its optically active 6a carbon. This retention of optical activity of apomorphine under such conditions parallels the observations of Kametani with the aporphine-like protoberberines[23] and 1-benzyltetrahydroisoquinolines.[24] It should be noted, however, that exposure of apomorphine[25] and related ring systems[23,24] to PtO_2 and hydrogen has been found to cause almost complete racemization of the 6a chiral center.

The successful use of **4** as a novel high-specific-activity, tritiated dopaminergic agonist has recently been documented.[26]

Experimental Section

General Methods. Evaporations were carried out on a Büchi rotary evaporator in vacuo at bath temperatures below 40 °C. TLC was performed on Analtech 5 × 15 cm (250 μm, analytical) and 20 × 20 cm (1000 μm, preparative) silica gel GF coated glass plates. Common solvent combinations were S_1 ($CHCl_3$–CH_3OH, 9:1), S_2 ($CHCl_3$–HOAc–CH_3OH, 10:2:2), S_3 (EtOH–HOAc–H_2O, 6:3:1), and S_4 (CH_3OH–PhH–H_2O–HOAc, 15:2:5:2). Autoradiography was performed at 0 °C after spraying the TLC plates with PPO (New England Nuclear) and exposing them to Eastman Kodak SB-5 film. TLC plates were also scanned for activity by using a Packard 7201 scanner. UV spectra were measured on a Beckman Model 25 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. The proton and triton magnetic resonance spectra were obtained on a Bruker WP 200-MHz NMR spectrometer. High-resolution mass spectra were performed by Shrader Analytical Laboratories. Preparative and analytical high-pressure LC was performed on a Waters high-pressure LC instrument using μ-Bondapak CN and μ-Bondapak C_{18} columns (Waters) eluted with S_5 [5% EtOH in 0.01 N KH_2PO_4 (pH 3) buffer] at 1.0 mL/min. Peak detection was performed at 280 nm by using a Waters 440 UV detector.

(-)-*N*-Allylnorapomorphine (3). A solution of (-)-nalorphine (**2**;[16] 75 mg, 0.22 mmol) in 1 mL of argon-degassed methanesulfonic acid was heated at 90 °C under argon for 0.5 h and then cooled in an ice bath. After the mixture cooled, 20 mL of a 0.1% $Na_2S_2O_5$ aqueous solution was slowly added to the reaction. It was basified to pH 8 with NH_4OH and then extracted with three 30-mL portions of S_1. The combined extracts yielded a residue upon evaporation which was preparatively chromatographed on a 1000-μm silica gel plate eluted with S_2. A major band (short-wave UV, R_f 0.63) was scraped off and eluted with S_1. Concentration of the eluent yielded a residue that was taken up in a solution of 5 mL of $CHCl_3$ and 25 mL of Et_2O. Millipore filtration and acidification with excess ethereal HCl yielded 20 mg (27%) of **3**·HCl as a white solid: mp 263–266 °C (lit.[18a] 265–266 °C); ^1H NMR (CD_3OD) δ 8.42 (dd, 1, J = 7.57, 0.98 Hz, H-1), 7.35 (dd, 1, J = 7.57, 0.49 Hz, H-2), 7.18 (dd, 1, J = 7.57, 0.98 Hz, H-3), 6.75 (m, 2, H-8,9), 6.10 (m, 1, $NCH_2CH{=}CH_2$), 5.70 (m, 2, $NCH_2CH{=}CH_2$), 4.50–3.20 (m, 8, H-4,5,7, $NCH_2CH{=}CH_2$), 2.80 (t, 1, J = 14.16 Hz, H-6a); UV (EtOH) λ_{max} 273 nm (ε 14 156), 281 (16 783), 320 (3015); $[\alpha]^{25}_D$ -66.1° (c 0.378, water) [lit.[18a] $[\alpha]^{30}_D$ -64.0° (c 0.328, water)].

Anal. Calcd for $C_{19}H_{19}NO_2$ (molecular ion): m/e 293.1414. Found: m/e 293.1401.

(-)-*N*-*n*-[^{3}H]Propylnorapomorphine (4). A solution of 8 mg (0.023 mmol) of **3** in 1.5 mL of EtOH with 3 mg of 10% Pd/C was stirred under an atmosphere of 75 Ci of tritium for 2 h at ambient temperature in the dark. Catalyst filtration and volatile removal with EtOH was performed. The resulting residue was dissolved in 20 mL of EtOH (total activity 474 mCi). This solution was concentrated to a volume of 0.5 mL and preparatively chromatographed on two 1000-μm silica gel plates eluted with S_3. The major band (short-wave UV R_f 0.84) was scraped off and eluted with EtOH (total activity 204 mCi). Final purification was performed by high-pressure LC using a μ-Bondapak CN column eluted at 1.0 mL/min with S_5. Typically, 204 mCi of prepurified **4** yielded 20 mCi of **4** displaying 98% radiochemical purity by silica gel TLC (S_3 and S_4) and high-pressure LC on μ-Bondapak CN and C_{18} eluted with S_5.[27] In both TLC and high-pressure LC analyses of radiolabeled **4**, it coeluted with cold standard (-)-*N*-*n*-propylnorapomorphine. The specific activity of **4** [ε (273 nm) 17 000[13b]] as measured by UV spectroscopy was 72 Ci/mmol.

(-)-*N*-*n*-[^{2}H]Propylnorapomorphine (5). A solution of 10 mg of **3** in 1.5 mL of EtOH with 4 mg of 10% Pd/C was stirred under an atmosphere of deuterium for 2 h at ambient temperature in the dark. Millipore filtration of the catalyst yielded a solution which was treated with excess ethereal HCl and concentrated to approximately 0.3 mL. The solution was diluted with 15 mL of Et_2O to yield 3.9 mg (41%) of **5** as a white solid.

Acknowledgment. The authors gratefully acknowledge the technical assistance of K. Bradley in the tritiation of **3** to **4** and H. Maksoud for supplying mass spectral data for **5**, the help of Professor L. J. Altman (Stony Brook) in obtaining the triton magnetic resonance spectrum of **4** and the consultation of Professor P. Vouros (Northeastern University) regarding the mass spectrum of **5**. The research at Northeastern University was supported in part by Contract NOI-CM-53741 from the National Cancer Institute and by a grant from the National Institutes of Health (NS 15439-01).

Registry No. **2**, 62-67-9; **3**·HCl, 1477-58-3; **4**, 73728-30-0; **5**, 73728-31-1.

(23) T. Kametani and M. Ihara, *J. Chem. Soc. C*, 191, (1968).
(24) T. Kametani, M. Ihara, and K. Shima, *J. Chem. Soc. C*, 1619 (1968).
(25) J. L. Neumeyer and P. Rice, unpublished results.
(26) (a) M. Titeler and P. Seeman, *Eur. J. Pharmacol.*, **56**, 291, (1979); (b) I. Creese, L. Padgett, E. Fazzini, and F. Lopez, *ibid.*, **56**, 411, (1979).
(27) The loss of product **4** attending this stage of the purification is undoubtedly due to product decomposition during rotary evaporator concentration of crude **4** in EtOH to a volume suitable for high-pressure LC injection, as well as peak shaving during the high-pressure LC of **4**.

Ene Reaction of Triazolinediones with Alkenes. 1. Structure and Properties of Products

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The structures of the ene products from reaction of triazolinediones with alkenes and polyisoprene were studied by using ^1H NMR. The pK_a values of the ene products were measured. The reactivity and stability of the ene products were also studied.

The ene reaction of 4-substituted-1,2,4-triazoline-3,5-diones (4-R-TD) with alkenes (eq 1) was first studied by Pirkle and Stickler[1] and 4-methyl-1,2,4-triazoline-3,5-dione (MeTD) was found to be at least 30 000 times more reactive

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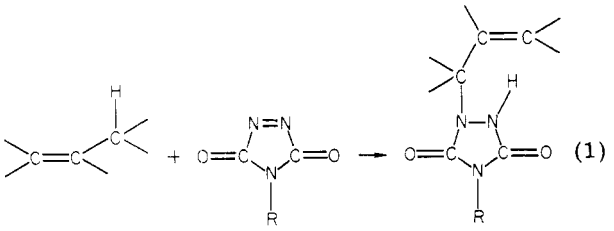


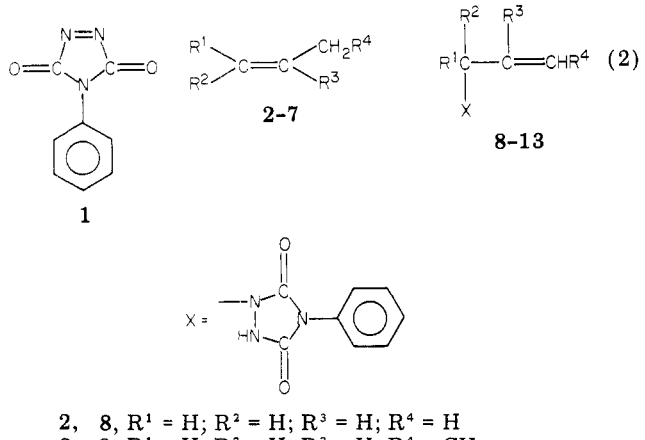
(1)

toward cyclohexene than is ethyl azodicarboxylate. Saville[2] used this reaction for cross-linking of natural rubber. We[3,4] have successfully used this reaction for modification of polybutadiene, polyisoprene, and copolymers of butadiene and isoprene. However, no systematic studies on this reaction itself have been reported. A study was undertaken to obtain fundamental background information on the ene reaction between TD and alkenes. In this paper we report the structures of the ene products for a series of model compounds as well as for polyisoprene. We also wish to report pK_a data and some reactions of the ene products.

Results and Discussion

Ene Reaction between PhTD and Alkenes. An excess (5–10 mol/1 mol of PhTD) of the alkene was permitted to undergo reaction with PhTD in dichloromethane at room temperature. Usually the typical red color of PhTD was quickly discharged when mixed with the alkenes. After removal of solvent and recrystallization of the residual solids, pure ene products were obtained. The products from certain alkenes (especially 1-alkenes) required chromatographic purification to obtain high purity. The structures of the products were confirmed by ^1H NMR analysis, and all alkenes which were studied gave normal ene reaction products. Yields and melting points of these products are listed in Table I and ^1H NMR data are shown in Table II. In the case of alkenes which may give several isomeric structures, the ^{1} H NMR spectrum of the crude product was also checked just after removal of solvent.

Alkenes **2**–**7** (eq 2) gave structures which could be predicted from the normal ene reaction. 2-Methyl-1-pentene



(2)

1 **2-7** **8-13**

2, 8, R^1 = H; R^2 = H; R^3 = H; R^4 = H
3, 9, R^1 = H; R^2 = H; R^3 = H; R^4 = CH_3
4, 10, R^1 = H; R^2 = H; R^3 = CH_3; R^4 = H
5, 11, R^1 = CH_3; R^2 = H; R^3 = H; R^4 = H
6, 12, R^1 = CH_3; R^2 = CH_3; R^3 = CH_3; R^4 = H
7, 13, R^1 = H; R^2 = H; R^3 = H; R^4 = $CH_2CH_2CH_3$

(**14**, eq 3) gave products consisting of almost equal amounts of **15** and **16**. *trans*-2-Hexene (**17**, eq 4) gave a slight excess of the internal olefin (**18**/**19** ratio of 2:3). However, 2-methyl-2-butene (**20**, eq 5) gave only one product, **21**. 1-Methyl-1-cyclohexene (**22**, eq 6) was attacked exclusively at the 2-position and the ratio between the two isomers, **23** and **24**, was 1:1.

The reaction between **1** and **25** (eq 7) gave a mixture of products, **26** and **27**. More than 80% of the product was the 1:2 adduct **27**. 3-Methyl-1-pentene (**28**, eq 8) gave a mixture of 25% of 1:1 adduct **29** and 75% of the 1:2 adducts **30** and **31**.

1,5-Hexadiene (**32**, eq 9) with PhTD at a molar ratio of 28:1 yielded only a 1:1 ene product, **33**. However, at a molar ratio of 1:2, the major product was **34**. Compound **34** was shown to be formed rather than **35** by NMR analysis, based upon integration of the allylic vs. nonallylic protons in the δ 1–3 region. A Diels–Alder reaction could have occurred on **34** to form the 1:3 adduct; however, this was not observed, probably due to steric effects.

From a qualitative comparison of the rate of color discharge of PhTD, the order of reactivity of the alkenes appears to be as follows: **2**, **3**, **7** < **5**, **14**, **17** ≪ **20** ≪ **6**. This qualitative comparison appears valid on the basis of the fact that the same molar ratio of alkene to PhTD was used for alkenes **7**, **14**, **17**, **20**, and **6**. This order is also supported by the kinetic study reported in the succeeding paper.[5] This order suggests that reactivity of the alkene increases markedly with increased substitution at the carbon–carbon double bond of the alkene. Taking this fact into consideration, the result that **25** and **28** gave more 1:2 adduct than 1:1 adduct can be easily understood. Since **25** and **28** are 1-alkenes, their reactivity is very low. On the other hand, the 1:1 adducts (**26** and **29**) have similar structures to that of **18** and are expected to have relatively high reactivity. Usually, the second addition is not fast enough to give an appreciable amount of the 1:2 adduct (for example **7** and **17**). However, in this case, once the 1:1 adduct is formed, it seems to react with another PhTD even faster than the starting alkene. That **34** is the major 1:2 adduct from **32** can be also explained by comparing the reactivity of two double bonds in **33**.

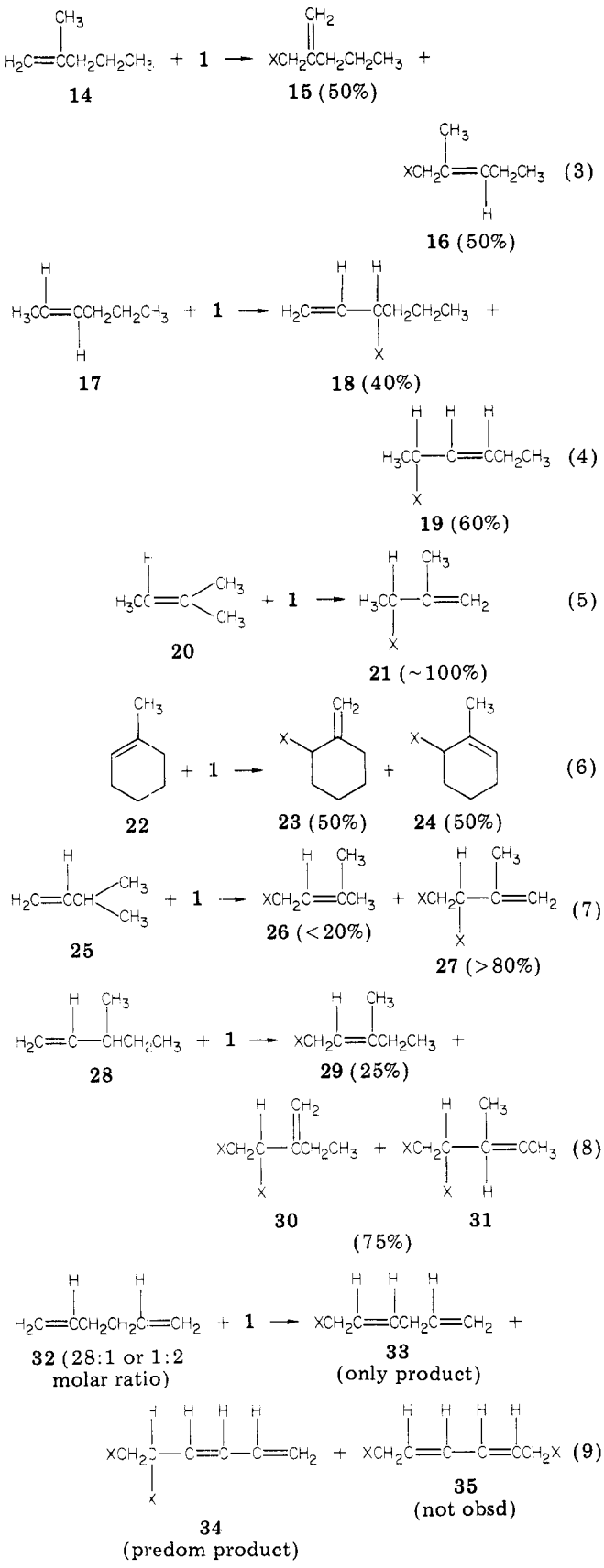
Elemental analyses of representative ene products are as follows. Anal. Calcd for **8** (1:1 propene–PhTD), $C_{11}H_{11}N_3O_2$: C, 60.83; H, 5.07; N, 19.35. Found: C, 60.59; H, 5.14; N, 19.28. Calcd for **27** (1:2 3-methyl-1-butene–

Table I. Yields and Melting Points of Products for the Ene Reaction[a] of Alkenes with PhTD

alkene	product	yield,[b] %	mp, °C
2	8	54	116.5-117.5
3	9	58	129-130
4	10	86	105-106
5	11	80	99-100
6	12	88	130-131
7	13	38	111-112
14	15 + 16	85	77-78
17	18 + 19	38	78-79
20	21	97	147-148.5
22	23 + 24	76	106-107
25	27		85-87
32[c]	33	87	102-105
51[d]	52	89	171-172

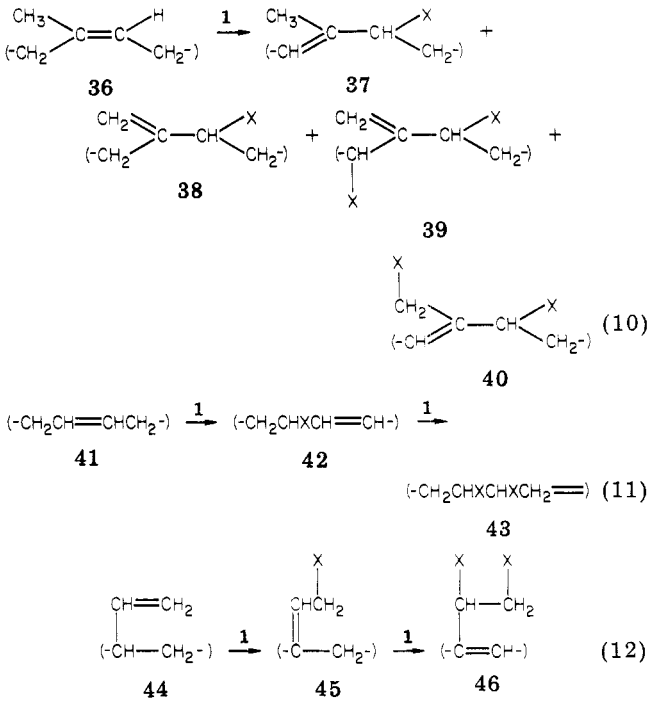
[a] Reaction in dichloromethane at room temperature. [alkene]/[PhTD] = 5–10. [b] After complete purification. [c] [Diene]/[PhTD] = 28. [d] Cyclohexene.

(1) Pirkle, W. H.; Stickler, J. C. *Chem. Commun.* **1967**, 760.
(2) Saville, B. *Chem. Commun.* **1971**, 635.
(3) Butler, G. B.; Williams, A. G.; Leong, K. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18*, 843.
(4) Leong, K.; Butler, G. B. *J. Macromol. Sci., Chem.*, in press.
(5) Ohashi, S.; Butler, G. B. *J. Org. Chem.*, companion paper in this issue.
(6) Wagener, K. B.; Turner, S. R.; Butler, G. B. *Polym. Lett.* **1972**, *10*, 805.
(7) Laitenen, H. A.; Harris, W. E. "Chemical Analysis", 2nd ed.; McGraw-Hill: New York, 1975; p 34.



PhTD), $C_{21}H_{20}N_6O_4$: C, 60.00; H, 4.76; N, 20.00. Found: C, 58.35; H, 4.97; N, 19.04. Calcd for **33** (1:1 1,5-hexadiene–PhTD), $C_{14}H_{15}N_3O_2$: C, 65.37; H, 5.84; N, 16.34. Found: C, 64.27; H, 5.93; N, 16.08.

Structure of Polymers Modified with Triazolinedione. Usually ^1H NMR spectra of polymers modified with TD are too complicated to give sufficient information for structural determination. However, if we use the results of the model studies, we can predict the structures reasonably well. 1,4-*cis*-Polyisoprene (**36**, eq 10) can give



several different structures by reaction with TD. But the results from **20** and **22** suggest that only two structures, **37** and **38**, should be formed. Furthermore, **39** seems to be the only 1:2 adduct likely to be formed, because **37** would be predicted to be much more reactive than **38**. On the basis of these assumptions, an attempt to calculate the ratio of each structure for 1,4-*cis*-polyisoprene modified with MeTD was made. Those peaks between δ 1 and 3, which should arise from allylmethyl, allylmethylene, and *N*-methyl protons, were used for the calculation. The results are shown in Table III. The ratio of **37** to **38** was found to be very close to 1:1 and in very good agreement with the model study.

From this study, it was found that substitution at the allyl methylene position by the urazole ring decreases the reactivity of allyl compounds to about $^1/_{50}$ of its original reactivity, so the ratio of **39** to **37** and **38** would be predicted to be less than 10%, even at high conversion.

In the cases of 1,4-*cis*- or -*trans*-polybutadiene (**41**, eq 11) and 1,2-polybutadiene (**44**), the structures can be predicted more easily. Structure **41** will give mostly **42** and only a small amount of **43** at the higher extent of modification. Structure **44** (eq 12) will give more of 1:2 adduct **46**, because of the high reactivity of structure **45**.

pK_a of Ene Products. The urazole derived via the ene reaction of TD with alkenes has one NH proton, which seems to be very acidic. Actually, we[3] have observed that polymers modified with TD are soluble in alkaline solution if the extent of modification is 40–50% or more. So the measurement of the pK_a of the ene products was considered to be very important in providing information on the properties of modified polymers.

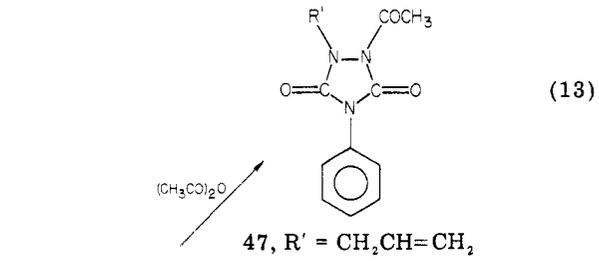
The pK_a of the ene products was measured by using an acid–base titration method. As most of the ene products are not soluble in pure water, an *N*,*N*-dimethylformamide–water mixed solvent was used, and the pK_a in pure water was estimated by the extrapolation method. The results are shown in Table IV.

As expected, these compounds are quite strongly acidic, and the pK_a of **8** is almost the same as that of acetic acid.

The increase of the number of substituents on the alkenyl group causes a decrease of acidity, but the difference is not so pronounced. Thus, polymers modified with TD are expected to have similar acidities to that of polyacrylic acid and can be converted to the polyanion which should be very stable even under strongly basic conditions.

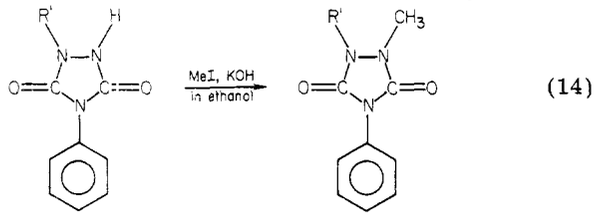
Reactivity of Ene Products. In order to get further information on the stability and reactivity of modified polymers, we studied reactions of the NH group and the carbon–carbon double bond by using model compounds.

As would be expected from its pK_a value, the NH group of the ene product is very reactive. Compound **8** reacts with acetic anhydride at room temperature to give an *N*-acetyl compound (**47**, eq 13). Compound **8** also reacts



(13)

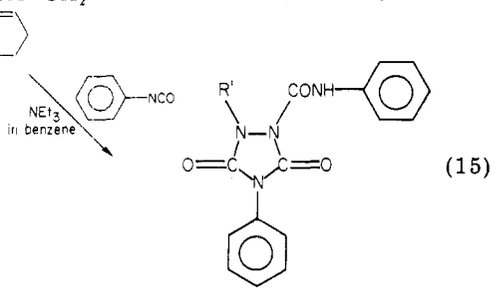
47, R′ = $CH_2CH{=}CH_2$



(14)

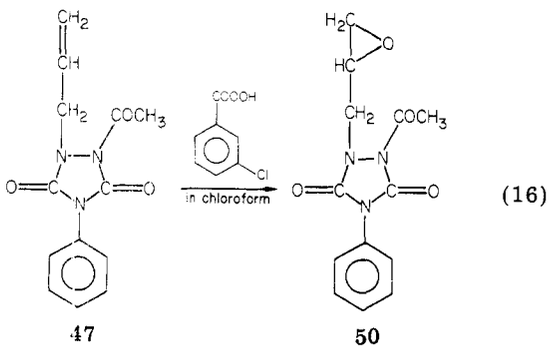
8, R′ = $CH_2CH{=}CH_2$ **48**, R′ = $CH_2CH{=}CH_2$

52, R′ =



(15)

49, R′ =



(16)

47 **50**

with methyl iodide in the presence of potassium hydroxide (eq 14) to give **48**, and the ene product, **52**, of the reaction of cyclohexene **51** with PhTD reacts with phenyl isocyanate in the presence of triethylamine as catalyst to give **49** (eq 15). These reactions could be useful for further modification of TD-modified diene polymers and TD copolymers.

The ene product still possesses a carbon–carbon double bond which should have interesting reactivity. This double bond can undergo reaction with bromine or another TD molecule. However, the reactivity is much lower than that of the corresponding simple alkene. N-Acetylated compound **47** (eq 16) yielded epoxy compound **50** by the action of *m*-chloroperoxybenzoic acid. Compound **50** could be useful as another type of monomer or modifier which has a urazole ring.

These ene products were found to be very stable. The ene product of the reaction of cyclohexene **51** with PhTD, **52**, was heated in 3 N potassium hydroxide in methanol–water (3:1 v/v) solution at 110 °C for 46 h or was treated with dinitrogen tetraoxide at room temperature to result in only the recovery of **52**. However, such an N-methylated compound as **48** was completely hydrolyzed by the action of potassium hydroxide at 110 °C.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were taken on a Varian A-60A spectrometer. A Corning pH meter, Model 125, was used for pH measurement. Microanalyses were performed by Atlantic Microlab, Inc.

Ene Reaction and Isolation of Products. The alkene was dissolved in or bubbled into dichloromethane (ca. 0.1 mol/L), and TD in the same solvent (ca. 0.01 mol/L; alkene/TD = 5–10 mol/mol) was added slowly to the alkene solution with stirring. After complete discharge of the red color of TD, the solvent was removed on a rotary evaporator. The residual slightly yellow oil or solid was purified by recrystallization from benzene–hexane or by column chromatography (silica gel). Yields and melting points of these products are shown in Table I and ^1H NMR data are shown in Table II.

The ratios of isomers for the products from alkenes **14**, **17**, **20**, **22**, **25**, **28**, and **32** were determined by comparing two peaks which are assigned to vinyl and vinylene protons, respectively, in the ^1H NMR spectra.

Modification of 1,4-*cis*-Polyisoprene by MeTD. A 0.97-g sample of polyisoprene was dissolved in 40 mL of CH_2Cl_2 during 20 h. MeTD (0.38 g) was dissolved in 8.3 mL of Me_2SO-d_6. To a known amount of the polymer solution was added the solution of MeTD dropwise with stirring, the solution being kept slightly pink. The color disappeared in less than 5 min when less than an equimolar amount of MeTD was added. No precipitation was observed. Dichloromethane was removed on a rotary evaporator, and Me_2SO-d_6 solutions of the modified polymers were tested by ^1H NMR. When the polymer was modified to an extent of less than 20% it was insoluble in pure Me_2SO. Thus chloroform-*d* (30% v/v) was added to give a homogeneous solution.

NMR analysis was used to assign structures for the modified polymers.

pK_a Measurement. The ene product (ca. 5×10^{-4} mol) was weighed accurately into a 100-mL beaker and dissolved in 50 mL of deionized water. In the case of the DMF–water mixed solvent, the sample was first dissolved in DMF, and then water was added to adjust the volume. The electrode of the pH meter was dipped into this solution, which was maintained at 25.0 °C by using a water bath. The pH of the solution was measured after each addition of 0.5 mL of 0.08 N aqueous sodium hydroxide solution. The pK_a was calculated at each point by using eq 17, and these

$$pK_a = pH + \log ([AH]_{st} - [H^+] + [OH^-]) - \log ([A^-]_{st} + [H^+] - [OH^-]) \quad (17)$$

values were averaged. In the case of the compounds which are insoluble in pure water, the pK_a in 10, 30, and 50% DMF–water was measured, and the pK_a in pure water was estimated by extrapolation.

1-(2-Propenyl)-2-acetyl-4-phenyl-1,2,4-triazolidine-3,5-dione (47). A 2.28-g (10.5 mmol) sample of **8** was dissolved in 50 mL of acetic anhydride and left at room temperature overnight. Excess acetic anhydride and acetic acid were removed on a rotary evaporator, and the residue was dried in vacuo. After chromatography (silica gel) and recrystallization from benzene–hexane, 2.1 g (77%) of **47** was obtained: mp 103–104 °C; NMR ($CDCl_3$) δ 2.58 (s, 3), 4.60 (d, 2), 5.27 (d, 1), 5.30 (d, 1), 5.83 (ddt, 1), 7.47 (s, 5).

Table II. ^{1}H NMR Data of Ene Products

	δ ($CDCl_3$)[a]									
product	CCH_3	>C=C<(CH3)	CH_2	>C=C<(CH2)	N-N (CH2)	N-N (CH)	$C=CH_2$	CH=C	Ph	N-N (H)
8					4.15 d		5.27 w	5.9 m	7.47 s	8.65 br s
9		1.70 d			4.17 d			5.73 m	7.52 s	8.9 br s
10		1.72 d			4.10 s		4.94 s		7.46 s	8.75 br s
11	1.35 d					4.80 m	5.15 m	5.83 m	7.47 s	8.4 br s
12	1.62 s	1.85 s					5.04 s		7.50 s	9.0 br s
13	0.85 t		1.37 m	1.99 q	4.13 d			5.65 m	7.48 s	9.0 br s
21	1.43 d	1.82 s				4.80 q	5.07 s		7.53 s	8.7 br s
26		1.72 s			4.20 d			5.28 t	7.48 m	8.8 br s
27		1.64 s			4.0 br m		4.87 br m		7.30 s	8.3 br s
33				2.70 t	4.05 d		4.7-6.05 m		7.40 s	9.0 br s
52			1.85 m	1.98 m		4.85 s		5.83 m	7.52 s	

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Table III. Structure of 1,4-*cis*-Polyisoprene Modified with MeTD

extent of modification, %	% products		extent of modification, %	% products	
	37	38		37	38
12.8	43	57	44.7	50	50
22.1	47	53	55.6	62	38
38.2	58	42	100.0		

Table IV. pK_a of PhTD–Alkene Ene Products

compd	pK_a[a] in water[b]	pK_a[a] in DMF–water (1:1)
8	4.71	5.97
10	(4.80)	6.05
21	(4.86)	6.16
12	(5.33)	6.72
52	(5.10)	6.31
phenylurazole	5.29	6.44

[a] Measured at 25 °C. [b] Values in parentheses were obtained by extrapolation.

Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05; N, 16.21. Found: C, 60.21; H, 5.09; N, 16.19.

1-(2-Propenyl)-2-methyl-4-phenyl-1,2,4-triazolidine-3,5-dione (48). A 0.75-g sample of potassium hydroxide was dissolved in 50 mL of ethanol, and 2.5 g (11.5 mmol) of **8** was added to this solution. After complete dissolution, 3.5 mL of methyl iodide was added, and the mixture was left at room temperature overnight. After separation of the salt, ethanol and excess methyl iodide were removed on a rotary evaporator. The residual oil was dissolved in ethyl acetate, washed with water, and dried with sodium sulfate. After removal of ethyl acetate, the product was purified by column chromatography (silica gel), and 2.64 g (82%) of colorless oil was obtained: NMR ($CDCl_3$) δ 3.22 (s, 3), 4.27 (d, 2), 5.32 (d, 1), 5.33 (d, 1), 5.92 (ddt, 1), 7.47 (m, 5). Anal. Calcd for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.67; N, 18.17. Found: C, 62.13; H, 5.73; N, 18.10.

1-(2-Cyclohexenyl)-2-[(phenylamino)carbonyl]-4-phenyl-1,2,3-triazolidine-3,5-dione (49). A 0.52-g (2 mmol) sample of **52** was dissolved in 10 mL of benzene, and 0.45 mL of phenyl isocyanate and 2 drops of triethylamine were added to the solution. After 1 day, the solvent was removed on a rotary evaporator, and the residual solid was recrystallized from benzene–hexanes: NMR ($CDCl_3$) δ 2.67 (s, 3), 2.70 (dd, 1), 2.86 (dd, 1), 3.22 (m, 1), 3.97 (dd, 1), 4.38 (dd, 1), 7.51 (s, 5).

Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.89; H, 4.82; N, 15.30.

1-Glycidyl-2-acetyl-4-phenyl-1,2,3-triazolidine-3,5-dione. To 1.04 g (4 mmol) of **47** dissolved in 15 mL of 1,2-dichloroethane was added 0.89 g of *m*-chloroperoxybenzoic acid in 20 mL of $CHCl_3$. The mixture was kept at room temperature for 3 h and then heated at 70 °C overnight. After cooling, the mixture was treated with sodium sulfite to remove excess peroxide and then washed with 5% sodium bicarbonate, followed by drying with sodium sulfate, and the solvent was removed. The residue was purified by column chromatography (silica gel) and recrystallized from benzene–hexanes to yield 0.62 g (56%) of white crystals: mp 116–118 °C; NMR ($CDCl_3$) δ 2.1 (br m, 6), 4.9 (br m, 1), 5.85 (br m, 2), 7.48 (m, 10), 9.55 (br s, 1).

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Registry No. **1**, 4233-33-4; **2**, 115-07-1; **3**, 106-98-9; **4**, 115-11-7; **5**, 590-18-1; **6**, 563-79-1; **7**, 592-41-6; **8**, 73970-92-0; **9**, 70353-81-0; **10**, 73970-93-1; **11**, 73970-94-2; **12**, 73970-95-3; **13**, 73970-96-4; **14**, 763-29-1; **15**, 73970-97-5; **16**, 73970-98-6; **17**, 4050-45-7; **18**, 73970-99-7; **19**, 73971-00-3; **20**, 513-35-9; **21**, 73971-01-4; **22**, 591-49-1; **23**, 73971-02-5; **24**, 73971-03-6; **25**, 563-45-1; **26**, 73971-04-7; **27**, 73971-05-8; **28**, 760-20-3; **29**, 73985-86-1; **30**, 73985-87-2; **31**, 73971-06-9; **32**, 592-42-7; **33**, 73971-07-0; **34**, 73985-88-3; **36**, 9003-31-0; **47**, 73971-08-1; **48**, 73971-09-2; **49**, 73971-10-5; **50**, 73971-11-6; **51**, 15971-69-4; **52**, 73971-12-7.