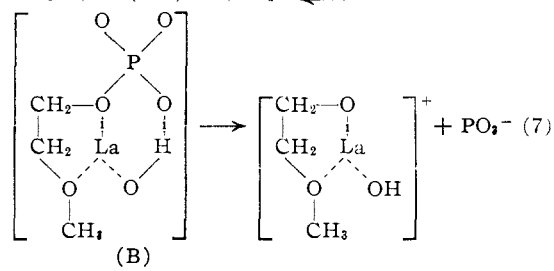
$ROPO_3H_2$ is present in high concentration, hydrolysis by way of an intermediate analogous to A would lead to the alcohol, ROH, and monomeric metaphosphoric acid, HPO_3. But presumably such an intermediate will not lose ROH, with the bonding electron pair accompanying oxygen, as readily as will the negatively charged intermediate, A. In strong acid, one or more additional mechanisms, which require C–O cleavage, dominate the hydrolysis. Thus the distinctive *p*H–rate profile for the phosphate hydrolysis may be explained provided that (at moderate acidities) proton transfer to the alcoholic oxygen atom is an obligatory part of the process.

The mechanism for the hydrolysis of simple phosphate esters also can be formulated without the additional water molecule postulated in A so that the hydrolysis goes by way of a four-membered, rather than a six-membered, ring. However, the intermediate A bears somewhat the same relationship to the zwitterion, $R-\overset{+}{\underset{H}{O}}-PO_3^=$, as the cyclic, hydrogen-bonded intermediate in the decarboxylation of beta ketoacids[21] bears to its corresponding zwitterion; the six-membered ring appears *a priori* more probable than the other possibilities. Alternatively, the hypothetical ion, PO_3^-, might be hydrated to $H_2\overset{+}{O}-PO_3^=$ simultaneously with the decomposition of A. These formulations can also explain the *p*H–rate profile.

A mechanism somewhat analogous to that shown in equations 5 and 6 can explain the hydrolysis promoted by lanthanum hydroxide gel. Since the rate is considerably increased (see Table IV) by a substituent in the β-position in the ester, the oxygen or nitrogen atom of this substituent is probably coördinated with lanthanum ion; since the methoxy group causes an increase in rate, the ionization of the substituent is certainly not a necessary part of the process. (Choline phosphate is a special case; perhaps here the positive charge of the nitrogen atom has a favorable electrostatic effect upon the rate of hydrolysis.) A plausible mechanism for the hydrolysis of methoxyethyl phosphate is shown in equation 7.

$$ROPO_3^= + La(OH)^{++} + H_2O \rightleftharpoons$$



(B)

$$PO_3^- + H_2O \longrightarrow H_2PO_4^- \qquad (6)$$

Alternatively, the postulated intermediate, B, may hydrolyze directly to $H_2PO_4^-$ or may rearrange directly to a lanthanum phosphate complex. In eq. 7 the positive lanthanum ion replaces, as to essential function, the proton of the monoanion, $ROPO_3H^-$, in the hydrolysis shown in eq. 5.

Bamann pointed out that the effect of lanthanum ion in promoting the hydrolysis of α-glyceryl phosphate can be observed only in alkaline solution where the gel, $La(OH)_3$, is present as a separate phase. The exact statement of mechanism for a heterogeneous reaction is extraordinarily difficult at the present time; a more accurate formulation must, in all probability, await a determination of the kinetics of metal-ion promoted hydrolysis of a phosphate ester in homogeneous solution.

CAMBRIDGE, MASS.

(21) F. H. Westheimer and W. A. Jones, THIS JOURNAL, **63**, 3283 (1941).

[CONTRIBUTION FROM THE ENTOMOLOGY RESEARCH BRANCH, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Insecticidal Phosphates Obtained by a New Rearrangement Reaction[1a]

BY W. F. BARTHEL, B. H. ALEXANDER, P. A. GIANG AND S. A. HALL

RECEIVED DECEMBER 10, 1954[1b]

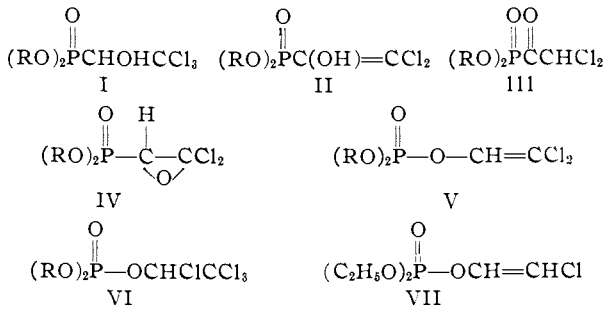
Dehydrochlorination of O,O-dialkyl 2,2,2-trichloro-1-hydroxyethylphosphonates causes rearrangement to dialkyl 2,2-dichlorovinyl phosphates. The products of dehydrochlorination were compared with compounds of known structure obtained by another synthesis and found to be identical. Other isomeric structures were considered and ruled out by chemical and physical data. New compounds are reported, several of which possess high insecticidal activity. O,O-Diethyl 2,2-dichloro-1-hydroxyethylphosphonate was converted to the systemic insecticide diethyl 2-chlorovinylphosphate.

In a previous paper[2] we described a series of O,O-dialkyl-2,2,2-trichloro-1-hydroxyethylphosphonates (I), which are readily prepared by condensing chloral with a dialkyl hydrogen phosphite. The lower members of this series possess insecticidal activity, and the methyl ester (I, R = CH_3), as "Bayer L $^{13}/_{59}$," has been widely tested. Recently Mattson, Spillane and Pearce[3a] have reported on their original discovery that "L $^{13}/_{59}$" undergoes dehydrochlorination in the presence of alkali, to yield a volatile, more highly insecticidal ester, to which they assigned the enol structure, II. They subsequently[3b] assigned the keto structure, III, to the dehydrochlorination product on the basis of infrared absorption data and formation of an

(1) (a) This work was conducted in part under funds allotted by the Department of the Army to the Department of Agriculture. (b) Original manuscript received November 11, 1954.

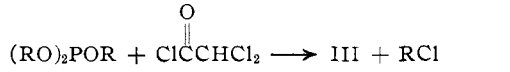
(2) W. F. Barthel, P. A. Giang and S. A. Hall, THIS JOURNAL, **76**, 4186 (1954).

(3) (a) A. M. Mattson, J. T. Spillane and G. W. Pearce. Abstract of paper for presentation at the 126th Meeting of the American Chemical Society at New York, N. Y., September 12–17, 1954; (b) *ibid.*, paper as actually presented.

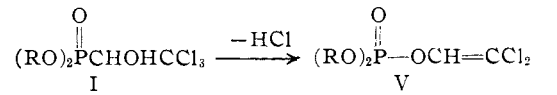


osazone with 2,4-dinitrophenylhydrazine. The osazone was described as identical with that of glyoxal. The same osazone is obtained from dichloroacetaldehyde. Presumably dichloroacetaldehyde was split off from the dehydrochlorination product on treatment with 2,4-dinitrophenylhydrazine.

We have prepared the dehydrochlorination products by treatment of I with aqueous sodium hydroxide, or in the case of higher members of the series (where R = C_3H_7 or above), with alcoholic sodium hydroxide, removing 1 mole of hydrogen chloride. The dehydrochlorination products of I, which distilled under vacuum, are mobile esters heavier than water. These did not react with 2,4-dinitrophenylhydrazine or semicarbazide hydrochloride. However, the dehydrochlorination product of "L 13/59" (I, R = CH_3) was cleaved with *p*-nitrophenylhydrazine to yield the corresponding glyoxal osazone. We then synthesized III (R = CH_3, C_2H_5), according to the general procedure described by Kabachnik and Rossiĭskaya[4] as



The α-ketophosphonic esters, III (R = CH_3, C_2H_5), thus obtained, readily reduced Fehling reagent and reacted vigorously with *p*-nitrophenylhydrazine to give the expected osazones. They also exhibited markedly different physical properties (including infrared spectra) from the isomeric compounds derived from I by dehydrochlorination. The keto structure III is, therefore, excluded for the dehydrochlorination compounds. The latter gave no active hydrogen by the Zerewitinoff method, nor could they be acetylated as could the parent compounds I. Infrared spectra also failed to show the presence of a hydroxyl group in the dehydrochlorinated derivatives of I. Thus, structure II is excluded. The epoxide structure, IV, was eliminated because of addition of 1 mole of chlorine with no formation of hydrogen chloride. The possibility of a rearrangement reaction on treatment of I with alkali to yield dichlorovinyl phosphates V was then considered. Perkow,[5] in connection with the preparation of some new anti-cholinesterases, recently described a rearrangement reaction between trialkyl phosphites and chloral with elimination of 1 mole of alkyl chloride, to yield what proved to be V. In support of the phosphate structure, Perkow found that acid hydrolysis of the esters yielded phosphoric acid. He also found that the esters took up 1 mole of chlorine to yield the expected tetrachloro derivatives VI. We repeated the preparation of V by the Perkow route from trialkyl phosphites and chloral, and found the physical properties of the liquids essentially the same as those of the corresponding esters obtained by dehydrochlorination of I. We then made tetrachloro derivatives VI (R = CH_3, C_2H_5) of the compounds made by each route and found them identical. The infrared spectra of the dimethyl esters prepared by the Perkow method, and the dehydrochlorination method were the same. Although we could find no other reports in the literature of a rearrangement of a phosphonate to a phosphate, it is evident that this rearrangement takes place



We also prepared diethyl 2-chlorovinyl phosphate (VII), (although in poor yield) by dehydrochlorination and rearrangement of O,O-diethyl 2,2-dichloro-1-hydroxyethylphosphonate, $(C_2H_5O)_2PCHOHCHCl_2$. We then prepared VII in fairly good yield by the Perkow route from triethyl phosphite and dichloroacetaldehyde. The esters obtained by both routes were identical. The vinyl rearrangement thus can be extended to β-dichloro-α-hydroxyphosphonates. It is of interest to note that VII has been reported[6] to be a systemic insecticide, although no preparative method is given.

The infrared spectra[7] of the dimethyl esters of I, III and V were compared. A peak at 3.21 μ of I is characteristic of an associated hydroxyl group; at one-tenth dilution this peak is diminished, while a sharp peak at 2.93 μ, characteristic of a free hydroxyl, is increased. In confirmation of this we acetylated I (R = C_2H_5) proving that it is indeed a phosphonate. The spectrum of III shows a band at 5.88 μ, attributable to the carbonyl group. This band is absent in V. The spectra of VA and VB, prepared, respectively, by dehydrochlorination and by Perkow's[5] method, are identical. In Table I we have listed the properties of the dialkyl chlorovinyl phosphates, V and VII, with the yields obtained by the dehydrochlorination procedure and by the Perkow method.

Experimental[8]

Dialkyl 2,2-Dichlorovinyl Phosphates (V). Method A. By Dehydrochlorination and Rearrangement of the Corresponding Dialkyl 2,2,2-Trichloro-1-hydroxyphosphonates.—The phosphonate I (0.1 mole) was partially dissolved in

(4) M. I. Kabachnik and P. A. Rossiĭskaya, *Izvestiya Akad. Nauk ot.kh.n.* (No. 4), 364 (1945).

(5) W. Perkow, *Ber.*, **87**, 755 (1954); W. Perkow, K. Utterich and Fr. Meyer, *Naturwissenschaften*, **39**, 353 (1952).

(6) R. A. Corey, S. C. Dorman, W. E. Hall, L. C. Glover and R. R. Whetstone, *Science*, **118**, 28 (1953).

(7) These infrared spectra have been deposited as Document number 4458 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Dr. Jonas Carol of the Food and Drug Administration kindly determined the infrared spectra.

(8) Physical properties, yield and analyses not shown are listed in Table I.

TABLE I

DIALKYL CHLOROVINYL PHOSPHATES $(RO)_2P(=O)—O—CH=CCl_2$

R	Method[a]	Yield,[b] %	B.p.,[c] °C	Mm.	$n^{25}D$	d^{25}_4	Formula	Phosphorus, % Calcd.	Phosphorus, % Found	Chlorine, % Calcd.	Chlorine, % Found
CH_3	A	57	120	14	1.4524	1.413	$C_4H_7Cl_2O_4P$	14.02	13.91	32.09	31.93
	B	86[d]	120[d]	14	1.4523	1.415[d]			13.89		32.42
C_2H_5	A	51	131–132	14	1.4479	1.295	$C_6H_{11}Cl_2O_4P$	12.45	12.35	28.47	28.51
	B	97[e]	132–133[e]	14	1.4475	1.295[e]			12.51		28.12
C_3H_7	A	36	107	0.3	1.4450		$C_8H_{15}Cl_2O_4P$	11.18	11.07	25.59	26.28
	B	70[f]	114	1.1	1.4440	1.215[f]			10.77		26.10
i-C_3H_7	A	26	99–105	0.7	1.4423		$C_8H_{15}Cl_2O_4P$	11.18	11.22	25.59	25.82
	B	75[g]	108–111[g]	0.9	1.4422	1.201[g]					25.79
C_4H_9	A	53	125–128	0.35	1.4487		$C_{10}H_{19}Cl_2O_4P$			23.24	23.35
	B	79	124–131	0.2	1.4487	1.166					23.56
$(C_2H_5O)_2P(=O)$—OCH=CHCl:											
	A	13	121–122	13	1.4345		$C_6H_{12}ClO_4P$			16.52	16.79
	B	53	121–122	11	1.4348	1.204					15.94

[a] A, prepared by the dehydrochlorination rearrangement; B, prepared by the Perkow synthesis (*Ber.*, 87, 755 (1954)). [b] Yield based on a single rapidly distilled product. [c] Physical constants taken on redistilled fraction. [d] Perkow (ref. 5) reported 60%, b.p. 100–104° (2.5 mm.), d^{21} 1.4243. [e] Perkow (ref. 5) 85–90%, b.p. 113–115° (2.0 mm.), d^{21} 1.299. [f] Perkow (ref. 5), 70%, b.p. 118–120° (0.7 mm.), d^{21} 1.216; [g] Perkow, ref. 5, 72%, b.p. 106–108° (0.8 mm.), d^{21} 1.210.

water at 40° (100 ml. of water for the more soluble dimethyl phosphonate; 500 ml. for the diethyl phosphonate), a few drops of phenolphthalein added and then 100 ml. of 1 *N* aqueous sodium hydroxide was run in. Dehydrochlorination took place rapidly, only a fleeting pink color of the phenolphthalein appearing. The turbid solution (final *p*H between 5 and 6) was transferred to a separatory funnel and the nearly colorless oil drawn off. The aqueous portion was extracted with chloroform, the extracts added to the oil, dried with anhydrous sodium sulfate and filtered through a fluted paper. After removal of the chloroform the residual mobile oil was distilled rapidly ***in vacuo*** and then fractionated. Homologs above ethyl, insoluble in water, were dehydrochlorinated with 2 *N* alkali solution prepared by dissolving commercial sodium methylate in methanol containing 10% water. This was added (1.25 moles) with stirring, at 40 to 50° to the phosphonate (1 mole) dissolved in 500 ml. of methanol. The reaction mixture was stirred for 5 minutes until the pink color of the phenolphthalein disappeared, and then poured into three times its volume of cold water, allowed to cool and extracted with chloroform. This was worked up in the usual way.

Method B.—Perkow's procedure[5] was slightly modified by adding the chloral in ether solution to the trialkyl phosphite at a lower temperature (0 to −5°), which gave somewhat better yields than reported.

Active hydrogen by the Zerewitinoff method was negative for dehydrochlorinated I (**R** = CH_3). This compound reacted with *p*-nitrophenylhydrazine (but not with 2,4-dinitrophenylhydrazine) to yield the osazone of glyoxal as red crystals from alcohol m.p. 310° dec. (reported[9] m.p. 311°).

Anal. Calcd. for $C_{14}H_{12}N_6O_4$: N, 25.59. Found: N, 25.20.

Dialkyl 1,2,2,2-Tetrachloroethyl Phosphates (VI, R = CH_3, C_2H_5).—These were prepared by Perkow's procedure,[5] by addition of chlorine to V prepared by both methods A and B above. The dimethyl derivative (not reported by Perkow) was obtained in 76% yield, b.p. 99–102° (0.2 mm.), $n^{25}D$ 1.4701, d^{25}_4 1.562. It crystallized on standing in the refrigerator. After one crystallization from Skellysolve A, fine white platelets, m.p. 42–43°, were obtained. A mixture melting point of the derivatives from starting material obtained by methods A and B showed no depression.

Anal. Calcd. for $C_4H_7Cl_4O_4P$: Cl, 48.59. Found: Cl, 48.34, 48.51.

The diethyl homolog was prepared in the same manner as above, b.p. 116–119° (0.4 mm.), $n^{25}D$ 1.4620, d^{25}_4 1.431, yield 42% (reported[5] b.p. 123–125° (1.2 mm.), d^{21} 1.392, yield 62%).

(9) A. Wohl and C. Neuberg, *Ber.*, **33**, 3107 (1900).

Anal. Calcd. for $C_6H_{11}Cl_4O_4P$: P, 9.68; Cl, 44.33. Found: P, 9.30; Cl, 44.44, 45.08.

O,O-Diethyl 2,2-Dichloro-1-hydroxyethylphosphonate.—This was prepared in the same manner as I,[2] except that dichloroacetaldehyde,[10] instead of chloral reacted with diethyl hydrogen phosphite. After standing overnight at 40–50° a quantitative yield of a viscous liquid, $n^{25}D$ 1.4638, was obtained. A portion was distilled and the fraction boiling at 142–144° (0.1 mm.), $n^{25}D$ 1.4678, taken for analysis.

Anal. Calcd. for $C_6H_{13}Cl_2O_4P$: Cl, 28.25. Found: Cl, 28.48.

Diethyl 2-Chlorovinyl Phosphite (VII). Method A. By Dehydrochlorination and Rearrangement of O,O-Diethyl 2,2-Dichloro-1-hydroxyethylphosphonate (Crude Material).—Methanolic sodium hydroxide was used. With aqueous sodium hydroxide only a very low yield of impure product was obtained.

Method B: prepared by a modified Perkow synthesis[5] using dichloroacetaldehyde[10] and triethyl phosphite.

Diethyl 1,2,2-Trichloroethyl Phosphate: prepared by chlorination of VII. The fraction boiling at 113–115° (0.05 mm.), $n^{25}D$ 1.4523, was analyzed.

Anal. Calcd. for $C_6H_{12}Cl_3O_4P$: Cl, 37.25; P, 10.85. Found: Cl, 37.41; P, 10.80.

O,O-Dialkyl 2,2-Dichloro-1-oxoethylphosphonates (III, R = CH_3, C_2H_5).—The dimethyl ester was prepared by slowly adding a solution of trimethyl phosphite (0.5 mole) in 150 ml. of Skellysolve A, with stirring, to a strongly cooled solution (−50° bath temperature) of dichloroacetyl chloride (0.5 mole) in 150 ml. of Skellysolve A. After two hours the reaction mixture was allowed to come to room temperature while stirring was continued. Solvent and low-boiling materials were removed at the water pump. The residual hygroscopic oil was distilled and the fraction boiling at 101° (0.3 mm.), $n^{25}D$ 1.4790, collected. The yield was only 3%.

Anal. Calcd. for $C_4H_7Cl_2O_4P$: P, 14.02; Cl, 32.09. Found: P, 13.82; Cl, 31.92.

***p*-Nitrophenyl osazone,** brilliant yellow crystals from alcohol m.p. 328° dec.

Anal. Calcd. for $C_{16}H_{17}N_6O_7P$: N, 19.27; P, 7.09. Found: N, 19.02; P, 6.79.

Diethyl Homolog.—It was found possible to alter the reaction conditions because of the greater stability of triethyl phosphite as compared to trimethyl phosphite. Triethyl phosphite (0.5 mole) was added, without solvent, to 0.5 mole of dichloroacetyl chloride, while refluxing. During

(10) Commercial dichloroacetaldehyde was distilled through a six-plate Snyder column and the fraction distilling at 86–87°, $n^{25}D$ 1.4550, was used.

the addition, which took 30 minutes, the temperature rose from an initial 105 to 140°, when evolution of ethyl chloride ceased. The reaction product was distilled rapidly at *ca.* 130° (0.2 mm.). The colorless hygroscopic distillate was fractionated and the fraction boiling at 148–152° (0.8 mm.), $n^{25}D$ 1.4699, collected, yield 50%.

Anal. Calcd. for $C_6H_{11}Cl_2O_4P$: Cl, 28.47; P, 12.45. Found: Cl, 27.31; P, 12.71.

p-Nitrophenyl osazone, red crystals from alcohol, m.p. 255° dec.

Anal. Calcd. for $C_{18}H_{21}N_6O_7P$: N, 18.11; P, 6.67. Found: N, 17.95; P, 6.61.

O,O-Diethyl 2,2,2-Trichloro-1-acetoxyethylphosphonate.—One-tenth mole of I (R = C_2H_5) was acetylated with acetic anhydride (sodium acetate catalyst) in 48% yield, b.p. 116–117° (0.05 mm.), $n^{25}D$ 1.4653.

Anal. Calcd. for $C_8H_{14}Cl_3O_5P$: Cl, 32.48. Found: Cl, 32.34.

BELTSVILLE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RAVENSHAW COLLEGE, UTKAL UNIVERSITY]

2-β-Naphthylimino-4-thiazolidone and its Derivatives

BY M. K. ROUT AND G. N. MAHAPATRA

RECEIVED AUGUST 16, 1954

An improved method of synthesis of thiazolidones is illustrated by the preparation of 2-β-naphthylimino-4-thiazolidone. The condensation products of the above thiazolidone with aldehydes and their bromine derivatives also are described. The bromine derivatives have been screened for fungicidal action and the arylidene derivatives for use as analytical reagents.

In view of the close relationship between thiazolidones and thiazoles, the presence of a thiazolidine moiety in Penicillin and the reported use of thiazolidone compounds as anesthetics,[1] anticonvulsants[2] and amebacidal agents,[3] it was of interest to explore newer methods of synthesis of thiazolidones and new applications of them.

Several methods are available for synthesis of thiazolidones.[4,5] The present method (illustrated by the preparation of 2-β-naphthylimino-4-thiazolidone) consists of heating arylthiocarbamides with chloroacetic acid in absolute alcohol in the presence of anhydrous sodium acetate and is superior to the method of Desai, Hunter and Koppar,[5] since the procedure adopted here is more rapid and does not involve the isolation of the intermediate substituted formamidinethiolacetic acid which was obtained by Desai and Hunter[5] by a rather prolonged operation. The thiazolidone structure for this compound to the exclusion of a possible thiohydantoin structure has been confirmed by establishing (a) the cyclic nature of the sulfur atom (by heating with mercuric oxide and chloroacetic acid), (b) by testing for the presence of S–CH_2–CO group by Andreasch's test,[6] (c) by boiling with hydrochloric acid and then establishing the structure of the glycolide formed by boiling with hydrochloric acid and then establishing the structure of the glycolide formed by its unambiguous synthesis from chloroacetic acid and β-naphthylthiourethan. When the reaction was carried out in refluxing alcohol, following the method of preparation of the diphenyl analog,[7] a compound fairly soluble in water and acidic in nature was obtained. It was found to be identical with β-naphthylformamidinethiolacetic acid hydrochloride prepared by Desai and Hunter[5] by a different procedure.

The thiazolidone compound thus prepared has been condensed with aldehydes. In view of the fact that closely related compounds like benzylidenerhodanine[8] and 2,5-dimercapto-1,3,4-thiodiazole[9] already have found use as analytical reagents, the thiazolidone compound and its condensation products have been tested for use in this direction. The condensation products with aldehydes are expected to be more effective reagents than the parent thiazolidones in view of the decided superiority of arylidenerhodanine over rhodanine as reagents in inorganic analysis.[10]

On screening the arylidene derivatives for use as analytical reagents, formation of metallic complexes was observed with silver, mercury and copper salts. Conditions of complete precipitation especially *p*H, were then studied with different arylidene derivatives and it was found that the *p*-dimethylaminobenzylidene derivative was more useful than others, effecting complete precipitation of the metal at all *p*H's in the acidic range and was therefore taken up for more detailed investigations. Results indicate that this is a very satisfactory reagent for estimation of silver.

The amount of silver found on ignition in the silver compound on the basis of the proposed structure agrees within 0.2% with the amount of silver added. Details of the analytical tests will be published elsewhere.

Both the thiazolidone compound and its arylidene derivatives also have been brominated in the hope of obtaining very powerful fungicides in view of the established fact that halogens confer fungicidal activity.[11] By undertaking bromination, it was possible also to test the validity of the assumption made by Hunter and co-workers[12] that the keto–enol system present in tetrahydrothiazole derivatives does not take part in the production of the bromine addition compound. Since the assumption was found to be correct in the present case

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(4) A. R. Surrey, *ibid.*, **69**, 2911 (1947).
(5) R. D. Desai, F. G. Hunter and L. G. Koppar, *Rec. trav. chim.*, **54**, 118 (1935).
(6) R. Andreasch, *Ber.*, **12**, 1385 (1879).
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(11) Goldsworthy and Green, *Phytopath*, **29**, 700 (1939).
(12) M. O. Farooq and R. F. Hunter, *J. Indian Chem. Soc.*, **9**, 545 (1932).