

## Ene Reaction of Triazolinediones with Alkenes. 2. Kinetics and Substituent Effects

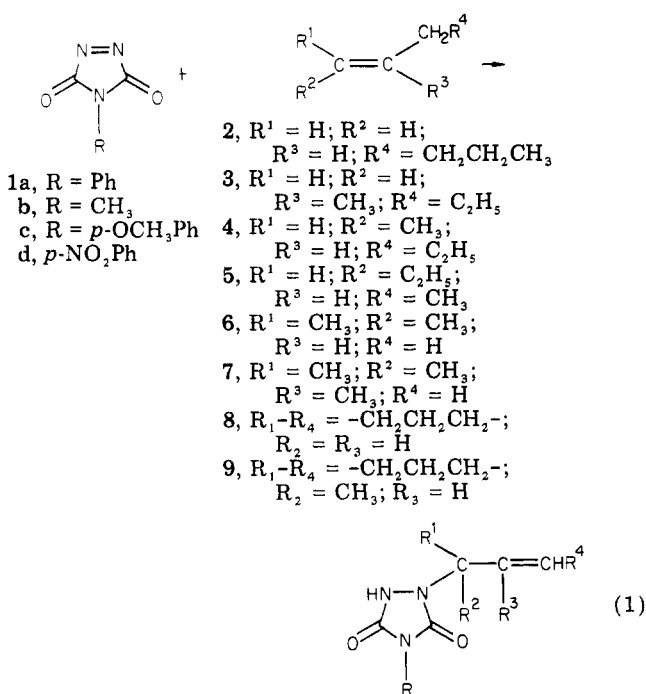
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The kinetic measurements for the reaction of 4-substituted-1,2,4-triazoline-3,5-diones (4-R-TD; R = Ph, Me, *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) with alkenes have been undertaken. The reactivity of alkenes was found to be very sensitive to substituent effects. The effects of solvent and substituent on TD were small. In the reaction of TD with ene products, side reactions as well as second-step ene reactions were observed. The reactions of 1-alkyl-4-phenyl-1,2,4-triazolidine-3,5-diones were investigated, and the reaction products were isolated.

Since Pirkle and Stickler<sup>1</sup> reported the high reactivity of 4-substituted-1,2,4-triazoline-3,5-diones (4-R-TD) as enophiles, the ene reaction of TD (eq 1) has been used for



synthesis of hydrazine derivatives,<sup>2</sup> synthesis of copolymers with styrene,<sup>3</sup> and modification of polydienes.<sup>4,5</sup> However, no systematic studies on this reaction have been reported.

In the previous paper, we<sup>6</sup> have reported the structure of ene products obtained from a series of alkenes as well as polyisoprene. In this paper, we would like to report the results of kinetic studies on the ene reaction of TD with a series of alkenes. Kinetic measurements have been made for the ene reaction of four different TDs (1a-d) with various alkene structures (2-9). The effect of the alkene structure as well as that of the TD and also the effect of solvent on the reaction rate have been studied. The reaction of TD with the ene product was also studied, and

the mechanism of the second step reaction is discussed.

### Results and Discussion

**Reactivity of Alkenes and Triazolinediones.** The reactivities of C<sub>5</sub> and C<sub>6</sub> alkenes in the ene reactions with TD were examined by measuring the reaction rates. The reaction of TD with an excess of alkene ([alkene]/[TD] = 5) was carried out in a UV cell by using benzene as solvent. The decrease of absorbance was recorded by use of a UV-visible photometer. It has been confirmed that under such conditions only the 1:1 reaction product is formed, especially during the early stages of the reaction.<sup>5</sup>

The reaction was treated as a second-order reaction. The second-order rate constant, *k*<sub>2</sub>, and the reactivity ratio (based on *trans*-3-hexene, 5) are shown in Table I. As shown, the reactivity of alkenes was markedly dependent on the structure. Compound 2 was the least active, and one substituent on the double bond increased the reactivity 10-20 times. Further substitution on the double bond increased the reactivity extraordinarily, and the reactivity of 2,3-dimethyl-2-butene (7) was too high to measure the reaction rate by the method used here. In the ene reaction of diethyl azodicarboxylate with C<sub>4</sub> and C<sub>5</sub> alkenes, a similar increase of reactivity of the alkenes was observed.<sup>7</sup> However, in that case, the difference of reactivity was very small, and the reactivity ratio of 2-methyl-2-butene (6) and 2-methyl-1-butene based on the reactivity of 1-pentene was 4.33 and 3.64, respectively. The reactivities of cyclohexene (8) and 1-methylcyclohexene were much lower than those of the corresponding linear alkenes (3 and 6).

As for the reactivity of TD, 1d was the most reactive and 1b was the least reactive. 1a and 1c showed similar reactivity. These results are quite reasonable if we consider the electron-donating or -withdrawing effect of the substituents at the 4-position of TD. A similar order of TD reactivities was also observed in the ene reaction by Butler and Williams<sup>8</sup> and in the Diels-Alder reaction by Burrage, Cookson, Gupte, and Stevens.<sup>9</sup> The effect of the structures of alkenes on *k*<sub>2</sub> was almost the same for all four triazolinediones studied.

In methylene chloride the reaction was about 5 times as fast as that in benzene. Since TD decomposes slowly in this solvent, accurate measurement of *k*<sub>2</sub> was not easy for such an inactive alkene as 2. However, quite similar tendencies were observed concerning the reactivity ratio of the alkenes and reactivity of the triazolinediones.

(1) Pirkle, W. H.; Stickler, J. C. *Chem. Commun.* 1967, 760.  
(2) Corey, E. J.; Snider, B. B. *Tetrahedron Lett.* 1973, 3091.  
(3) Wagener, K. B.; Turner, S. R.; Butler, G. B. *J. Polym. Sci., Part B* 1972, 10, 805.  
(4) Butler, G. B.; Williams, A. G.; Leong, K. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1977, 18, 843.  
(5) Leong, K.; Butler, G. B. *J. Macromol. Sci., Chem.*, in press.  
(6) Ohashi, S.; Leong, K.; Matyjaszewski, K.; Butler, G. B. *J. Org. Chem.*, companion paper in this issue.

(7) Thaler, W. A.; Franzus, B. *J. Org. Chem.* 1964, 29, 2226.  
(8) Butler, G. B.; Williams, A. G. *J. Polym. Sci., Polym. Chem. Ed.* 1979, 17, 1117.  
(9) Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* 1975, 1325.

Table I. Second-Order Rate Constants ( $10^2 k_2$ , L/(mol s))<sup>b</sup> for the Ene Reactions<sup>a</sup> of Triazolinedione

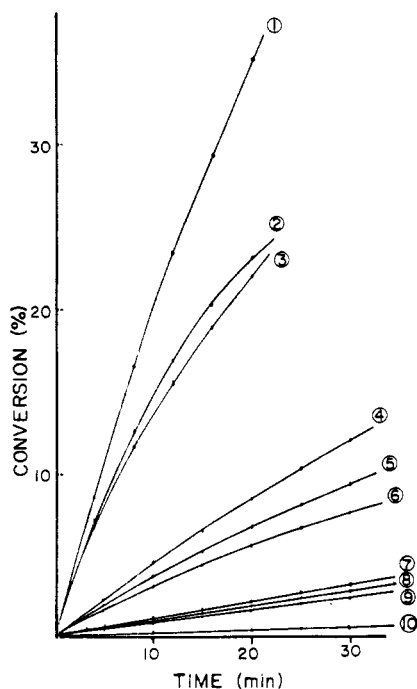
olefin	substituent (R)							
	benzene as solvent				methylene chloride as solvent			
	Ph	CH <sub>3</sub>	<i>p</i> -OCH <sub>3</sub> Ph	<i>p</i> -NO <sub>2</sub> Ph	Ph	CH <sub>3</sub>	<i>p</i> -OCH <sub>3</sub> Ph	<i>p</i> -NO <sub>2</sub> Ph
2	0.29 (0.08)	0.13 (0.09)	0.28 (0.10)	0.94 (0.07)	1.1 (0.07)		13.8 (1.00)	
4	3.54 (1.03)	1.77 (1.24)	3.30 (1.15)	14.3 (1.10)	16.5 (1.01)	7.8 (1.13)	18.8 (1.05)	75.6 (1.07)
5	3.44 (1.00)	1.43 (1.00)	2.87 (1.00)	13.0 (1.00)	16.4 (1.00)	6.9 (1.00)	13.1 (1.00)	70.4 (1.00)
3	5.46 (1.59)	1.95 (1.36)	4.39 (1.53)	17.8 (1.37)	21.1 (1.29)	9.4 (1.36)	18.0 (1.37)	95.4 (1.36)
6	157.3 (45.7)	47.8 (33.4)	116.0 (40.1)	609.0 (46.8)	<sup>c</sup>	300 (43.5)	<sup>c</sup>	<sup>c</sup>
8	1.12 (0.33)	0.56 (0.39)	0.93 (0.32)	4.37 (0.34)	5.4 (0.33)	2.5 (0.36)	4.4 (0.34)	25.5 (0.36)
9	7.86 (2.28)	2.64 (1.85)	6.22 (2.17)	36.6 (2.82)				

<sup>a</sup> At 25 °C. <sup>b</sup> The values in parentheses are reactivity ratios based on the reactivity of 5. <sup>c</sup> The reaction was too fast to measure by the method used.

Table II. Reaction of PhTD with Alkenes.<sup>a</sup> Solvent Effects on Second-Order Rate Constants

solvent	$10^2 k_2$ , <sup>b</sup> L/(mol s)			
	5	4	3	6
dichloromethane	16.4 (1.0)	16.5 (1.0)	21.1 (1.3)	<sup>c</sup>
1,2-dichloroethane	14.4 (1.0)	15.3 (1.1)	20.4 (1.4)	<sup>c</sup>
benzene	3.44 (1.0)	3.54 (1.0)	5.46 (1.6)	157 (45.6)
nitrobenzene	5.18 (1.0)	5.82 (1.1)	7.57 (1.5)	208 (40.2)
ethyl acetate	0.46 (1.0)	0.51 (1.1)	0.65 (1.4)	16.5 (35.9)
tetrahydrofuran	0.32 (1.0)	0.38 (1.2)	0.39 (1.2)	9.58 (29.9)

<sup>a</sup> At 25 °C. <sup>b</sup> The values in parentheses are reactivity ratios based on the reactivity of 5. <sup>c</sup> The reaction was too fast to measure by the method used.



**Figure 1.** Reactions of ene products with PhTD in benzene at 25 °C: [PhTD] =  $4.60 \times 10^3$  M; [ene products] =  $2.30 \times 10^{-2}$  M. Refer to structure I for the assignments of the following curves: 1, R = CH<sub>2</sub>C(CH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>CH<sub>3</sub>; 2, R = CH<sub>2</sub>CH=CHCH<sub>3</sub>; 3, R = CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; 4, R = CH<sub>2</sub>CH=CH<sub>2</sub>; 5, R = CH<sub>2</sub>C(CH<sub>3</sub>)=CH<sub>2</sub>; 6, R = CH(CH<sub>3</sub>)C(H)=CHCH<sub>2</sub>CH<sub>3</sub> and CH(CH=CH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; 7, R = CH(C-H<sub>2</sub>CH<sub>3</sub>)CH=CHCH<sub>3</sub>; 8, R = CH(CH<sub>3</sub>)C(CH<sub>3</sub>)=CH<sub>2</sub>; 9, R = CH(CH<sub>3</sub>)CH=CH<sub>2</sub>; 10, R = C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)=CH<sub>2</sub>.

In order to get further information on the reaction mechanism, we examined the effect of solvent. 1,2-Dichloroethane (DCE), tetrahydrofuran (THF), ethyl acetate, and nitrobenzene as well as benzene and dichloromethane were used as solvents. In nitrobenzene, dichloromethane, and tetrahydrofuran, **1a** decomposed gradually, so the rate constants in these solvents were corrected for such decomposition. Concentrations of TD in these studies were

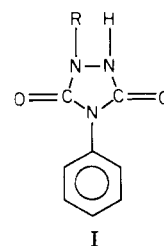
on the order of  $5 \times 10^{-3}$  mol/L. The results are shown in Table II.

Solvent effects, in general, were small. Even in such a polar solvent as nitrobenzene,  $k_2$  was not greatly different from that in benzene. The reaction in THF and ethyl acetate was slower than that in other solvents. As shown in Table IV,  $\lambda_{\max}$  of TD in THF and ethyl acetate is almost 15 nm lower than  $\lambda_{\max}$  in benzene. This result indicates a strong donor-acceptor complex interaction between TD and the solvent, which seems to cause the lower reactivity of TD, possibly via an increase in the electron density of the N=N system. Recent evidence has shown that **1a** undergoes a slow reaction with THF to yield *N*-(2-tetrahydrofuryl)urazole.<sup>12</sup> Also, this interaction between TD and solvent seems to affect the reactivity ratio of alkenes. The reactivity ratio of 6 ( $K_6/K_5$ ) in these solvents is obviously lower than that in benzene.

Considering such a small effect of solvent and the results of studies on the structure of ene products,<sup>6</sup> it appears that the reaction proceeds via a concerted mechanism.

**Second Step of the Ene Reaction.** The ene products of alkenes with TD still have carbon-carbon double bonds which may react with another TD. In the reaction of TD with inactive alkenes like **2**, the presence of unknown impurities suggested the possibility of other side reactions. In order to investigate these possibilities, we studied the reaction of TD with 1:1 ene product.<sup>6</sup>

Figure 1 shows the time-conversion curves for the reaction of **1a** with ene products (see structure I for identity



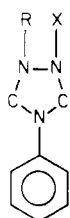
of ene products). Although the reactivity of most of the ene products was lower compared with that of the corre-

sponding simple alkenes, they obviously undergo reaction with another TD. However, the reactions were too complicated to permit reliable rate constants to be calculated.

Among the 1:1 ene products, those obtained from 1-alkenes showed reasonably high reactivity. Especially, **10** showed comparable reactivity with that of propylene itself. If we consider the order of reactivity of alkenes shown in Table I, the results are rather unusual. Furthermore, all attempts to isolate the reaction products resulted in failure. These reactions gave very complicated mixtures even in such simple reactions as those of **10** with **1a-c**. Careful attempts to purify the products via liquid column chromatography were unsuccessful, and their NMR spectra gave very broad peaks; however, no evidence for simple 1:2 ene reaction products was obtained.

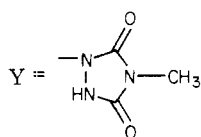
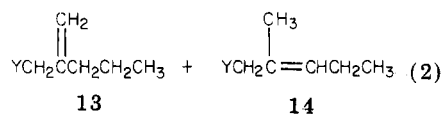
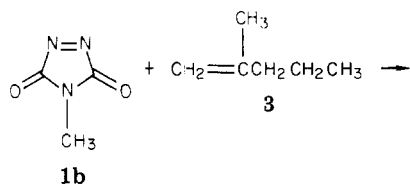
It is well-known that TD has a high capability for hydrogen abstraction. TD reacts with hydrazine derivatives<sup>10</sup> and alcohol,<sup>11</sup> and even with ethers<sup>13</sup> like THF or diethyl ether. Taking this fact into consideration, it seems more probable that TD reacts with the NH hydrogen of the urazole ring.

In order to prove this possibility, we substituted the NH group of **10** by an acetyl group (**11**) or a methyl group (**12**). As expected, **11** and **12** showed no detectable reactivity toward **1a** (Figure 2, curves 4 and 5; compounds **11** and **12**).



- 10**, R = CH<sub>2</sub>CH=CH<sub>2</sub>;  
X = H  
**11**, R = CH<sub>2</sub>CH=CH<sub>2</sub>;  
X = COCH<sub>3</sub>  
**12**, R = CH<sub>2</sub>CH=CH<sub>2</sub>;  
X = CH<sub>3</sub>  
**22**, R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>;  
X = COCH<sub>3</sub>

The reaction of **1b** with **3** (eq 2) gave two isomers, **13** and **14**, in a ratio of 1:1. Structures **13** and **14** were sep-



arated from each other by recrystallization. The results

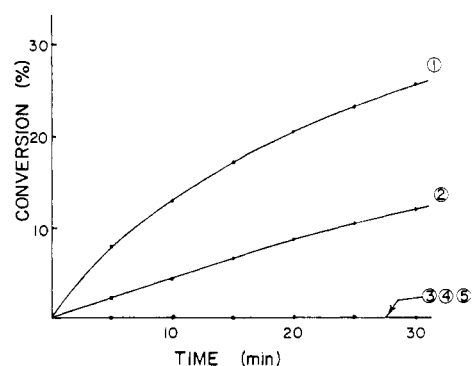


Figure 2. Reaction of PhTD with N-substituted urazole in benzene at 25 °C. The following curves represent the reaction with the urazole given: 1, **21**; 2, **10**; 3, **22**; 4, **11**; 5, **12**.

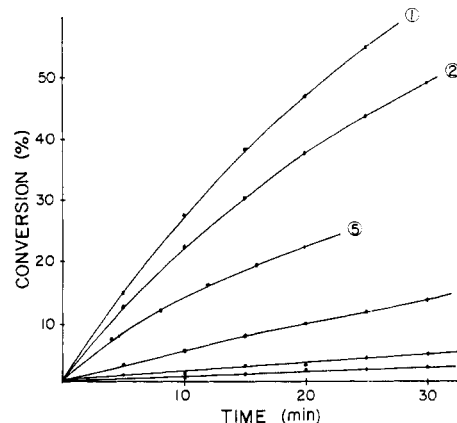
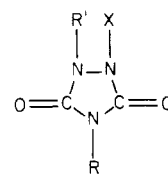


Figure 3. Reaction of PhTD with ene products **14-18** in benzene at 25 °C. The following curves represent the reaction with the ene product given: 1, **14**; 2, **16**; 3, **13**; 4, **17**; 5, **15**; 6, **18**.

of the reaction of **13** and **14** with **1a** are shown in Figure 3 along with that of the product (**15**) from **1a** and **2**. In



- 15**, R = Ph; R' = CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; X = H  
**16**, R = CH<sub>3</sub>; R' = CH<sub>2</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>CH<sub>3</sub>; X = COCH<sub>3</sub>  
**18**, R = Ph; R' = CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; X = COCH<sub>3</sub>

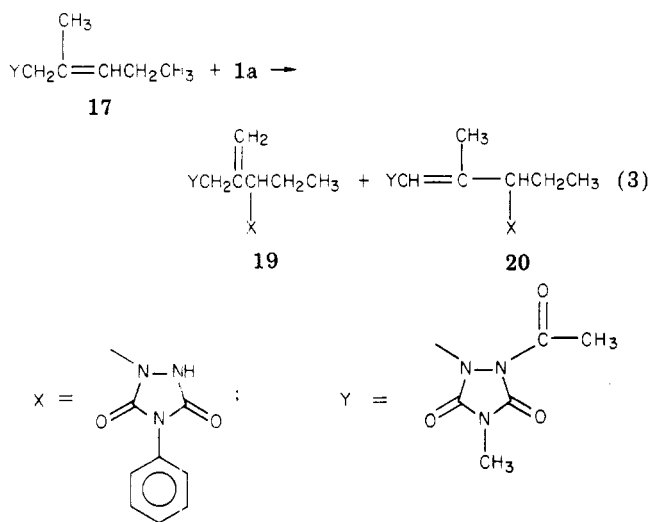
the case of these compounds, even the acetylated compounds (**16-18**) reacted with PhTD. The reaction product (**19** and **20**) from **1a** and **17** was purified by column chromatography and confirmed to be the 1:2 ene product (eq 3). The initial ratio of **19** to **20** was about 1:1 before purification. However, since **19** was less soluble, the final ratio of **19** to **20** was found to be 3:2 from NMR analysis. These reactions were treated as second-order reactions, and  $k_2$  values for **16-18** were  $1.07 \times 10^{-3}$ ,  $2.23 \times 10^{-2}$ , and  $4.3 \times 10^{-4}$  L/(mol s), respectively. By comparing the reactivities of **17** and **18** with those of **6** and **4**, respectively, we can estimate that substitution at the allyl position by the urazole ring causes a decrease of reactivity by at least  $1/50$ . The reaction of isoprene with **1a** gives the Diels-Alder product, which has a similar structure to **9**. Synthesis of this Diels-Alder adduct followed by a study of its reactivity

(10) Koch, K. H.; Fahr, E. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 634.

(11) Cookson, R. C.; Stevens, I. D. R.; Watts, C. T. *Chem. Commun.* 1966, 744.

(12) Wamhoff, H.; Wald, K. *Chem. Ber.* 1977, 110, 1699.

(13) Wamhoff, H.; Wald, K. *Chem. Ber.* 1977, 110, 1716.



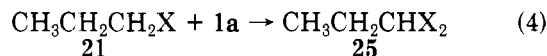
with TD showed that no reaction occurred, probably because the deactivation effect of the urazole ring is even stronger than that in the case of 17.

**Reaction of 1-Alkyl-4-phenyl-1,2,4-triazolidine-3,5-dione with PhTD.** As described above, it was found that side reactions were caused by the presence of the NH group of the ene products. However, the reaction between the ene products and 1a was so complicated that the structure of the products could not be determined.

In order to simplify the system, we synthesized 1-propyl-4-phenyl-1,2,4-triazolidine-3,5-dione (1-propyl-4-phenylurazole, 21) by the reaction of 1-iodopropane with the potassium salt of 4-phenylurazole and permitted it to react with 1a in benzene. Structure 21 does not have a carbon-carbon double bond, so only the reaction between NH and 1a was expected to occur.

As shown in Figure 2, 21 reacted with 1a even faster than 10. On the other hand, the N-acetylated derivative (22) of 21 did not react with 1a.

In order to determine the structure of the reaction product, we carried out an equimolar reaction between 21 and 1a in DCE at 60 °C. The reaction gave white crystals (25), which are soluble in Me<sub>2</sub>SO and slightly soluble in acetone and water, in very high yield (ca. 85%). The same reaction at room temperature also gave 25 in high yield; however, the reaction was very slow (after 10 days the solution was still red). NMR analysis of 25 indicated the structure shown in eq 4. Elemental analysis also supported this structure.



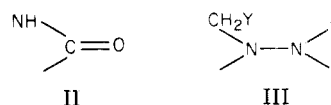
In the reaction of 1-ethyl-4-phenylurazole (23) with 1a the same type of product was obtained. On the other hand, the reaction of 1-methyl-4-phenylurazole (24) with 1a was much slower than that of 21 or 23. The <sup>1</sup>H NMR peaks of the product from 24 were very broad, and a very small peak for methyl protons was observed.

1a is reported to form adducts with ether<sup>12</sup> by heating or irradiation with UV light ( $\lambda > 313$  nm) and with 1,3-dimethyluracil<sup>13</sup> by heating. However, 22 did not react with 1a, which suggests that the reaction mechanism of 21 with 1a is different from these examples. 1a is also known to react with hydrazine derivatives or 4-phenylurazole to form radicals. In the case of 21, the NH group appears to react or at least to have a very strong interaction with PhTD. This reaction or interaction would make the hydrogen abstraction from the methylene group adjacent to the urazole ring easier.

Table III. Visible Absorption of 4-Substituted-1,2,4-triazoline-3,5-diones in Dichloromethane and Benzene

R	dichloromethane		benzene	
	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$
CH <sub>3</sub>	537.5	185.9	540	247.0
Ph	546	160.0	543.5	240.7
<i>p</i> -OCH <sub>3</sub> Ph	549	181.5	546	242.9
<i>p</i> -NO <sub>2</sub> Ph	540	170.9	541	240.7

In the case of 24, hydrogen abstraction from the methyl group appears to be more difficult, and the radical which would be formed by hydrogen abstraction could disappear by a different pathway. Structure 10 has a carbon-carbon double bond, which seems to make the reaction of the radical much more complicated. Thus, these ene products are shown to undergo reaction with TD via several routes: (1) with the N-C-C=C-R or more highly branched system if present; (2) with the function II, if present; (3) with the  $\alpha$ -protons of system III, the reaction being enhanced if X = H but decreased if Y = vinyl.



### Experimental Section

Visible spectra were recorded on a Beckman ACTA V photometer. <sup>1</sup>H NMR spectra were obtained by use of a Varian A-60 spectrometer. All melting points were taken on Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc.

**Preparation of the Triazolinediones.** 4-Substituted-1,2,4-triazolidine-3,5-diones (4-substituted urazoles) were synthesized according to the procedure described in ref 14. These urazoles were dispersed in dichloromethane with anhydrous sodium sulfate and oxidized at 0 °C by bubbling dinitrogen tetroxide<sup>15</sup> to give 4-substituted-1,2,4-triazoline-3,5-diones (1a-d). These triazolinediones were purified by sublimation under reduced pressure. Values for  $\lambda_{\text{max}}$  and  $\epsilon$  in the visible region are shown in Tables III and IV.

**Kinetic Measurements.** An alkene solution (1 mL) and 2 mL of TD solution were mixed in a 1-cm, cubic UV cell. The TD absorbance at  $\lambda_{\text{max}}$  in the visible region was measured vs. time. The reaction was determined to be second order overall by fitting the data to eq 5. In eq 5,  $A_t$  = the absorbance at time  $t$ ,  $a$  = the

$$\log \left( 1 + \frac{K}{A_t} \right) = \frac{b-a}{2.30} k_2 t + \log \frac{b}{a} \quad (5)$$

initial concentration of TD,  $b$  = the initial concentration of alkene,  $k_2$  = the second-order rate constant, and  $K = [(b-a)/a]A_0$ , where  $A_0$  is the initial absorbance.

**Ene Products.** The 1:1 ene products of PhTD with alkenes were prepared according to the procedure described in ref 6.

**1-(2-Methylenepentyl)-4-methyl-1,2,4-triazolidine-3,5-dione (13) and 1-(2-Methyl-2-pentenyl)-4-methyl-1,2,4-triazolidine-3,5-dione (14).** To 10.3 g (0.12 mol) of 2-methyl-1-pentene in 100 mL of 1,2-dichloroethane (DCE) was added 2.80 g (0.025 mol) of 1a in 150 mL of DCE slowly at room temperature with stirring. After 3 h, the color of 1a had been completely discharged to result in a slightly yellow solution. DCE was removed on a rotary evaporator. The resulting yellow oil was dissolved in benzene, and hexane was added to the solution until the solution became cloudy. After 1 day in a refrigerator, the solution gave 1.81 g (36.7%) of white needlelike crystals which were found to

(14) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* 1971, 15, 121.

(15) Stickler, J. C.; Pirkle, W. H. *J. Org. Chem.* 1966, 31, 3444.

Table IV. Visible Absorption of  
4-Phenyl-1,2,4-triazoline-3,5-dione

solvent	$\lambda_{\max}$ , nm	$\epsilon_{\max}$
dichloromethane	546	160.0
1,2-dichloromethane	544.5	183.0
benzene	543.5	240.7
nitrobenzene	538	178.8
ethyl acetate	531	170.8
tetrahydrofuran	528	171.9

be almost pure 13 (purity >95%).

The filtrate was concentrated, and the yellow oil was purified by column chromatography on silica gel with chloroform and 5% methanol in chloroform as eluents. The main fractions were combined and concentrated. The almost colorless oil was dissolved in benzene, and hexane was added. From this solution, 1.89 g (38.3%) of white needlelike crystals were obtained. These crystals consisted of 75% of 14 and 25% of 13. For 13: mp 77–78 °C dec; NMR (CDCl<sub>3</sub>)  $\delta$  0.93 (t, 3), 1.51 (hexet, 2), 2.06 (t, 2), 3.10 (s, 3), 4.13 (s, 2), 5.04 (s, 2), 8.44 (br s, 1). For 14: mp 51.53 °C dec; NMR (CDCl<sub>3</sub>)  $\delta$  1.00 (t, 3), 1.65 (s, 3), 2.10 (q, 2), 3.08 (s, 3), 4.06 (s, 2), 5.48 (t, 1), 8.4 (br s, 1).

1-(Methylenepentyl)-2-acetyl-4-methyl-1,2,5-triazolidine-3,5-dione (15) and 1-(2-Methyl-2-pentenyl)-2-acetyl-4-methyl-1,2,4-triazolidine-3,5-dione (16). Compound 13 was treated with acetic anhydride,<sup>6</sup> and 15 was obtained as a colorless oil after chromatographic purification. Compound 16 was also synthesized from 14.

**Reaction of 16 with 1a.** A 370-mg (1.54 mmol) sample of 16 and 245 mg (1.40 mmol) of 1a were dissolved in 30 mL of DCE, and the mixture was left at room temperature. After 3 days, DCE was removed on a rotary evaporator, and the residue was purified by column chromatography (silica gel). The main fractions were combined and concentrated. After two recrystallizations from benzene-hexane, 433 mg (74.6%) of a mixture of 19 and 20 was obtained. The ratio of 19 to 20 was found to be 3:2 from <sup>1</sup>H NMR analysis.

The data for the mixture of 19 and 20 are as follows: mp 166.5–167.5 dec; NMR (CDCl<sub>3</sub>)  $\delta$  0.93 (t), 0.97 (t), 1.90 (quintet), 1.97 (s), 2.53 (s), 2.58 (s), 3.10 (s), 3.13 (s), 4.45 (t), 4.6 (s), 5.33 (d), 5.98 (s), 7.48 (s). Anal. Calcd for C<sub>19</sub>H<sub>22</sub>N<sub>6</sub>O<sub>5</sub>: C, 55.06; H, 5.35; N, 20.98. Found: C, 54.54; H, 5.37; N, 20.12.

1-Propyl-4-phenyl-1,2,4-triazolidine-3,5-dione (21). To 5.26 g of potassium hydroxide (85% purity, 0.080 mol) in 200 mL of ethanol was added 14.16 g (0.08 mol) of 4-phenylurazole. To this

solution, which was heated to 60–65 °C, was added 41.0 g (0.24 mol) of 1-iodopropane. The mixture was kept at 70 °C for 3 h, during which the salts precipitated. The mixture was left at room temperature overnight. After filtration, ethanol and excess of 1-iodopropane were removed on a rotary evaporator. The resulting yellow oil was dissolved in ethyl acetate, and the ethyl acetate solution was washed with water and then dried over anhydrous sodium sulfate. The slightly yellow solid residue, after evaporation of the ethyl acetate, was purified by column chromatography (silica gel). After concentration and recrystallization from benzene-hexane, 8.78 g (50.7%) of pure 21 was obtained: mp 98–99 °C dec; NMR (CDCl<sub>3</sub>)  $\delta$  0.90 (t, 3), 1.66 (six peaks, 2), 3.56 (t, 2), 7.49 (s, 5), 8.6 (br s, 1). Anal. Calcd for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.90; H, 6.17; N, 19.30.

1-Propyl-2-acetyl-4-phenyl-1,2,4-triazolidine-3,5-dione (22). Compound 21 was acetylated by using acetic anhydride: mp 107–108 °C; NMR (CDCl<sub>3</sub>)  $\delta$  0.93 (t, 3), 1.64 (six peaks, 2), 2.65 (s, 3), 4.04 (t, 2), 7.50 (s, 5).

1-Methyl-4-phenyl-1,2,4-triazolidine-3,5-dione (24). The potassium salt of 4-phenylurazole was permitted to react with methyl iodide in ethanol to give, after purification, 24: mp 158–160 °C; NMR (acetone-*d*<sub>6</sub>)  $\delta$  3.23 (s, 3), 7.48 (m, 5).

**Reaction of 21 with 1a.** To 2.00 g (0.1 mmol) of 21 in 150 mL of DCE was added 1.59 g (9.1 mmol) of PhTD at 60 °C. After 1 day, the red color was completely discharged, and a large amount of white crystals was formed. The crystals were collected by filtration and washed with dichloromethane to give 2.79 g (77.8%) of 25. The filtrate was concentrated, and the residue was washed with benzene to give 0.28 g (7.8%) of 25: mp 193–195 °C dec; NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  1.03 (t, 3), 2.23 (quintet, 2), 5.63 (t, 1), 7.45 (s, 10). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>6</sub>O<sub>4</sub>: C, 57.86; H, 4.60; N, 21.31. Found: C, 57.72; H, 4.64; N, 21.29.

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## Fluorine Magnetic Resonance Spectra of Monofluoro- and Difluoro-Substituted Hydrocarbons

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Fluorine chemical shifts have been measured for some simple mono- and difluorides. Substituent effects analogous to those in carbon NMR have been developed for aliphatic, phenyl, and fluorine substituents. The substituent parameters for individual compounds are interpreted in terms of conformational effects, and the general parameters are compared with those of other nuclei.

Fluorine NMR, although indispensable to the fluorine chemist,<sup>1,2</sup> is not as useful as it might be in distinguishing between alternative structures. In part, this problem has arisen because, in contrast to carbon NMR,<sup>3,4</sup> the basic

rules governing fluorine chemical shifts, as would be determined from simple compounds, have never been elucidated. Carbon chemical shifts have been correlated with substituent parameters derived from rigid molecules and rotamer populations derived from regression analyses. This ideal approach is more feasible for carbon than for

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