow} [(C_6H_5)_3\overset{+}{P}CH_2CH_2OAc\cdot\overset{-}{Cl}] \xrightarrow[fast]{(C_6H_5)_3P} (C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\cdot\overset{-}{Cl},\ \overset{-}{O}Ac$$

Step 3 requires that under conditions used for quaternization sthe following equilibrium be established.

$$R_3\overset{+}{P}CH_2CH_2\overset{+}{P}R_3 + R_3'P \rightleftharpoons R_3\overset{+}{P}CH_2CH_2\overset{+}{P}R_3' + R_3P$$

This was confirmed by a reaction between 1,2-ethylenebis(tributylphosphonium iodide) and trioctylphosphine in the presence of acetate ion in a refluxing methanol–isopropyl alcohol mixture. The rapid appearance of tributylphosphine was established by vapor phase chromatography. Acetate ion was required to establish the equilibrium suggesting a possible elimination–addition mechanism. Tributylphosphine was not detected when 1,2-ethylenebis(tributylphosphonium iodide) was treated with sodium acetate alone under these conditions.

Experimental[5]

Materials.—The dialkylphosphines were prepared by the method of Stiles, Rust, and Vaughan.[2] 2,4,6-Triisopropyl-

---

[3] P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2971 (1947).

[4] G. Aksnes, *Acta Chem. Scand.*, **15**, 438 (1961).

[5] Melting points and boiling points are uncorrected.

TABLE II

1,1,4,4-TETRAALKYL-1,4-DIPHOSPHONIACYCLOHEXANE SALTS

R	X^-	Recrystallization solvent	M.p., °C.	Analyses, %									
				Carbon		Hydrogen		Phosphorus		Halogen		Mol. wt.	
				calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found
n-C_4H_9	OAc	Benzene–ethanol	195 dec.	62.04	60.76	10.84	11.05	13.33	13.65	...	...	465	369[a]
n-C_4H_9	Br	1-Butanol	316–319 dec.	...	...	...	...	12.23	12.20	31.56	31.15	...	...
n-C_4H_9	I	Water	>335	40.01	39.92	7.38	7.52	...	...	43.58	43.71	...	...
i-C_4H_9	OAc	None	157–158 dec.	62.04	62.34	10.84	11.28	13.33	13.14	...	...	465	604[b]
i-C_4H_9	I	Dimethylformamide	337 dec.	40.01	40.40	7.38	7.34	10.63	10.52	...	...	...	...
n-C_8H_{17}	I	Ethanol	298–299 dec.	...	...	...	...	7.51	7.55	30.77	30.89	825	511[a]
C_6H_{11}	OAc	Methyl isobutyl ketone	221–223 dec.	67.57	66.49	10.27	10.59	10.89	10.92	...	...	704	450[c]
$NCCH_2CH_2$	OAc	2-Propanol–acetone	149–150 dec.	...	...	...	...	13.69	13.60	...	...	...	...
$NCCH_2CH_2$	Cl	Methanol–water	286–288 dec.	47.41	47.13	5.97	6.21	15.28	15.52	17.49	17.54	135	168[d]
$NCCH_2CH_2$	Br	Water	303–304 dec.	...	...	...	...	12.53	12.94	32.34	32.81	...	...
$NCCH_2CH_2$	I	Water	320 dec.	...	...	...	...	10.53	10.60	43.15	43.19	...	...
$HOOCCH_2CH_2$	Cl	Acetone–water	280–282	39.93	39.83	5.86	6.05	12.87	12.85	14.73	14.72	...	...

[a] Boiling point rise in ethanol. [b] Vapor pressure thermister method[8] in methylene chloride. [c] Vapor pressure thermister method[8] in chloroform. [d] Boiling point rise in water.

1,3-dioxa-5-phosphacyclohexane was prepared by the acid-catalyzed reaction of phosphine with isobutyraldehyde.[6] Bis-(2-cyanoethyl)phosphine was prepared by the base-catalyzed addition of phosphine to acrylonitrile.[7] Ethylenebis[bis(2-cyanoethyl)phosphine] was prepared from ethylenebis[tris(2-cyanoethyl)phosphonium bromide].[1] Other starting materials were obtained from conventional sources.

Dialkylacetoxyalkylphosphines.—The acetoxyalkylphosphines were prepared in general by adding 21.6 g. (0.25 mole) of vinyl acetate dropwise during 10 min. to a stirred solution of 0.25 mole of the secondary phosphine and 1.0 g. of α,α'-azobisisobutyronitrile in 75 ml. of the solvent at 78° under nitrogen. The mixtures were then stirred at 80–82° for an additional period to insure complete reaction. The addition reactions were essentially quantitative as indicated by the infrared spectra of the crude products; absorption bands corresponding to unchanged secondary phosphine or to vinyl acetate could not be detected, and bands at 1750 $cm.^{-1}$ and 1240 $cm.^{-1}$ corresponding to an acetate ester were present.

Di-*n*-butyl-2-acetoxyethylphosphine, b.p. 62–66° (0.005 mm.), 60% yield, was prepared in 2-propanol during 30 min. It was distilled after removal of solvent, in 10- to 15-ml. batches; the distillation could not be prolonged without vigorous quaternization taking place in the distillation flask.

Anal. Calcd. for $C_{12}H_{25}O_2P$: C, 62.04; H, 10.85; P, 13.34. Found: C, 62.45; H, 10.88; P, 13.13.

Diisobutyl-2-acetoxyethylphosphine, b.p. 80–84° (0.3 mm.), 82% yield, was prepared in acetonitrile during 60 min.

Anal. Calcd. for $C_{12}H_{25}O_2P$: C, 62.04; H, 10.85; P, 13.34. Found: C, 62.28; H, 10.85; P, 13.38.

2,4,6-Triisopropyl-5-(2-acetoxyethyl)-1,3-dioxa-5-phosphacyclohexane, b.p. 123° (0.3 mm.), 74% yield, was prepared in acetonitrile during 60 min.

Anal. Calcd. for $C_{16}H_{31}O_4P$: C, 60.35; H, 9.81; P, 9.73. Found: C, 59.64; H, 9.78; P, 9.62.

Di-*n*-butyl-3-acetoxypropylphosphine, b.p. 98–102° (0.1 mm.), 82% yield, was prepared in heptane during 60 min.

Anal. Calcd. for $C_{13}H_{27}O_2P$: C, 63.39; H, 11.05; P, 12.57. Found: C, 63.23; H, 11.25; P, 12.79.

Di-*n*-octyl-2-acetoxyethylphosphine, prepared in 2-propanol during 120 min., **dicyclohexyl-2-acetoxyethylphosphine**, prepared in 2-propanol during 150 min., and bis(2-cyanoethyl)-2-acetoxyethylphosphine quaternized below their distillation temperatures.

Quaternization Reactions of Dialkyl-2-acetoxyethylphosphines.—Individual experiments are described in Table I. The cyclic phosphonium salts are described in Table II; the halide salts were precipitated from aqueous solutions of the acetates by adding saturated aqueous solutions of the corresponding sodium halide. Representative experiments are described in this Experimental section.

Di-*n*-butyl-2-acetoxyethylphosphine.—A solution of 116 g. (0.50 mole) of the phosphine Ia in 50 ml. of heptane was heated at 105° under nitrogen. After 15 min. a vigorous reaction occurred leaving a dark red solution. The solution was cooled to room temperature, diluted with 150 ml. of anhydrous ether, and filtered to obtain 30.0 g. (26%) of 1,1,4,4-tetrabutyl-1,4-diphosphoniacyclohexane diacetate (IIIa), m.p. 193–194° dec. Recrystallization from benzene containing a little ethanol gave material melting at 195° dec.

The filtrate from the diphosphonium diacetate was freed of solvents under reduced pressure, and the residue was treated with 900 ml. of acetone. The precipitated solid was collected, washed with acetone and with anhydrous ether, and dried in a vacuum desiccator over phosphorus pentoxide to obtain 53.0 g. (46%) of white polymer, m.p. 156–157° dec. The polymeric acetate was deliquescent and was characterized as the halide salts.

Ten grams of the polymeric acetate was dissolved in 125 ml. of cold water and the solution was treated with saturated aqueous sodium bromide solution until precipitation was complete. The yellow gum which separated was dissolved in 50 ml. of acetone, and the solution was decolorized with activated charcoal. The solution was poured into excess ether and the precipitated white polymer was collected and washed with ether to obtain material melting at 258–270° dec.

Anal. Calcd. for $(C_{10}H_{22}BrP)_n$: C, 47.43; H, 8.75; P, 12.23. Found: C, 47.34; H, 8.73; P, 11.90; mol. wt., >3000 (vapor pressure thermister method in chloroform at 30°).[8] The intrinsic viscosity determined in water at 30° was 0.267.

A solution of 10.0 g. of the polymeric acetate in 150 ml. of water was treated with saturated aqueous sodium iodide solution until precipitation was complete. The precipitated iodide (11.8 g.) was reprecipitated from acetone with ether to obtain a white solid melting at about 310–315° dec.

Anal. Calcd. for $(C_{10}H_{22}IP)_n$: C, 40.01; H, 7.38; P, 10.32. Found: C, 40.98; H, 8.44; P, 9.81; mol. wt., >2120 (boiling point rise in ethanol).

Diisobutyl-2-acetoxyethylphosphine.—A solution of 70 g. (0.30 mole) of the phosphine Ib and 0.5 g. of the phosphonium acetate polymer from di-*n*-butyl-2-acetoxyethylphosphine (IIa) in 200 ml. of 2-propanol was heated at 80–84° under nitrogen for 560 min. The reaction mixture was concentrated to a thick sirup under reduced pressure. The sirup was treated with 700 ml. of anhydrous ether to precipitate 10.6 g. (15%) of 1,1,4,4-tetra-

---

(6) S. A. Buckler and V. P. Wystrach, *J. Am. Chem. Soc.*, **83**, 168 (1961).

(7) M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *ibid.*, **81**, 1103 (1959).

(8) A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961).

isobutyl-1,4-diphosphoniacyclohexane diacetate (IIIb), m.p. 157–158° dec.

The ethereal filtrate from the diphosphonium diacetate was extracted with three 50-ml. portions of water. The combined extracts were diluted with water to 500 ml., and the solution was treated with excess aqueous potassium iodide. The precipitated solid was extracted with 150 ml. of hot acetone to obtain 8.4 g. (10%) of the insoluble diphosphonium diidodide IIIb, m.p. 319–323° dec. The filtrate was diluted with 1 l. of ether. An oil separated and solidified when washed with ether. The solid (33.5 g., 38%) was reprecipitated from acetone with ether to obtain an analytical sample of the polymeric phosphonium iodide IIb, m.p. 292–296° dec.

Anal. Calcd. for $(C_{10}H_{22}PI)_n$: C, 40.01; H, 7.38; P, 10.63. Found: C, 41.42; H, 7.14; P, 10.82; mol. wt., >3900 (vapor pressure thermister method[8] in methanol).

Di-*n*-octyl-2-acetoxyethylphosphine.—The reaction mixture from 69 g. (0.2 mole) of the phosphine IIIc quaternized in the absence of solvent at 120° during 120 min. was treated with 100 ml. of ether to obtain a homogeneous solution. The solution was extracted with eight 100-ml. portions of water, and the combined extracts were treated with excess aqueous potassium iodide. The precipitated solid (26.8 g., 33%) was recrystallized from ethanol to obtain the crystalline diphosphonium diiodide IIIc, m.p. 298–299° dec.

In another experiment a solution of 69 g. (0.2 mole) of the phosphine Ic and 0.5 g. of the phosphonium acetate polymer from di-*n*-butyl-2-acetoxyethylphosphine (IIa) in 200 ml. of 2-propanol was heated under nitrogen at 82° for 330 min. The reaction mixture was cooled and poured into 1 l. of water. The precipitated solid was collected to obtain 58 g. (84%) of the phosphonium acetate polymer IIc, m.p. 142–144° dec. Two reprecipitations from 2-propanol with acetone gave material melting at 154–156°.

Anal. Calcd. for $(C_{20}H_{41}O_2P)_n$: C, 69.72; H, 11.99; P, 8.55. Found: C, 65.14; H, 12.14; P, 7.56; mol. wt., >1375 (boiling point rise in ethanol).

Five grams of the phosphonium acetate polymer in 10 ml. of 2-propanol treated with excess aqueous potassium iodide gave 5.2 g. of the phosphonium iodide polymer, m.p. 293–294° dec., after reprecipitation from 2-propanol with water. In contrast to the diphosphonium diidodide, the polymer was soluble in acetone. A mixture melting point of the two phosphonium iodides was depressed to 270–291°.

Anal. Calcd. for $(C_{18}H_{38}IP)_n$: C, 52.24; H, 9.28; I, 30.77; P, 7.51. Found: C, 52.63; H, 9.11; I, 30.36; P, 7.51; mol. wt., >2259 (boiling point rise in ethanol).

Dicyclohexyl-2-acetoxyethylphosphine.—A solution of 50.0 g. (0.18 mole) of the phosphine Id and 0.5 g. of poly(dibutyl)-ethylenephosphonium acetate (IIa) in 50 ml. of 2-propanol was stirred under nitrogen at 80–84° for 16 hr. The infrared spectrum of the solution indicated that acetate ester was still present, although at a substantially reduced concentration. The solution was cooled and diluted with 900 ml. of anhydrous ether. After standing at 0° overnight the solution deposited 4.2 g. (8%) of 1,1,4,4-tetracyclohexyl-1,4-diphosphoniacyclohexane diacetate (IIId), m.p. 221–223° dec.

The filtered reaction mixture was concentrated to a sirup under reduced pressure. Addition of 500 ml. of anhydrous ether precipitated an additional 12.5 g. (25%) of the diphosphonium diacetate, m.p. 216–218° dec.

1,1,4,4-Tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane Diacetate (IIIe) from Bis(2-cyanoethyl)-2-acetoxyethylphosphine.—A solution of 18.9 g. (0.22 mole) of vinyl acetate and 1.5 g. (0.01 mole) of α,α'-azobisisobutyronitrile in 20 ml. of acetonitrile was added dropwise with stirring during 20 min. to 28.0 g. (0.20 mole) of bis(2-cyanoethyl)phosphine which had been preheated to 76° under nitrogen. The reaction temperature was held at 78–83° by intermittent cooling in a water bath. At the end of the addition, the exotherm subsided and heat was applied to maintain the temperature at 83°. After about 10 min. a vigorous reaction began spontaneously. Although an ice bath was applied immediately the temperature rose to 95° and the reaction mixture boiled violently. When the reaction subsided the opaque, tan, viscous mixture was cooled to room temperature and stirred into 250 ml. of acetone. Much of the reaction mixture dissolved leaving 22.5 g. (50%) of a white crystalline solid, m.p. 150–151° dec. A portion of the product was dissolved in hot 2-propanol, containing a few drops of water, and the solution was diluted with 2 volumes of acetone. After standing several days at −10° crystals were obtained which after drying at 53° over phosphorus pentoxide melted at 149–150° dec.

Reaction of Bis(2-cyanoethyl)phosphine with 1,2-Dibromoethane.—A solution of 28.0 g. (0.20 mole) of bis(2-cyanoethyl)-phosphine, 9.4 g. (0.05 mole) of 1,2-dibromoethane, and 50 ml. of acetonitrile was refluxed for 2 hr. under nitrogen. The reaction mixture was cooled and filtered to obtain 0.4 g. of white solid. Recrystallization from water gave 0.1 g. of crystalline solid, m.p. 300–305°. A mixture melting point with authentic 1,1,4,4-tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane dibromide was not depressed and the infrared spectra were identical. Other products from the reaction were gums which were not identified.

Reaction of Bis(2-cyanoethyl)phosphine with Vinyl Bromide.—A slow stream of vinyl bromide was passed during 30 min. into a stirred solution of 12.5 g. of bis(2-cyanoethyl)phosphine and 0.80 g. of α,α'-azobisisobutyronitrile in 35 ml. of acetonitrile heated at 80°. An oil began to separate almost immediately. The oil congealed to a white gum when cool. Extraction of the gum with hot water gave 1.8 g. of crystalline solid, m.p. 300–303° dec. A mixture melting point with authentic 1,1,4,4-tetrakis-(2-cyanoethyl)-1,4-diphosphoniacyclohexane dibromide was not depressed, and the infrared spectra of the two products were identical.

1,1,4,4-Tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane Dibromide from 1,2-Ethylenebis[bis(2-cyanoethyl)phosphine] and Ethylene Dibromide.—A solution of 6.1 g. (0.02 mole) of 1,2-ethylenebis[bis(2-cyanoethyl)phosphine] and 3.8 g. (0.02 mole) of ethylene dibromide in 25 ml. of acetonitrile was refluxed for 1 hr. A white solid began to separate almost at once. The hot solution was filtered to obtain 1.2 g. of 1,1,4,4-tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane dibromide, m.p. 303–305° dec. A mixture melting point with the bromide salt of the product obtained from the reaction of bis(2-cyanoethyl)phosphine with vinyl acetate was not depressed and the infrared spectra of the two products were identical. The filtrate when cooled to 0° deposited 5.1 g. of unchanged 1,2-ethylenebis[bis(2-cyanoethyl)-phosphine], m.p. 98–102° (lit.[1] m.p. 101–102°).

1,1,4,4-Tetrakis(2-carboxyethyl)-1,4-diphosphoniacyclohexane Dichloride.—Five grams (0.01 mole) of 1,1,4,4-tetrakis(2-cyanoethyl)-1,4-diphosphoniacyclohexane diacetate was dissolved in 10 ml. of warm concentrated hydrochloric acid. After refluxing 5 min. the solution congealed to a white mass. An additional 20 ml. of concentrated hydrochloric acid was added and the mixture was then refluxed for 1 hr.

After cooling to room temperature, the solid was collected and washed with acetone. Recrystallization from dilute hydrochloric acid followed by recrystallization from aqueous acetone gave 3.7 g. (70%) of 1,1,4,4-tetrakis(2-carboxyethyl)-1,4-diphosphoniacyclohexane dichloride, m.p. 280–282°.

Anal. Calcd. for $C_{16}H_{28}Cl_2O_8P_2$: C, 39.93; H, 5.86; P, 12.87; Cl, 14.73. Found: C, 39.83; H, 6.05; P, 12.85; Cl, 14.72.

Rearrangement of Poly(di-*n*-butyl)ethylenephosphonium Acetate to 1,1,4,4-Tetra-*n*-butyl-1,4-diphosphoniacyclohexane Diacetate.—Three grams of the polymer was heated under nitrogen for 20 min. in a bath at 160–165°. The resulting red-brown melt was cooled and dissolved in 75 ml. of water. The solution was treated with saturated aqueous potassium iodide solution until precipitation was complete, and the solid was collected and washed with acetone to obtain 1.2 g. (32%) of the iodide salt of the cyclic dimer, m.p. 337–338° dec. A mixture melting point with authentic material was not depressed.

Tributyl-2-acetoxyethylphosphonium Bromide.—A mixture of 204 g. (1.01 moles) of tributylphosphine, 133 g. (1.06 moles) of 2-bromoethanol, and 275 ml. of dry 1,2-dimethoxyethane was heated at reflux under nitrogen for 18 hr. Tributyl-2-hydroxyethylphosphonium bromide separated as a heavy oil. Isopropenyl acetate (320 g., 3.2 moles) and 3 drops of 48% hydrobromic acid were added, and the mixture was stirred at reflux for 18 hr. Volatile components were removed under reduced pressure leaving the product as a viscous, hygroscopic oil. A solution of the oil in benzene was freeze-dried to obtain the very hygroscopic, solid phosphonium salt.

Anal. Calcd. for $C_{16}H_{34}O_2Br$: C, 52.04; H, 9.28; P, 8.38; Br, 21.64. Found: C, 52.55; H, 9.72; P, 8.59; Br, 21.40.

Reaction of Tributyl-2-acetoxyethylphosphonium Bromide with Tributylphosphine.—A solution of 0.74 g. of the phosphonium bromide and 1.6 g. of tributylphosphine in 25 ml. of 2-propanol was heated at 76° under nitrogen for 30 hr. Solvent and excess tributylphosphine were distilled under reduced pressure and the oily residue was dissolved in 50 ml. of water. Addition of 5% aqueous potassium iodide precipitated 1.3 g. (92%) of ethylenebis(tributylphosphonium iodide). Recrystallization from a mixture of ethanol and acetonitrile gave material melting at 194–195°.

Anal. Calcd. for $C_{26}H_{58}I_2P_2$: C, 45.49; H, 8.51; I, 36.95; P, 9.04. Found: C, 45.25; H, 8.05; I, 37.05; P. 9.24.

Reaction of Triphenylphosphine with 2-Chloroethylacetate.—A mixture of 50 g. (0.2 mole) of triphenylphosphine and 30 g. (0.25 mole) of 2-chloroethylacetate was stirred at 150° under nitrogen for 2 hr. The mixture was cooled and treated with 50 ml. of acetone and with 100 ml. of ether. The crude product precipitated and was recrystallized two times from a 1,2-dimethoxyethane-nitromethane mixture to obtain 18.1 g. (30%) of ethylenebis(triphenylphosphonium chloride), m.p. 282–285°. An additional recrystallization from 2-propanol gave material melting at 287–289°.

Anal. Calcd. for $C_{38}H_{34}Cl_2P_2$: C, 73.19; H, 5.49; Cl, 11.37; P, 9.95. Found: C, 72.97; H, 5.64; Cl, 11.29; P, 9.76.

The infrared spectrum did not contain carbonyl bands, and the product was identical to material prepared from triphenylphosphine and ethylene dichloride. No attempt was made to isolate the corresponding ethylenebis(triphenylphosphonium acetate).

Reaction of Ethylene(tributylphosphonium Iodide) with Trioctylphosphine and Acetate Ion.—A mixture of 3.45 g. (0.005 mole) of ethylenebis(tributylphosphonium iodide), 3.7 g. (0.01 mole) of trioctylphosphine, 0.2 g. (0.0024 mole) of anhydrous sodium acetate, 15 ml. of methanol, and 20 ml. of 2-propanol was refluxed under nitrogen for 1 hr. The presence of tributylphosphine in the mixture was established by gas chromatography, using an Aerograph Model A-100-C gas chromatograph with a 5-ft. long, 0.25-in. diameter Apiezon L column operated at 204° with a helium flow rate of 60 ml./min. The retention time for tributylphosphine under these conditions was 7.0 min.

Tributylphosphine could not be detected in these reaction mixtures when either acetate ion or trioctylphosphine was omitted. But tributylphosphine was detected when sodium acetate was replaced by 1,1,4,4-tetra-*n*-butyl-1,4-diphosphoniacyclohexane diacetate.

Acknowledgment.—We are indebted to Dr. Robert Stern for first preparing analytically pure di-*n*-butyl-2-acetoxyethylphosphine and to Mrs. Alice T. Tsilibes for some of the experiments with this compound. Analyses were carried out under the direction of Dr. J. A. Kuck and molecular weight determinations were by Mr. E. O. Ernst. We are indebted to Dr. Martin Grayson for his interest and encouragement.

Diels–Alder Reactions. II. The Independence of Reaction Temperature and Mode of Addition in the Isoprene–Methyl Acrylate Diels-Alder Reaction

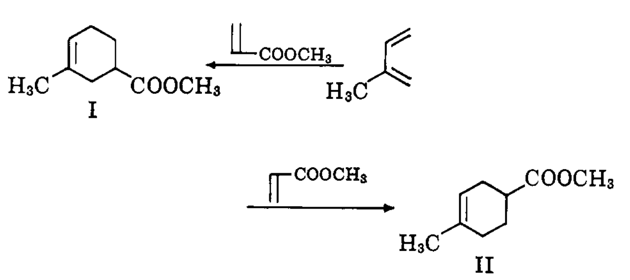
HENRY E. HENNIS

Benzene Research Laboratory, Midland Division, The Dow Chemical Company, Midland, Michigan

Received February 13, 1963

The isoprene–methyl acrylate Diels–Alder reaction was studied at reaction temperatures of 25–350°. No significant differences in the relative amounts of the two structural isomers could be detected by capillary column gas chromatography or infrared absorption spectroscopy analyses. These results are not in agreement with the data published by Nazarov, Titov, and Kuznetsova[1] who claimed that the ratio of 3-isomer to 4-isomer increased with increasing reaction temperature.

The Diels–Alder reaction of isoprene and methyl acrylate is typical of the reaction of an unsymmetrical diene and dienophile. Two structural isomers, the 3-isomer (I) and the 4-isomer (II), may be formed because two modes of addition are possible.[2] Both isomers have been detected in a number of these reactions. Specifically, Alder and Vogt[3] reported that the product of the reaction of isoprene and methyl acrylate contained about 18% of the 3-isomer. Nazarov, *et al.*[4] proved the presence of both structural isomers and later repeated the work to determine more precisely the composition of the product. This investigation was extended to include the effect of the reaction temperature on the mode of addition of this reaction and some other Diels–Alder reactions.



Of particular interest was the claim of Nazarov, Titov, and Kuznetsova[1] that the composition of the product mixture was dependent on reaction temperature. For example, their data indicated the ratio of 4- and 3-isomers of the isoprene–methyl acrylate adduct decreased from 5.1 to 1.4 as the reaction temperature was increased from 20 to 400°. This article did not suggest if the adducts were initially formed and remained at these ratios or whether these ratios were characteristic of a thermally equilibrated mixture. For example, equilibration would be feasible *via* a reverse Diels–Alder reaction.[5]

The latter explanation was initially accepted for two reasons. First, extension of prior work in this Laboratory[6] indicated that the isoprene–methyl acrylate reaction would proceed very rapidly at elevated temperatures and that Nazarov, Titov, and Kuznetsova[1] very likely used a considerably longer reaction time than necessary. Second, the use of an oven temperature as a reaction temperature guide of a highly exothermic reaction is not a sound experimental technique. In

---

[1] I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* (Eng. Transl.), 1412 (1959).

[2] The 3- and 4-isomers are often referred to in the literature as the *meta* and *para* isomers, respectively. The latter designation has been avoided because of possible confusion with the nomenclature of aromatic compounds.

[3] K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949).

[4] I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *Zh. Obshch Khim.*, **25**, 88 (1955); *J. Gen. Chem. USSR* (Eng. Transl.), **25**, 75 (1955); *Chem. Abstr.*, **50**, 1623 (1956).

[5] For an excellent review of the stereochemistry of the Diels–Alder reaction, see J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[6] H. E. Hennis, *Ind. Eng. Chem. Process Design Develop.*, **1**, No. 1, 71 (1962).