TABLE I

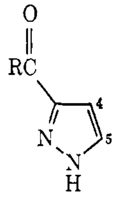
PREPARATION OF 3-SUBSTITUTED PYRAZOLES (**7a–e**) FROM VINYL SALT **1** AND SUBSTITUTED DIAZOMETHANES

Product	Ratio of **1**:**4**	Time, days	Yield, %	Yield of **8**, %	Anal. sample **7**, mp, °C	Analysis, %			Rel rate
							C	H	
7a	2:1	2	56		93–94	Calcd	65.34	4.98	50
						Found	64.94	5.00	
7a	1:1	2	34						
7b	2:1	2	67		130–132	Calcd	70.95	5.41	47
						Found	70.85	5.41	
7c	2:1	3	64	96	94–95[a]				26
7c	1:1	3	24	54					
7d	2:1	4	58	85	190–191	Calcd	55.30	3.25	1
						Found	55.24	3.18	
7e	2:1	1 (15)	20 (51)	55	155–157[b]				
9e	1:1	0.5	90[c]		*c*				

[a] Lit. mp 95–96°: J. Elguero and R. Jaquier, *Bull. Soc. Chim. Fr.*, 2832 (1966). [b] Lit. mp 155–157°: J. Elguero, G. Guirand, and R. Jaquier, *ibid.*, 619 (1966). [c] See Experimental Section.

TABLE II

SPECTRA OF PYRAZOLES



Product	Nmr				Ir		
	C-4	C-5	Phenyl	Other	NH	C=O	C=N
7a	6.85 (d) J = 2.4 Hz	7.65	6.95 (d), 8.15 (d) J = 8.5 Hz		3200	1630	1600
7b	6.92 (d) J = 2.7 Hz	7.91	7.26 (d), 7.84 (d) J = 9.5 Hz	CH_3O, 2.40 (s)	3150	1640	1600
7d	7.26 (d) J = 2.3 Hz		8.0–8.65 (m)		3250	1660	1600

mol of the diazo compound, and 10 ml of dried chloroform. The reaction mixture was stirred for the required amount of time at room temperature, concentrated to half volume, filtered to remove 1,2-ethylenebis(triphenylphosphonium bromide), mp 285–290° (lit.[3] in A mp 297–300°), and further concentrated to an oil. This material was placed on a Florisil column (4 × 25 cm) and eluted with ethyl acetate. The first fraction (200 ml) was concentrated, petroleum ether (bp 30–60°) was added to precipitate the product, and the pyrazole was filtered and collected. The product was recrystallized from benzene–petroleum ether. The physical data are given in Tables I and II. The results of experiments run with equimolar quantities of the species **1** and **4** are also listed in Table I. Examination of the crude reaction mixture from the equimolar experiments, by nmr, shows none of the expected peaks for the intermediate **9**. The nmr shows only pyrazole **7**, disalt **8**, and some starting material **4**.

5-Carbethoxy-2-pyrazolin-3-yltriphenylphosphonium Bromide (9e).—In a three-necked 100-ml flask with a drying tube and addition funnel was placed ethyl diazoacetate (0.57 g, 0.005 mol) in 5 ml of methylene chloride. Vinyl salt (1.85 g, 0.005 mol) in 5 ml of methylene chloride was added slowly over a 12-hr period and the solution was allowed to stir for an additional 2 hr. The reaction mixture was poured into ethyl acetate and the residue was recovered by filtration. The salt was recrystallized from methylene chloride–ethyl acetate at room temperature. An analytical sample could not be obtained owing to ready decomposition. The nmr was consistent with the assigned structure: nmr ($CDCl_3$) δ 1.25 (t, 3, CH_3, J = 7 Hz), 3.25 (2 d, 2, C-4, J = 9, 12 Hz), 4.15 (q, 2, OCH_2, J = 7.0 Hz), 5.1 (dd, 1, C-5, J = 9, 12 Hz), 7.6–8.1 ppm (m, 15, phenyl).

Attempted Phosphonioethylation of 5-Carbethoxy-2-pyrazolin-3-yltriphenylphosphonium Bromide (9e).—Vinyltriphenylphosphonium bromide (0.001 mol), **9e** (0.001 mol), and 10 ml of chloroform were refluxed for 24 hr, concentrated to half volume, and filtered. The white solid collected was disalt **8** in a 73% yield. There was no phosphonioethylated product found.

Kinetic Data.—The sample for the kinetics was obtained from the reaction mixture as soon as the chloroform had been added and the mixture was homogeneous. The sample was placed in a liquid cell and the change in absorbance of the diazo peak was followed with time on a Perkin-Elmer 421 spectrophotometer. A plot of the reciprocal of the absorbance *vs.* time in minutes gave the straight-line plot. The relative rates reported are the slopes of these plots.

Pyrolysis of 5-Carbethoxy-2-pyrazolin-3-yltriphenylphosphonium Bromide (9e).—In an nmr tube some of **9e** was heated to a melt for 5 min. $CDCl_3$ was added and an nmr was taken. The pyrazole hydrobromide could not be isolated pure but the nmr was consistent with that of a sample prepared from **7e** (Table I): nmr ($CDCl_3$) δ 1.35 (t, 3, CH_3, J = 7 Hz), 4.4 (q, 2, DCH_3 J = 7 Hz), 6.95 (d, 1, C-4, J = 2.8 Hz), 8.05 (d, 1, C-3, J = 2.8 Hz), 10 ppm (s, 2, NH solvent dependent, exchanges with D_2O).

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Registry No.—**1**, 5044-52-0; **4a**, 6832-17-3; **4b**, 4250-01-5; **4c**, 3282-32-4; **4d**, 4203-31-0; **4e**, 623-73-4; **7a**, 19854-93-4; **7b**, 40711-94-2; **7c**, 19854-92-3; **7d**, 40711-96-4; **7e**, 5932-27-4; **8**, 1519-45-5; **9e**, 40711-97-5.

Kinetic Evidence for the Existence of a 1,4 Dipole

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Recently we presented experimental evidence for the rearrangement of a proposed 1,4 dipole (**1**), gen-

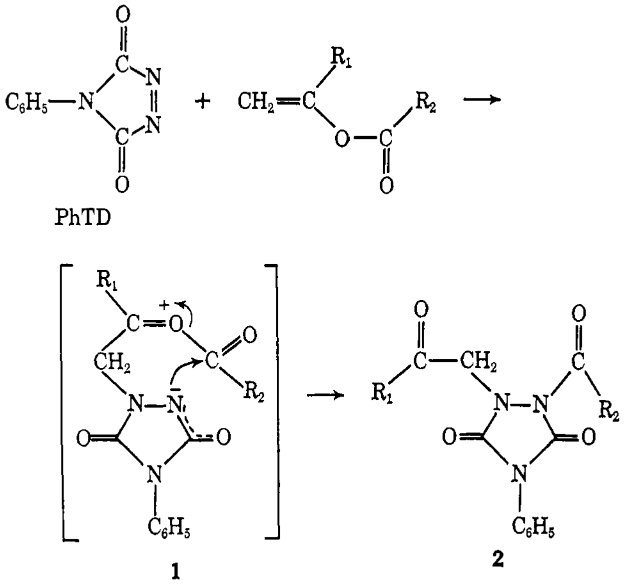
TABLE I

Registry no.	Vinyl ester	R_1	R_2	k, l./mol sec	ΔE_{act}, kcal/mol (c of c)[a]
108-22-5	Isopropenyl acetate	CH_3	CH_3	2.7×10^{-1}	7.4 (0.977)
108-05-4	Vinyl acetate	H	CH_3	4.2×10^{-2}	12
2424-98-8	Vinyl isobutyrate	H	$CH(CH_3)_2$	5.9×10^{-2}	12 (0.997)
3377-92-2	Vinyl pivalate	H	$C(CH_3)_3$	4.0×10^{-2}	12
2549-51-1	Vinyl chloroacetate	H	CH_2Cl	8.1×10^{-4} [b]	14 (0.997)
769-78-8	Vinyl benzoate	H	C_6H_5	4.3×10^{-2} [b]	11 (0.988)

[a] c of c refers to the coefficient of correlation, calculated for each set of data, reflecting the accuracy of the results. The closer the value is to unity, the better the straight-line fit. If no value is shown in the table, the c of c is 0.999 or better. [b] These values were obtained from an Arrhenius plot of second-order rate constants measured at four other temperatures.

erated by reaction of 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD) and vinyl esters (Scheme I), and suggested that the apparent rate of reaction was a function of the vinyl ester employed.[1] These reactions have been studied spectroscopically[2] and the results lend additional support for the existence of the 1,4 dipole.

SCHEME I



Assuming irreversibility, the reactions have been found to be second order overall—first order in each reactant—as might be expected in the formation of an adduct. Table I lists the second-order rate constants at 60° along with the energies of activation for each vinyl ester.

The size of R_2 has no effect on the energy of activation, as shown by the R_2 = alkyl series. This is indicative of an intermediate being formed, followed by nucleophilic attack by the dipole effecting rearrangement. Since the relative yield of **2** decreases as the size of R_2 increases,[1] the product ratios must be determined by the activation energies in the second step. This is exemplified in the energy diagram (Figure 1) for the vinyl isobutyrate reaction, which has a product ratio of 10:2:1 for 1-formylmethyl-2-(2-methylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione:copolymer:3-phenyl-6-(2-methylpropionyloxy)-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione.[1] The possibility of product formation occurring from other than a common intermediate was considered, *i.e.*, formation of rearranged product and polymer *via* ring opening of the corresponding 1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione. This pathway was eliminated by heating to 60° a solution of the three products resulting from the vinyl pivalate reaction for 16 hr to determine if the product ratio would change. No change was observed.

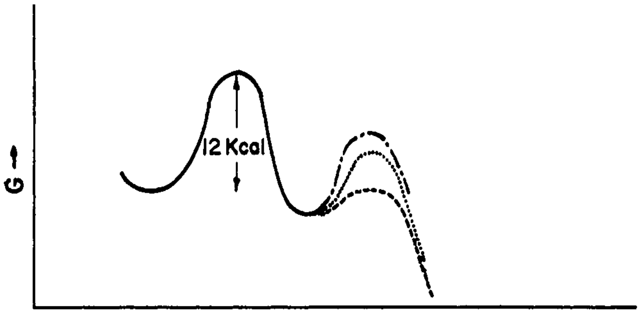


Figure 1.—Probable energy pathways: - - - - - - -, 1-formylmethyl-2-(2-methylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione (**2** in Scheme I); ·········, copolymer; —·—·—, 3-phenyl-6-(2-methylpropionyloxy)-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione. The second step is not necessarily lower in energy than the first step.

The stability of the 1,4 dipole is directly affected by the inductive effects of R_1 and R_2. Changing R_1 from methyl to hydrogen increases the activation energy *ca.* 4.5 kcal/mol, demonstrating the importance of cation stabilization. The dipole is destabilized further by placing a chloromethyl group at R_2, a phenomenon analogous in the opposite sense to the increase of the acidity of chloroacetic over acetic acid. The activation energy for the vinyl benzoate reaction is slightly lower than for the R_2 = alkyl series, possibly owing to conjugation of the ester carbonyl with the aromatic ring allowing increased lone-pair sharing by the ester oxygen.

Experimental Section

Kinetics Procedure.—Portions (1 ml) of equimolar solutions of vinyl ester and PhTD in 1,1,2,2-tetrachloroethane were pipetted into a pressure-resistant uv cell. Visible spectra were recorded and the PhTD absorbance at 545 nm was measured *vs.* time. A minimum of seven readings were taken during each run. The reaction was determined to be second order overall by fitting the data in the second-order rate expression (eq 1), which assumes formation of the 1,4 dipole to be irreversible.

$$\frac{1}{A_t} = \frac{k}{a}t + \frac{1}{A_0} \qquad (1)$$

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[1] K. B. Wagener, S. R. Turner, and G. B. Butler, *J. Org. Chem.*, **37**, 1454 (1972).

[2] Visible spectra were recorded on a Beckman DK-2A Ratio recording spectrophotometer. All straight-line slopes were calculated by the least squares method.

Table II[a]

Vinyl ester	Temp, °C	k, l./mol sec (c of c)[b]	ΔE_{act}, kcal/mol
Isopropenyl acetate	34.8	1.0×10^{-1}	7.44
	40.6	1.5×10^{-1}	
	48.1	2.0×10^{-1}	
Vinyl acetate	44.5	1.7×10^{-2} (0.998)	11.9
	68.3	6.1×10^{-2}	
	74.9	9.1×10^{-2}	
Vinyl isobutyrate	69.7	9.9×10^{-2}	11.6
	78.8	1.8×10^{-1}	
	90.0	2.5×10^{-1} (0.998)	
Vinyl pivalate	51.1	2.6×10^{-2}	12.1
	73.1	8.5×10^{-2}	
	80.2	1.2×10^{-1}	
Vinyl chloroacetate	71.3	1.8×10^{-2}	13.6
	78.3	2.7×10^{-2}	
	90.0	5.0×10^{-2}	
	101.5	9.0×10^{-2}	
Vinyl benzoate	62.5	3.8×10^{-2}	10.7
	69.0	5.7×10^{-2}	
	75.7	7.2×10^{-2}	
	80.0	8.4×10^{-2}	

[a] Since the third decimal place in the absorbance readings was estimated, these values are accurate to two decimal places only, as reported in Table I. [b] Coefficient of correlation, as in Table I.

In eq 1, A_t = absorbance at time t, a = PhTD absorptivity coefficient × cell path length, k = second-order rate constant, and A_0 = initial absorbance.

The reaction was determined to be first order in each reactant by first noting a tenfold increase in rate when using a 10:1 molar ratio of vinyl ester:PhTD, indicating the reaction to be first order in vinyl ester. The results were double checked by fitting the 10:1 molar ratio data in the first-order rate expression (eq 2),

$$\ln \frac{A_t}{a} = kt + A_0 \qquad (2)$$

demonstrating the reaction to be pseudo first order in PhTD under these conditions.

Energies of activation, calculated by the Arrhenius method, are listed to three significant figures in Table II. Second-order rate constants measured at temperatures other than 60° are reported also.

Check of Triazabicycloheptadiene Stability.—A sample of the solid resulting from reaction of 4-phenyl-1,2,4-triazoline-3,5-dione and vinyl pivalate was dissolved in chloroform-d_1 and its nmr taken. The nmr appeared as a superimposition of the nmr spectra of the three pure products. Of special note was the ratio (1:2) of the *tert*-butyl singlets of the monomeric products, one at δ 1.37 corresponding to the *tert*-butyl group of the rearranged product, the other at δ 1.20 caused by the *tert*-butyl of the triazabicycloheptadione. The nmr tube was heated to 60° for 16 hr, followed by nmr analysis. No change in the *tert*-butyl ratio occurred, and there was no noticeable increase in polymer; thus, the triazabicycloheptadiene did not ring open.

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Registry No.—PhTD, 4233-33-4.