phonate, b.p. 110–112° (6 mm.), and 16 g. of a residue. The residue was treated with 30 g. (0.14 mole) of phosphorus pentachloride to yield 8 g. of the dichlorodifluoroethylphosphonic dichloride, which was confirmed with the authentic sample prepared as mentioned below.

Using the same procedure, other dialkyl phosphonates were added to 1,2-dichloro-1,2-difluoroethylene. The addition reactions to other chlorofluoroolefins were carried out under similar conditions. In the case of 1,1-difluoro-2,2-dichloroethylene, the telomers were obtained with the 1:1 adduct. The dichloride of 1:2 adduct was isolated by distillation after the treatment of dialkyl ω-hydroperhaloalkylphosphonates with phosphorus pentachloride.

The irradiation conditions and yields based on the amounts of olefins added for each run are shown in Table I.

Chlorofluoroethylphosphonic Acids.—The hydrolysis of chlorofluoroethylphosphonates was carried out by the procedure of Brace.[8] In a flask fitted with a reflux condenser were added 25 g. (0.09 mole) of diethyl 1,2,2-trichloro-1-fluoroethylphosphonate and 60 ml. of concentrated hydrochloric acid. The mixture was refluxed at 80–110° for 5 hr. In 1 hr., a homogeneous solution was obtained. After ether extraction of the unchanged phosphonate, the aqueous solution was distilled under reduced pressure to remove hydrogen chloride and water. A trace of water remained and was removed by the azeotropic distillation with benzene. The liquid residue, 1,2,2-trichloro-1-fluoroethylphosphonic acid, 18.5 g. (0.08 mole, 92% yield), crystallized on standing. It was hygroscopic and liquefied on absorbing moisture in the air at room temperature. 1,2-Dichloro-1,2-difluoroethylphosphonic acid and 1,1-difluoro-2,2-dichloroethylphosphonic acid were prepared in an analogous fashion.

Chlorofluoroethylphosphonic Dichlorides.—To 16 g. (0.07 mole) of 1,1,2-trichloro-2-fluoroethylphosphonic acid in a flask with a reflux condenser was added 15 g. (0.07 mole) of phosphorus pentachloride in portions. A mixture was heated mildly and, in 0.5 hr., phosphorus oxychloride began to reflux. After heating for 1 hr., phosphorus oxychloride was distilled. To the residue, 15 g. (0.07 mole) of an additional phosphorus pentachloride was added and heated for 1 hr. Distillation of the products, after the removal of phosphorus oxychloride, gave 13 g. (0.05 mole) of 1,2,2-trichloro-1-fluoroethylphosphonic dichloride, b.p. 85–88° (8 mm.), and 3 g. of a solid residue.

Using the same procedure, 1,2-dichloro-1,2-difluoroethyl- and 1,1-difluoro-2,2-dichloroethylphosphonic dichlorides were prepared. Table III summarizes the physical properties of chlorofluoroethylphosphonic dichlorides.

Basic Hydrolysis of Chlorofluoroethylphosphonic Acids.—1,2,2-Trichloro-1-fluoroethylphosphonic acid, 10 g. (0.04 mole), and 30 ml. of 10% aqueous sodium hydroxide solution were added to a flask fitted with a reflux condenser, which was in turn connected to a trap cooled in Dry Ice–acetone. The mixture was heated at 50–100° for 30 min. to yield 1 g. (0.009 mole) of an olefin. The infrared spectrum and gas chromatogram of the olefin were compared with those of 1,2-dichloro-1-fluoroethylene which was prepared by the dechlorination of 1,1,2,2-tetrachlorofluoroethane.[16]

The Reaction of Ethyl Azodicarboxylate with Monoolefins

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The reaction of monoolefins with ethyl azodicarboxylate has been investigated. Acyclic monoolefins react by a nonradical process to give additive-substitution products with a shift of the double bond. Cyclic olefins, on the other hand, react predominantly by a free-radical process. The relative reactivity of C_4 and C_5 olefins (with ethyl azodicarboxylate) and the structure of the resultant products are all consistent with a concerted "addition–abstraction" mechanism involving a six-membered transition state. The data have been interpreted in terms of charge stabilization and steric interactions in the transition state.

The additive-substitution reaction of azodiformic acid esters with olefins was first observed in 1927 but received little attention[1,2] until recently.

Huisgen and Pohl were the first to present evidence for the mechanism of azo ester–olefin reactions. They demonstrated that aromatically conjugated olefins, such as 1,2- and 1,4-dihydronaphthalene and unsymmetrically substituted 1,3-diarylpropenes, underwent substitution in the allylic position with a shift of the double bond. Free-radical initiators and inhibitors had no effect on the rate or course of the reaction with these conjugated olefins; however, the reactions of azoformate ester with cyclopentene and cyclohexene were initiated by peroxide and retarded by radical inhibitors. The authors concluded that aromatically conjugated olefins react by a multicenter process involving a cyclic electron shift while nonconjugated olefins react by a free-radical chain process.

Levina, *et al.*,[4] reported that 1,1-disubstituted 1,3-dienes, whose steric hindrance precluded the usual Diels–Alder reaction, also underwent allylic substitution. However, they did not locate the positions of the double bond in the products and assumed that it occupied the same position as in the parent diene.

Cinnamon and Weiss[5] found that the reaction of cycloheptatriene with ethyl azodicarboxylate gave the diethyl ester of cycloheptatrienylbicarbamic acid instead of the customary Diels–Alder adduct which is roduced by reaction with other dienophiles such as aleic anhydride. They suggested that the driving rce for this reaction was the stability of the tropylium radical or tropylium ion which could be formed through hydrogen abstraction or hydride ion abstraction, respectively, followed by collapse to the allylic-substituted cycloheptatriene.

Franzus and Surridge[6a] demonstrated that 1,3- and 1,4-cyclohexadiene, which were neither sterically hindered nor capable of producing an unusually stable species, underwent substitution at the allylic position with a corresponding shift of double bond instead of the anticipated Diels–Alder reaction which is observed with cyclopentadiene. They also demonstrated the insensitivity of this reaction to radical initiators and inhibitors. Gillis and Beck[6b] found that the reaction of sterically hindered dienes such as 2,5-dimethyl-2,4-hexadiene, which was studied previously by Russian

(1) O. Diels and K. Alder, *Ann.*, **450**, 237 (1927).
(2) K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943).
(3) R. Huisgen and H. Pohl, *ibid.*, **93**, 527 (1960).
(4) R. Y. Levina, U. S. Shabarov, and M. G. Kuzmin, *Dokl. Akad. Nauk SSSR*, **131**, 1080 (1960).
(5) J. M. Cinnamon and K. Weiss, *J. Org. Chem.*, **26**, 2644 (1961).
(6) (a) B. Franzus and J. H. Surridge, *ibid.*, **27**, 1951 (1962); (b) B. T. Gillis and P. E. Beck, *ibid.*, **27**, 1947 (1962).

TABLE I

ADDUCTS FROM THE REACTION OF ETHYL AZODICARBOXYLATE AND BUTENES (80°)[a]

	Monoadduct[b]							Diadduct[c]						
			Analysis,[e] %							Analysis,[f] %				Total yield[d] of mono- and
Olefin	Product	Yield, %[d]	C	H	N	B.p. °C., (mm.)	$n^{20}D$	Product	Yield (%)[d]	C	H	N	Mol. wt.	diadduct (%)
1-Butene	1	63.5	51.93	7.75	12.58	120 (0.025)	1.4590	2	25.0	47.43	7.10	13.92	398	88.5
cis-2-Butene	3	77.8	51.92	7.93	12.38	110–115 (0.025)	1.4565	4	15.6	47.35	6.88	13.97	403	93.4
trans-2-Butene	3	95.0	52.26	8.18	12.54	110–115 (0.025)	1.4562	...	...	...	...	...	...	95.0
Isobutylene	5	77.8	52.08	7.86	12.52	110–115 (0.025)	1.4581	6 and 7	11.2	47.66	6.78	13.28	376	89.0

[a] 100 mole % excess of olefin, reacted until azo ester was consumed. [b] 1:1 azo ester–olefin adduct. [c] 2:1 azo ester–olefin adduct. [d] Based on azo ester. [e] Calcd. for $C_{10}H_{18}O_4N_2$: C, 52.16; H, 7.88; N, 12.17. [f] Calcd. for $C_{16}H_{28}O_8N_4$: C, 47.52; H, 6.98; N, 13.86; mol. wt., 404.

TABLE II

MONOADDUCTS FROM THE REACTION OF ETHYL AZODICARBOXYLATE WITH PENTENES (80°)[a]

	Monoadduct							Hydrogenated monoadduct				
			Analysis[f]						Analysis,[g] %			
Olefin	Products	Yield, %[b]	C	H	N	B.p. °C., (mm.)	$n^{20}D$	Products	C	H	N	$n^{20}D$
1-Pentene	8	78.0	53.53	8.18	11.43	118 (0.025)	1.4590	...	...	...	...	...
2-Pentene[e]	9 and 10	92.2	53.78	8.10	11.47	122 (0.05)	1.4590	11 and 12	53.66	8.97	11.71	1.4477
trans-2-Pentene	9 and 10	90.2	53.99	8.11	11.48	110 (0.025)	1.4587	...	...	...	...	...
cis-2-Pentene	9 and 10	76.5	53.98	7.98	11.63	107 (0.025)	1.4620	11 and 12	52.96	9.02	11.16	1.4498
2-Methyl-2-butene	13	85.8	54.43	8.02	11.81	107 (0.025)	1.4608	15	53.58	8.89	11.56	1.4490
2-Methyl-1-butene	16 and 17	84.3	54.35	8.23	11.46	120–130 (0.05)	1.4604	18	53.42	8.91	11.50	1.4465
3-Methyl-1-butene	20[c]	*d*	...	...	...	...	...	...	...	...	...	...

[a] 100 mole % excess of olefin, reacted until azo ester was consumed. [b] Based on azo ester. [c] 90% yield of diadduct (2 moles of azo ester to 1 mole of olefin) isolated from the reaction of a 2:1 mole ratio of olefin to azo ester. *Anal.* Calcd. for $C_{17}H_{30}N_4O_8$: C, 48.79; H, 7.23; N, 13.37; mol. wt., 418. Found: C, 48.83; H, 7.14; N, 13.29; mol. wt., 430. [d] Monoadduct (19) isolated from 20:1 olefin–azo ester reaction mixture. *Anal.* Found: C, 54.07; H, 8.19; N, 11.69. [e] Mixture, 58% *cis*- and 42% *trans*-2-pentene (99% pure). [f] Calcd. for $C_{11}H_{20}N_2O_4$: C, 54.08; H, 8.25; N, 11.47. [g] Calcd. for $C_{11}H_{22}N_2O_4$: C, 53.64; H, 9.00; N, 11.37.

workers,[4] gave 83% of the 3-substituted product with a shifted double bond. They attributed this product to a cyclic process similar to that proposed by Huisgen.[3] The simultaneous formation of the 1-substituted diene without any shift of the double bond (15%) was attributed to a competing free-radical process.

They also demonstrated that 1,3-cyclohexadiene gave allylicly substituted 1,4-cyclohexadiene as the principal product of the reaction with ethyl azodicarboxylate, and pointed out that retention of conjugation was not a requisite for adduct formation.

Results

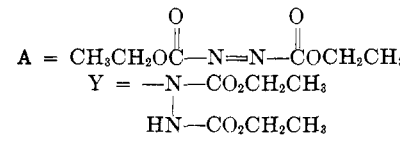
Effect of Structure on Products —It was considered that the reaction of azoformate ester with monoolefins warranted further investigation, and might provide an interesting system for expanding our knowledge of the properties of allylic free radicals whose reactions have been an object of interest for one of the authors.[7]

In the course of this investigation it soon became apparent that the reaction of ethyl azodicarboxylate with simple olefins (contrary to Huisgen's conclusions based on studies with cyclopentene and cyclohexene[3]) did not involve a free-radical path as the principal mode of reaction.

Reactions of ethyl azodicarboxylate with excess C_4 and C_5 monoolefins (2 moles/mole of azo ester) were carried out at 80° in sealed tubes in the presence of air. The 1:1 adducts isolated in excellent yields by distillation were water white, moderately viscous liquids. The nonvolatile distillation residues (viscous yellow oils) which proved to be diadducts containing 2 moles of ethyl azodicarboxylate per mole of olefin required no further purification. The yields, physical properties, and elemental analyses for these reactions are presented in Table I (C_4 olefins) and Table II (C_5 olefins).

The monoadducts were resolved analytically by capillary v.p.c. for the purpose of identification and quantitative analysis. These products were readily amenable to n.m.r. analysis which was used for the assignment of molecular structure and the semiquantitative analysis of mixtures, permitting direct comparison with v.p.c. determinations. N.m.r. analyses and parameters for monoadducts of ethyl azodicarboxylate with these monoolefins are presented in Tables III and IV, respectively.

The reaction of ethyl azodicarboxylate (**A**) with the four isomeric butenes (eq. 1-3) gave a total of four isomeric allylic substituted ethyl bicarbamates (monoadducts) which were resolved by capillary v.p.c.



(7) (a) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961); (b) A. A. Oswald, K. Griesbaum, W. Thaler, and B. E. Hudson, *ibid.*, **84**, 3897 (1962); (c) W. Thaler, A. A. Oswald, and B. E. Hudson, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, p. 65.

TABLE III

N.M.R. ANALYSIS OF MONOADDUCTS[a]

Olefin	Product(s)	—Methyl + methylene— Theory	Found	—Allyl[b]— Theory	Found	—$-OCH_2-$ + $-NCH_2-$[c] Theory	Found	Vinyl + $-NCH<$[c] Theory	Found	—>NH— Theory	Found
1-Butene	1	33.3	33.7	16.7	15.6	33.3	34.6	11.1	10.6	5.6	5.5
cis-2-Butene	3	50.0	49.3	...	...	22.2	22.8	22.2	22.6	5.6	5.3
trans-2-Butene	3	50.0	49.1	...	...	22.2	23.4	22.2	22.6	5.6	4.9
Isobutylene	5	33.3	32.4	16.7	16.7	33.3	33.7	11.1	11.6	5.6	5.6
1-Pentene	8	45.0	46.4	10.0	10.0	30.0	30.0	10.0	9.0	5.0	4.6
2-Pentene	9 and 10[d]	45.0	46.0	15.0	13.0	20.0	20.7	15.0	15.4	5.0	4.9
2-Methyl-2-butene	13	45.0	45.4	15.0	14.6	20.0	21.2	15.0	14.1	5.0	4.7
2-Methyl-1-butene	16 and 17[e]	37.5	37.1	20.0	21.7	30.0	29.2	7.5	7.4	5.0	4.6
3-Methyl-1-butene	19	30.0	32.8	30.0	29.4	30.0	29.0	5.0	4.2	5.0	4.6

[a] Comparison of area per cent with calculated values. [b] Allyl hydrogens except on carbons bearing a nitrogen. [c] Allyl hydrogens on carbons bearing a nitrogen. [d] Theory calculated for the major product (9). [e] Theory calculated for 1:1 mixture of products 16 and 17.

TABLE IV

N.M.R. PARAMETERS OF OLEFIN–ETHYL AZODICARBOXYLATE MONOADDUCTS

Olefin	Product(s)	Methyl[d]	—Methyl[e]—	Allyl-CH_3	Allyl-CH_2[f]	$-OCH_2-$	$-N-CH_2-$[g]	$>C=CH_2$	$>C=C<_{H}$ or $-CH=CH-$[h]	>NH[i]
1-Butene	1	...	1.2[a] (7)[b] t[c]	1.7 (5.5) d	...	4.1 (7) q	4.0 ± 0.2	...	5.5 ± 0.2	7.7–7.9 s
2-Butene	3	1.2 (7) d	1.2 (7) t	...	...	4.1 (7) q	...	...	...	7.4–7.7 s
Isobutylene	5	...	1.2 (7) t	1.6 s	...	3.9 (7) q	3.8 ± 0.2	4.5 s	...	7.2–7.5 s
1-Pentene	8	0.9 (7) t	1.2 (7) t	...	1.9[m]	4.0 (7) q	3.9 ± 0.2	...	5.5 ± 0.2	7.8 s
2-Pentene	9 and 10	1.1 (7) d	1.2 (7) t	1.6 (4) d	...	4.1 (7) q	...	...	5.5 ± 0.2	7.5 s
2-Methyl-2-butene	13	1.3 (7) d	1.2 (7) t	1.7 s	...	4.1 (7) q[j]	...	4.9 s	...	7.6 s
						4.2 (7) q				7.4 s
2-Methyl-1-butene	16 and 17	1.1 (7) t	1.2 (7) t	1.6 s[k]	2.1 (7) q[l]	4.1 (7) q[m]	4.0 ± 0.2	4.9 s	5.4 ± 0.2	7.7 s
				1.6 (7) d		4.2 (7) q				7.8 s
3-Methyl-1-butene	19	...	1.2 (7) t	1.5 s[n]	...	3.9 (7) q	3.8 ± 0.2	..	...	6.9 s
				1.6 s						

[a] Chemical shift in p.p.m. to nearest 0.1 p.p.m.; TMS = 0 (all spectra were run in CCl_4 solution). [b] Parenthesis indicate spin-spin splitting in c.p.s. [c] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [d] Methyl hydrogens from hydrocarbon moiety. [e] Methyl hydrogens from ethyl azodicarboxylate moiety. [f] Does not include allyl next to nitrogen. [g] Under part of OCH_2 quartet. [h] Complicated multiplet. [i] Chemical shift dependent on concentration probably due to hydrogen bonding. [j] Resolution between two $-OCH_2-$ of azo ester have been observed infrequently (see ref. 8). [k] Two allyl methyls of 16. [l] Allylmethylene from 17. [m] 1.5-c.p.s. resolution between OCH_2 of 16 and 17. [n] 3.5-c.p.s. resolution between two different allyl methyls of 19.

$$CH_3CH_2CH{=}CH_2 + A \longrightarrow CH_3CH{=}CHCH_2Y \xrightarrow{A} \text{diadduct} \quad (1)$$
(1 = $CH_3CH{=}CHCH_2Y$; 2 = diadduct)

$$\textit{cis}\text{- or }\textit{trans}\text{-}CH_3CH{=}CHCH_3 + A \longrightarrow CH_3\underset{\displaystyle Y\ 3}{CH}{=}CH_2 \xrightarrow{A} \text{diadduct} \quad (2)$$
(4 = diadduct)

$$CH_3C(CH_3){=}CH_2 + A \longrightarrow CH_2{=}C(CH_3)CH_2Y \quad (3)$$
(5 = $CH_2{=}C(CH_3)CH_2Y$)

$$5 + A \longrightarrow YCH_2C(CH_2)CH_2Y + YCH_2C(CH_3){=}CHY \quad (4)$$
(6 = $YCH_2C(CH_2)CH_2Y$; 7 = $YCH_2C(CH_3){=}CHY$)

1-Butene gave a monoadduct which could be partially resolved by capillary v.p.c. into two peaks (83 and 17 area %). Infrared absorption at 10.3 μ indicated that the principal product was a substituted *trans*-2-olefin. N.m.r. (Tables III and IV) substantiated the presence of an internal double bond and confirmed structure **1**. It was concluded that 1-butene gave 1-(ethyl bicarbamyl)-2-butene (**1**) (about 83% *trans* and 17% *cis*).

cis- and *trans*-2-butene both formed the same product which gave a single new v.p.c. peak. The infrared showed typical absorption at 10.1 and 10.9 μ attributable to a monosubstituted ethylene (α-olefin). The n.m.r. spectrum of the 2-butene monoadduct was qualitatively and quantitatively consistent with 3-(ethyl bicarbamyl)-1-butene (**3**).

The n.m.r. spectra of the monoadducts from 1- and 2-butenes are presented in Fig. 1 and 2, respectively. They illustrate many of the typical proton resonance absorptions which were encountered in this study, and demonstrate the utility of this method for assigning structures to the allylic bicarbamic acid diethyl esters. Compound **1** clearly shows allylic methyl (1.7 p.p.m.) which is absent in **3**, while the remaining allylic hydrogens which are on a carbon bonded to nitrogen absorb further downfield (4 p.p.m.) and do not interfere in this region. In addition to the triplet methyl (1.2 p.p.m.) and quartet OCH_2 (4.1 p.p.m.) which are always present from the ethyl alcohol moiety of the ester, compound **3** shows a doublet methyl (1.2 p.p.m.) consistent with a 3-substituted butene-1 structure.

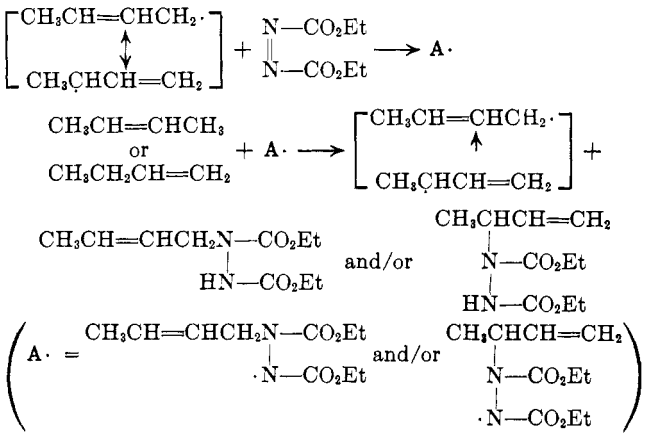
Substitution in isobutylene (eq. 4) also occurred at the allylic position to give product **5**; however, owing to the symmetry of the isobutylene molecule it was not possible to determine whether its reaction with **A** involved a shift of the double bond in a fashion analogous to the reactions with the linear C_4 olefins.

Yields of diadducts ranging from 0–25%, depending on the structure of C_4 olefin reacted, were isolated when a twofold excess of olefin was used (Table I). Larger quantities of excess olefin increased the yield of mono-

adduct at the expense of diadduct. Discussion of the effect of olefin structure on diadduct yield is best deferred to the section dealing with the relationship between olefin structure and reactivity.

The demonstration that 1- and 2-butenes gave completely different products, which contained double bonds adjacent to their original position in the parent olefin, is significant because it precludes the formation of these products by means of a free-radical chain mechanism.

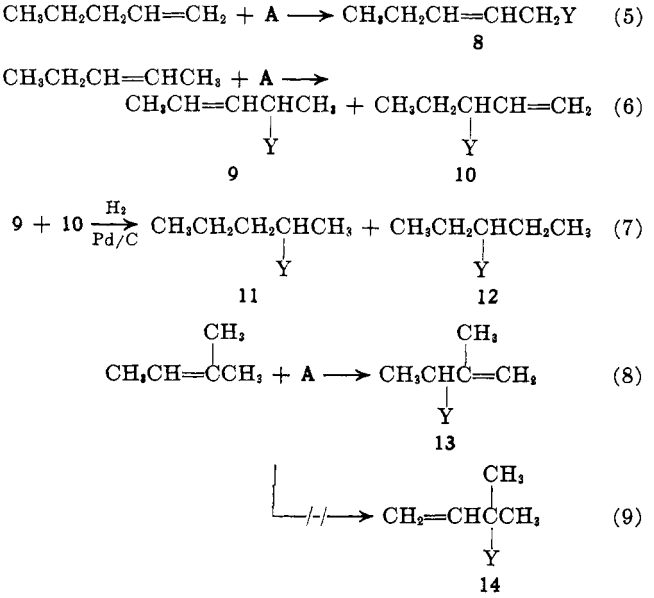
A radical chain mechanism would involve the formation of an intermediate allylic radical followed by addition of this radical across the azo double bond. The



resulting product(s) from the reactions of either 1- or 2-butene would of necessity be the same, since the same allylic radical intermediate(s) would be formed from both.

A situation in which stereochemically different intermediate allylic radicals are produced from *trans*- and *cis*-2-butene is somewhat more complicated. However, at least one intermediate allylic radical from 1-butene must still be the same as an intermediate radical derived from *cis*- or *trans*-2-butene.[7a] Therefore, the conclusion, that if a free-radical process were involved 1-butene would give the same product(s) as derived from *trans*- or *cis*-2-butene, remains unaltered.

The reaction of ethyl azodicarboxylate with a twofold excess of acyclic C_5 olefins similarly gave allylic bicaramates with a shifted double bond exclusively.



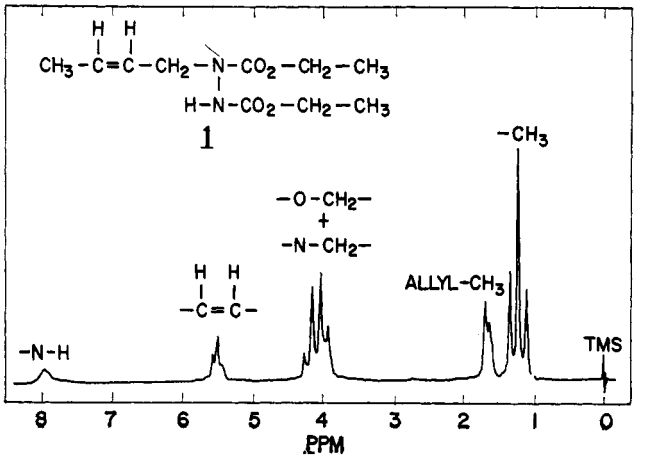


Fig. 1.—N.m.r. of adduct from 1-butene.

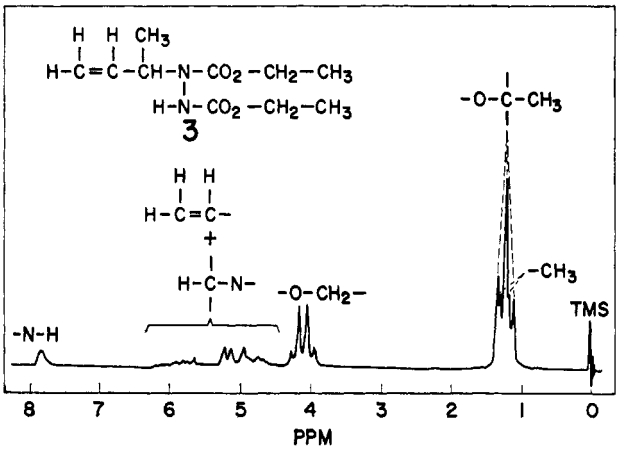
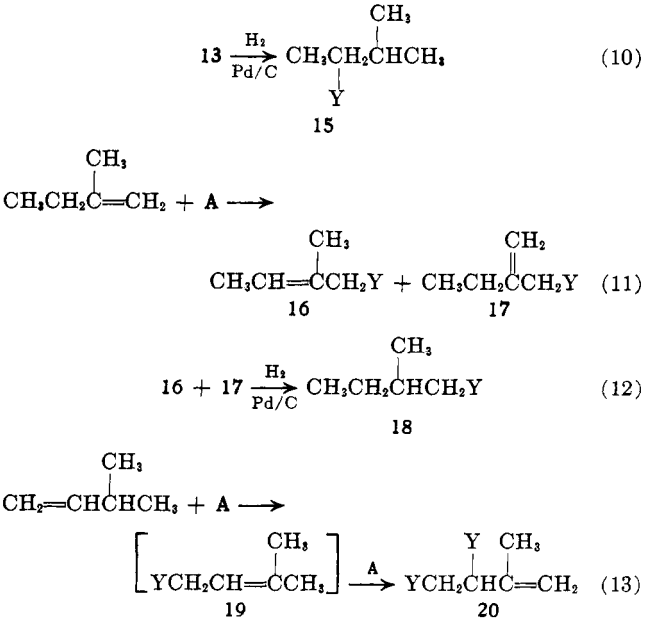


Fig. 2.—N.m.r. of adduct from 2-butene.

Pentene-1 (eq. 5) gave a single peak in the capillary v.p.c. and was shown by n.m.r. to be a 1-substituted 2-pentene. *cis*- and *trans*-pentene-2 (eq. 6) each gave the same three capillary v.p.c. peaks. Some difference in composition was observed for the product peaks from *trans*- and *cis*-olefin: *trans*-2-pentene showed P_1 30%, P_2 8%, P_3 62%; *cis*-2-pentene showed P_1 19%, P_2 16%, P_3 65%. N.m.r. indicated that these mixtures were



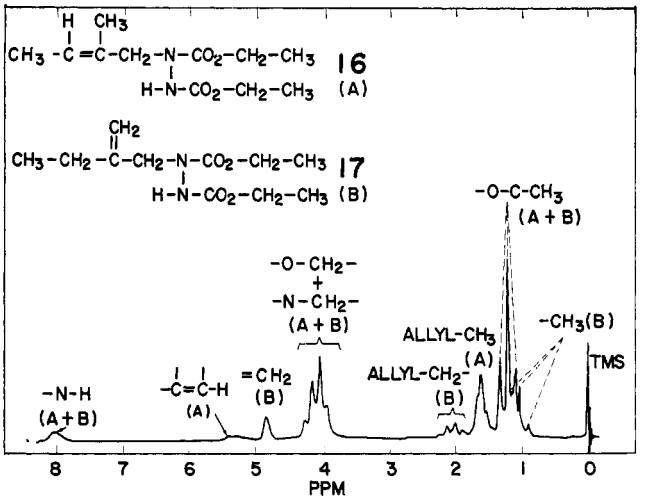


Fig. 3.—N.m.r. of adducts from 2-methyl-1-butene.

mostly 4-substituted 2-olefin with lesser quantities of 3-substituted 1-olefin. Hydrogenation (eq. 7) of a distilled fraction containing 30% P_1, 4% P_2, and 66% P_3 gave two new products, P_1' 30% and P_1' 70%. The results suggest that P_1 is 3-(ethyl bicarbamyl)-1-pentene (**10**) while P_2 and P_3 are *cis*- and *trans*-4-(ethyl bicarbamyl)-2-pentene (**9**). Their infrared spectra support these assignments.

2-Methyl-2-butene upon reaction (eq. 8) gave a single product (capillary v.p.c.). N.m.r. evidence also supported the formation of a single product of structure **13** indicating that the reaction of this branched chain olefin similarly involved a shift of the double bond. No evidence could be found for the presence of any **14** which would require shifting the double bond in the opposite direction (eq. 9) to give the less stable of the two possible olefinic products. Hydrogenation of the product from reaction 8 gave only one product (**15**).

2-Methyl-1-butene was examined to discern any trend toward the formation of the thermodynamically more stable product (olefin with greatest number of alkyl substituents). To the contrary, n.m.r. showed that equal quantities of **16** and **17** were produced (Fig. 3) without regard for the stability of the double bond in the product. Capillary v.p.c. showed three peaks, P_1 48%, P_2 17%, and P_3 35%, which were consistent with a mixture of 48% **17** and 52% *cis* and *trans* **16**. Proof that **16** and **17** differed only by the position of the double bond was obtained when it was shown that all three products could be hydrogenated to a single product (**18**), whose v.p.c. retention time was quite different from isomeric **15**.

The reaction of 3-methyl-1-butene with ethyl azodicarboxylate (eq. 13) under the same conditions (twofold excess of olefin) gave only a diadduct consisting of 2 moles of ethyl azodicarboxylate to 1 of olefin. N.m.r. was consistent with structure **20**. It was possible to isolate the monoadduct **19** when a large excess (twentyfold) of olefin was used.

The observation that the 3-methyl-1-butene reacted more slowly than the olefinic monoadduct (**19**) gave qualitative evidence that 3-methyl-1-butene is a comparatively unreactive olefin, despite the fact that of all the systems investigated this product contained the most stable double bond relative to reactant. The thermodynamic stability of the products does not, therefore, appear to be an important factor directing the course of this reaction.

V.p.c. examination of the recovered excess olefin after each reaction demonstrated that no isomerization of olefin occurred under the conditions of these reactions.

In order to obtain information regarding the effect of free-radical initiators and inhibitors on the structure and distribution of products from the reaction of ethyl azodicarboxylate with C_4 and C_5 olefins, the reactions were run in the presence of benzoyl peroxide, *t*-butylcatechol, and 2,2-diphenyl-1-picrylhydrazyl. The reactions were run in degassed sealed tubes with a tenfold excess of olefin over azo ester (to avoid diadduct formation) together with each of the above modifiers at 4% of the azo ester concentration.

The free-radical inhibitors (*t*-butylcatechol and 2,2-diphenyl-1-picrylhydrazyl) were found to have no effect on the products of these reactions. The same allylic ethyl bicarbamates with their double bond shifted to the adjacent position were produced as in the previous experiments. In the presence of free radicals, generated from the decomposition of benzoyl peroxide, the principal products (>85%) remained the same as in the noncatalyzed and inhibited reactions. In addition to the customary (thermal) products, small quantities (0–15%) of products attributable to a free-radical chain process were identified. This can be exemplified by the reaction of *trans*-2-butene which customarily gave 3-(ethyl bicarbamyl)-1-butene (**3**) as the sole product. In the presence of free-radical initiator, 13% 1-(ethyl bicarbamyl)-2-butene (**1**, usual product from 1-butene) was produced along with 87% of **3**. Production of **1** from *trans*-2-butene is ascribed to an allylic radical precursor ($CH_3CH{=}CHCH_2 \cdot \leftrightarrow CH_3\dot{C}HCH{=}CH_2$) which adds across the nitrogen–nitrogen double bond to give a bicarbamyl radical. The bicarbamyl radical then abstracts a hydrogen atom from the olefin giving allylic bicarbamate products and regenerating the allylic radical intermediate.

It is significant that the relative amounts of the usual products formed under nonradical conditions, in those reactions that customarily gave more than one product, remained essentially unchanged when the reaction was run under free-radical conditions. This suggests that only a very small amount of the products which can be produced thermally are also produced by a simultaneous free-radical process. Table V gives the yield of additional products formed under radical conditions which were not produced under the usual thermal conditions. The "new" products were readily identified since all were obtainable from the nonradical (thermal) reaction with a different isomeric olefin.

TABLE V

ADDITIONAL PRODUCTS FOUND ONLY IN THE PRESENCE OF BENZOYL PEROXIDE INITIATION

Reactant	Additional Product	Yield, %
2-Butene	1	12–15
Isobutylene	...	...
Pentene-1	10	13
Pentene-2	...	...
2-Methyl-1-butene	13	6
2-Methyl-2-butene	...	...

Since it could be demonstrated that free-radical initiator caused no isomerization of olefin, it would appear safe to conclude that in the presence of free-radical initiator these small quantities of new products were formed by means of a competing free-radical process.

The failure of free-radical inhibitors to alter the usual thermal reaction, coupled with the observation that this thermal process always proceeds with a shifting of double bond and is relatively unaffected by radical initiators, provides compelling evidence for the nonradical nature of the reaction of azodiformic acid ester with *acyclic monolefins*.[8]

Structure and Reactivity in Azoformate Ester Reactions.—The effect of olefin structure on reactivity toward ethyl azodicarboxylate was examined using competitive kinetic techniques. Relative reactivities were determined by following both the rates of disappearance of olefinic reactants and the rates of appearance of products, in different experiments, using vapor phase chromatographic analysis. The relative reactivity for two different olefins, determined from the disappearance of olefinic reactants, was calculated using the expression

$$k_A/k_B = \log \frac{(A_I)}{(A_F)} \Big/ \log \frac{(B_I)}{(B_F)}$$

where k_A/k_B is the relative rate constant for reaction with olefin A and olefin B, while $(A_I)/(A_F)$ and $(B_I)/(B_F)$ are the ratios of the initial to final olefin concentrations for olefins A and B, respectively. The initial/final olefin concentrations were calculated from the ratios of each of the olefins to an inert internal standard (such as *n*-pentane) before and after reaction. Relative reactivities for pairs of olefins, determined by following product formation, were calculated using the expression

$$k_A/k_B = \frac{(A')}{(B')} \Big/ \frac{(B)}{(A)}$$

where (A')/(B') is the molar ratio of the products after reaction and (B)/(A) is the ratio of olefinic reactants (which is essentially constant at low conversions) before reaction. Relative reactivity experiments requiring calculations based on the consumption of olefin were carried to about 50% conversion of olefinic reactants, whereas experiments using the formation of products were carried to about 5% conversion.

Results from both techniques were in fairly good agreement and gave the same order of olefin reactivities as shown in Table VI. The relative reactivities determined by following product formation gave very reproducible self-consistent results while the determination using olefin disappearance, which required cumbersome mechanical techniques, were less precise. Therefore, the data presented in Table VI were calculated from the relative rates of product formation from pairs of reacting olefins.

The absolute rate constant[9] of 1.64×10^{-4} (8 °) for the reaction of ethyl azodicarboxylate with 1,4-cyclohexadiene can, therefore, be utilized to calculate absolute rate constants from these relative reactivity data.

The greater tendency of some olefins towards diadduct formation (Table I) is in agreement with this relative reactivity data. Thus *trans*-2-butene, which forms a less reactive α-type olefinic product, gave essentially no diadduct, while isobutylene which gives the same type of double bond in the product as in the parent olefin exhibits a tendency towards diadduct formation. *cis*-2-Butene and 1-butene, whose adducts possess more reactive double bond types than the parent olefin, like isobutylene, show an increased tendency towards diadduct formation. In the sluggish 3-methyl-1-butene system, the reactivity of the initial product is so large, relative to the parent olefin, that under these same conditions (2:1 olefin-azo ester) it is almost entirely converted to diadduct.

TABLE VI

RELATIVE REACTIVITIES OF OLEFINS WITH ETHYL AZODICARBOXYLATE (80°)

C_4 Olefins (Relative to *cis*-2-Butene)	
Isobutylene	17.2
trans-2-Butene	3.73
1-Butene	2.57
cis-2-Butene	1.00
C_5 Olefins (Relative to 1-Pentene)[a,b]	
2-Methyl-2-butene	4.33
2-Methyl-1-butene	3.64
trans-2-Pentene	2.13
1-Pentene	1.00
3-Methyl-1-butene	Slow

[a] *cis*-2-Pentene reacted more slowly than 1-pentene but the very reactive 2-methyl-2-butene impurity in the 95% pure *cis*-2-pentene interfered with an accurate determination. [b] 1,4-Cyclohexadiene had an over-all reactivity of 14.7 ± 1.17 relative to pentene-1.

The amount of diadduct formation is, therefore, not only dependent on the ratio of hydrocarbon (olefin) to azoformate ester but also upon the relative reactivity of the olefinic bond types of the hydrocarbon and the monoadduct.

The reaction of ethyl azodicarboxylate with cyclopentene gave the expected 2-(ethyl bicarbamyl)-1-cyclopentene as reported by Huisgen and Pohl.[3] When cyclopentene was reacted competitively with some of the aforementioned acyclic olefins, the relative reactivities showed poor reproducibility. Since all of the competitions between acyclic olefins afforded results with excellent precision, a comparison of the effects of free-radical initiator on competitions between two acyclic olefins with the effects of initiator on competitions between cyclic and acyclic olefins was made.

The data in Table VII reveal that the rates of reaction of the acyclic monoolefins were, as expected, not affected by free-radical initiator. On the other hand, the rate of reaction of cyclopentene was markedly increased by conditions favoring free-radical reaction. The poor precision observed between unmodified competitions of pentene-1 with cyclopentene can be ascribed to varying quantities of peroxidic impurity which could have been present.

The rather surprising conclusion which can be drawn from these results is that cyclopentene, unlike the acyclic olefins examined, reacts with azoformate ester preferentially by a free-radical path. This conclusion is in agreement with the observation of Huisgen and Pohl that cyclopentene and cyclohexene reacted with ethyl azodicarboxylate in a reaction that was enhanced by initiators and retarded by inhibitors of free-radical

(8) After the present work had been concluded, Polish workers reported the results of ozonolysis experiments which confirm the shifting of the double bond position: O. Achmatowicz and O. Achmatowicz, Jr., *Roczniki Chem.* **37**, 317 (1963).

(9) B. Franzus, *J. Org. Chem.*, **28**, 2954 (1963).

TABLE VII

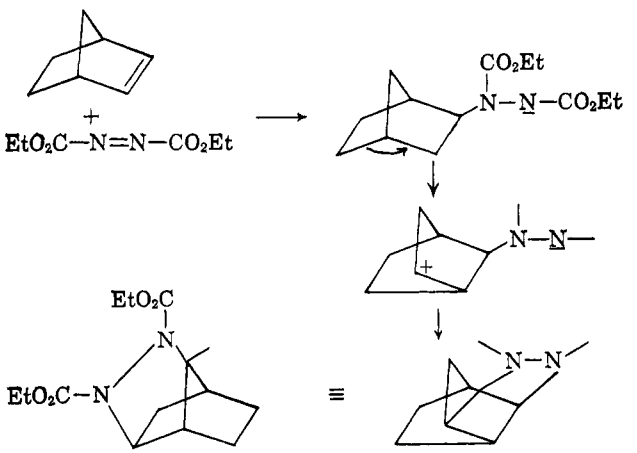
A COMPARISON OF THE EFFECTS OF FREE-RADICAL INITIATORS ON THE RELATIVE REACTIVITIES OF CYCLIC AND ACYCLIC OLEFINS TOWARD ETHYL AZODICARBOXYLATE (80°)

Olefin A / Olefin B	k_A/k_B: Free-radical[a] inhibitor	Nothing added	Free-radical[b] initiator
Pentene-1 / Cyclopentene	3.70 ± 0.05	1.70 (1.18)[c]	0.300 ± 0.006
Pentene-2 / Pentene-1		2.13 ± 0.02	2.11 ± 0.01

[a] 2,2-Diphenyl-1-picrylhydrazyl and *t*-butylcatechol were each used in duplicate runs. [b] Benzoyl peroxide. [c] Poor reproducibility presumably due to varying traces of hydrocarbon peroxide.

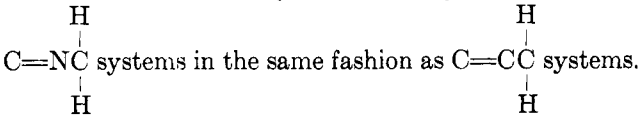
reactions.[3] It is now apparent, however, that their conclusion that nonconjugated monoolefins react by a free-radical mechanism resulted from generalization of the findings of what appears, in light of the present investigation, to be a rather special case.

The reaction of ethyl azodicarboxylate with norbornylene (95°), which cannot proceed with a shift of the double bond (Bredt's rule), gave a monoadduct whose n.m.r. is consistent with a tricyclic compound produced by the following sequence.



It would appear that in the absence of easily abstractable allylic hydrogens as in the case of norbornylene and norbornadiene a "free" carbonium ion is formed thereby permitting rearrangements of carbon skeletons.[10]

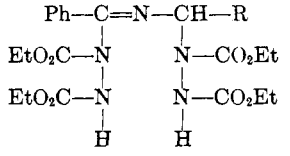
Some exploratory experiments with azomethine systems indicated that ethyl azodicarboxylate reacts with



systems in the same fashion as

systems.

When ethyl azodicarboxylate reacted with the condensation product from benzaldehyde and an aliphatic amine, a diadduct of the structure (**21**) was formed. This structure was confirmed by n.m.r. and ultraviolet



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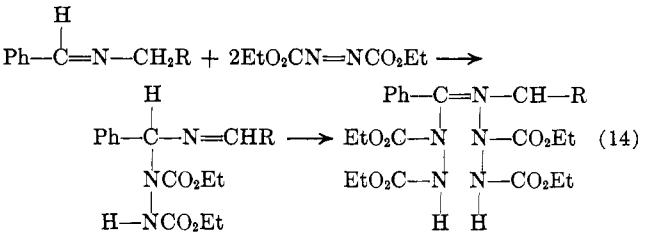
(10) S. J. Cristol, E. L. Allred, and D. L. Wetzel, *J. Org. Chem.*, **27**, 4058 (1962).



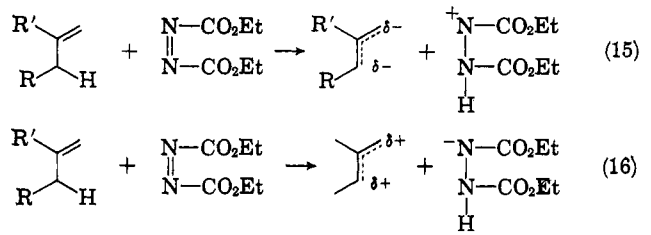
analysis. The ultraviolet showed the same absorption wave length and an almost identical molar extinction coefficient for both starting imine and diadduct. The nonconjugated monoadduct first formed is in all probability more reactive toward azo ester adduct than the conjugated starting compound accounting for the sole formation of diadduct.

Some experiments with methyl and ethyl phenylazoformate (Ph—N=NCO$_2$R,R = Me or Et) indicated that these compounds gave 1:1 adducts with simple monoolefins, with somewhat greater difficulty then the azoformate diesters. Higher reaction temperatures were required and the reactions were not so selective and had poorer yields. These condensation products were also more difficult to purify.

Discussion

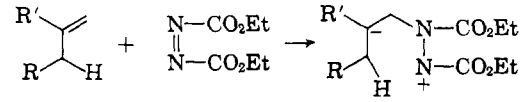
The evidence regarding product structure and the effects of initiators and inhibitors on the course and rates of the reaction of ethyl azodicarboxylate with acyclic monoolefins appears to preclude a free-radical chain mechanism. While it is not possible to describe accurately the transition state for this reaction without thoroughly investigating its kinetics, examination of the effect of olefin structure on reactivity (relative) and product structure has enabled us to make several generalizations: the relative thermodynamic stability of the olefinic product (number of alkyl substituents about the double bond) and the type of abstracted hydrogen (primary, secondary, tertiary) influences neither the reaction rate nor the structure of the product; the rate of reaction is increased by the presence of alkyl substituents on the vinyl carbon adjacent to the one which becomes bound to nitrogen; *trans* olefins are more reactive than *cis* olefins; the presence of several alkyl substituents on the allylic carbon greatly reduces the reactivity of the olefin; when more than one potential point of attack is available, attack occurs at the least hindered vinyl carbon.

Several heterolytic processes involving a sequence of two reactions can be written. The two steps involve hydrogen transfer and attack on vinyl carbon (double bond). The former may take the form of either proton transfer (eq. 15) or hydride transfer (eq. 16), while the latter may involve either nucleophilic (eq. 17) or electrophilic (eq. 18) attack upon the double bond as the rate-determining step.

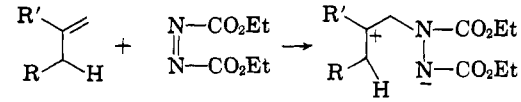


Each of these hydrogen-transfer reactions would be expected to give two different allylic bicarbamate products, since the intermediate allylic carbonium ions or carbanions have a delocalized charge and, therefore, two reactive sites. Furthermore, neither of these two reactions explains the observed increase in rate when an alkyl group (R′) is introduced onto a vinyl carbon.

Nucleophilic attack by ethyl azodicarboxylate upon the olefinic bond (eq. 17) would be expected to give the opposite of the observed increase in rate when alkyl substituents (R′) are placed on the vinyl carbon. Furthermore, nucleophilic attack by azoformate ester is out of character for such an excellent dienophile with its electron-withdrawing substituents.



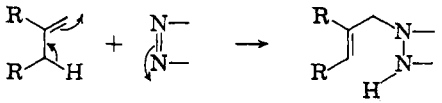
(17)



(18)

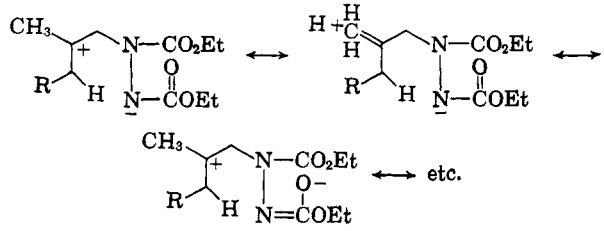
An electrophilic attack upon an olefin (eq. 18) is consistent with the observations which have been made, for example, rate enhancement by electron-donating alkyl substituents. However, electrophilic substitution like the other stepwise processes, which involve a large degree of charge formation is not consistent with the failure to incorporate deuterium in the product when the reaction is run in deuterio alcohol, as well as the comparatively small increase in rate (twentyfold) when the reaction is run in solvents of widely different polarity (cyclohexane and ethanol).[9]

It, therefore, appears that the process is a concerted one, involving a cyclic transition state similar to that first described by Arnold[11] to account for the condensation reactions of maleic anhydride with olefins, and by Huisgen[3] to explain the reaction of azoformates with aromatic olefins.



(19)

The large negative entropy of activation (about −40 e.u.) observed by Franzus[9] with azo ester–cyclic diene reactions is strongly indicative of such a concerted process (eq. 19) involving a rather rigid transition state. This process should not be interpreted as being completely synchronous; indeed, some charge development in the transition state would be anticipated. Contributing resonance structures of the type that follows



(11) R. T. Arnold and J. F. Dowdall, *J. Am. Chem. Soc.*, **70**, 2590 (1948).

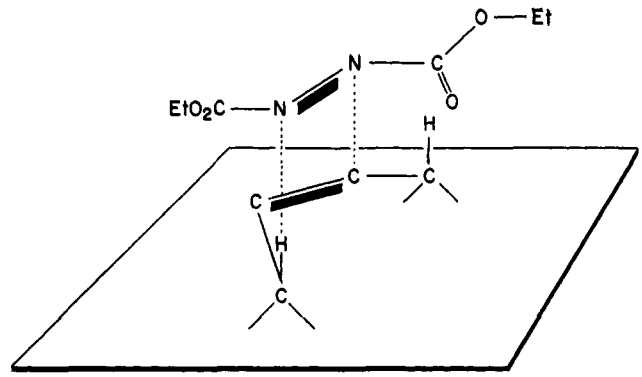
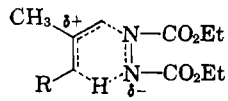


Fig. 4.—Steric interaction of carbethoxyl group with methyl group of *cis* olefin.

can be drawn for the transition state (22), which explain among other things the enhancement of reactivity by alkyl group substituents on the vinyl carbon *via* inductive and hyperconjugative stabilization of the incipient positive charge.[12]



22

The involvement of the depicted cyclic transition state (22) with its stringent steric requirements can account for such phenomena as the exclusive attack at the least hindered vinyl carbon of 2-methyl-2-butene, the greater reactivity of *trans* olefins compared with *cis* olefins, as well as the low reactivity of the 3-methyl-1-butene system.

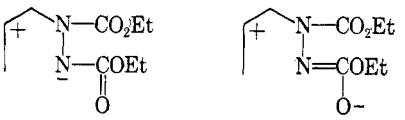
In Fig. 4 it can be seen that the steric interaction of the carbethoxyl group of ethyl azodicarboxylate (which is assumed to have the lower energy *trans* configuration) with an alkyl substituent, is a rate-diminishing feature in the reaction of *cis* olefins which does not come into play with *trans* olefins.

Similarly, examination of models suggests that the low reactivity of 3-methyl-1-butene can be attributed to the strained conformation, having a tertiary hydrogen coplaner with the p-orbitals of the olefinic bond, required for reaction. The assumption of such a conformation would involve considerable steric interaction between the methyl group and terminal vinyl hydrogens of 3-methyl-1-butene; it is not very favorable.

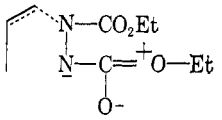
One might predict from the mechanistic picture proposed here, that the ability of such an electrophilic reagent to stabilize the negative charge developed in the transition state would be an important factor in determining its ability to participate in additive substitutions involving the addition–abstraction (cyclic) mechanism depicted (eq. 19). The greater stability of a negative charge on nitrogen compared with carbon may be one of the important features which makes azo ester–olefin reactions considerably more facile than the analogous reactions with unsaturated carbon compounds such as fumarates and maleates (as well as maleic anhydride).

(12) Similar transition state structures involving unpaired electrons instead of charge separation can also be drawn. Some uncertainty is involved in distinguishing between these two transition states; however, the twentyfold increase in rate with increased solvent polarity would appear to make the diradical type of transition state less likely.

The correctness of our emphasis on the importance of change delocalization in lowering the energy of the transition state and therefore the importance of the contribution of resonance structures, such as is shown,



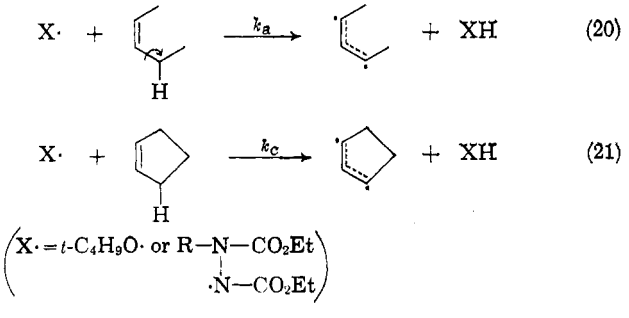
should be capable of verification. The presence of an oxygen adjacent to the carbonyl group enhances cross-conjugation structures, such as the one that follows,



which decrease the ability of the carbonyl group to delocalize the negative charge on nitrogen in the transition state relative to the ground state, thereby increasing the energy between the ground and the transition state. If this mechanistic picture is correct, replacement of the oxygen with elements less capable of interaction with the carbonyl group should enhance delocalization of the negative charge on nitrogen and should result in analogous azo compounds with enhanced reactivity. A comparison of the kinetics of the reaction of olefins with such modified azoformate esters is currently under investigation.

One is tempted to predict that a variety of unsaturated electrophilic reagents which possess the ability to delocalize effectively this incipient negative charge will prove effective in participating in additive-substitution reactions by means of such an addition–abstraction mechanism.

The preference for reaction of ethyl azodicarboxylate with cyclic olefins *via* a free-radical chain mechanism can be rationalized by comparison with data on the relative rates of allylic hydrogen atom abstraction from cyclic and acyclic olefins by *t*-butoxy radical. The preferential abstraction by *t*-butoxy radicals of allylic hydrogens from cyclohexene and cyclopentene compared with secondary and even tertiary allylic hydrogens from acyclic olefins has been attributed to the loss of a rotational degree of freedom from the acyclic system only.[7a]



Proceeding from the ground state to the transition state for the formation of an acyclic allylic radical such as 2-pentenyl free radical, which is capable of maintaining its geometry, involves the loss of a rotation about the C-3–C-4 bond. The cyclic olefin does not encounter this unfavorable entropy change between ground and transition state. Thus, the cyclic olefin has a lower free energy of activation for the abstraction of a hydrogen atom.

Similar considerations are applicable for the abstraction of allylic hydrogen atoms by RN(COOEt)NCOOEt radical. Evidently, the decreased reactivity of the *cis*-olefinic systems toward a concerted addition–abstraction type process, coupled with a more favorable entropy of activation for the formation of an allylic radical, is sufficient to make cyclic olefins such as cyclopentene react with azoformate ester preferentially by a free-radical path.

Experimental

All the hydrocarbons used in this study, with the exception of pentene-2, were Phillips Pure Grade (99% minimum purity). *trans*-2-Pentene of high purity was obtained from Farchan Research Laboratories. Phillips *cis*-2-pentene practical grade (95%) and pure grade pentene-2 (58% *cis*, 42% *trans*) were also used. Ethyl azodicarboxylate (diethyl azodicarboxylate) was purchased from Aldrich Chemical Co. and distilled before use. N.m.r. spectra were obtained using a Varian A-60 spectrometer. V.p.c. analyses were performed on a Perkin-Elmer 226 vapor fractometer using a 200-ft. capillary column coated with Surfonic TD 300 (a tridecyl alcohol–ethylene oxide adduct) operated at 160°. Several of the olefin competitions could be followed using packed column v.p.c. (1.5-m. ethylene glycol succinate on Chromsorb W, 170°); however, capillary v.p.c. was used for all purity evaluations and for a large majority of the relative rate measurements.

Noncatalyzed Reactions.—Ethyl azodicarboxylate, 34.8 g. (0.2 mole), together with 0.4 mole of olefin was placed in a glass-lined bomb (C_4 olefin) or sealed ample (C_5 olefin) and heated at 80° until the color of azo ester was essentially absent. The reaction mixtures were analyzed by v.p.c. both prior and subsequent to distillation. The monoadducts were isolated by distillation, whereas the distillation residues proved to be diadducts of high purity (Tables I and II).

Reactions in the Presence of "Modifiers".—Each of the C_4 and C_5 olefins mentioned in this study were reacted with ethyl azodicarboxylate at 80° in the presence of each of the three modifiers: benzoyl peroxide (free-radical initiator), *t*-butylcatechol, and 2,2-diphenyl-1-picrylhydrazyl (free-radical inhibitors).

Olefin (50 mmoles), 5 mmole of ethyl azodicarboxylate, and 0.2 mmole of modifier (about 4% based on azo ester) were placed in a Pyrex ampoule and degassed by alternately evacuating and pressuring with nitrogen. The tubes were then sealed and placed in a thermostated bath at 80° until azo ester had been consumed. The time necessary for complete reaction in the presence of 2,2-diphenyl-1-picrylhydrazyl was estimated from other runs (in the presence and absence of modifiers) in which color changes could be observed.

Competitions.—Approximately 50 mmoles of each of two olefins was accurately measured into a Pyrex ampoule, several microliters of the mixture were removed (for v.p.c. analysis to confirm relative concentration of the two olefins), and then approximately 5.0 mmoles of ethyl azodicarboxylate was added (20:1 olefin–azo ester). The tubes were degassed and sealed using liquid nitrogen coolant. After thawing, the contents were thoroughly mixed and placed in a constant temperature bath at 80° until azo ester was consumed. The tubes were cooled, cut open, and the ratio of the products formed determined by v.p.c. analysis. V.p.c. analyses were performed at least in triplicate for each run. Competitions with the same pair of olefins were run at least in duplicate.

Competitions which were run in the presence of initiator or inhibitor were carried out in the same manner except 5 mole % of modifier based on azo ester was added.

Reaction with Bicyclo[2.2.1]heptene-2 (Norbornylene).—Norbornylene, 12.06 g. (0.128 mole), together with 5.3 g. (0.03 mole) of ethyl azodicarboxylate was refluxed (92–95°) with 50 ml. of cyclohexane for 482 hr. after which time v.p.c. analysis indicated no further reaction was taking place. The solvent and some unreacted olefin were removed by distillation. Vapor phase chromatographic analysis (1 m. × 0.25 in. ethylene glycol succinate column at 170°, 200 cc./min. He flow) of this

TABLE VIII

N.M.R. ANALYSIS OF NORBORNYLENE ADDUCT

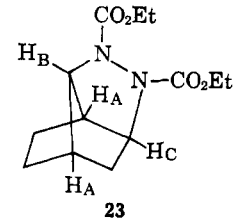
	Analysis, % Calcd.	Found	δ, p.p.m. from TMS
CH_3 + ring hydrogens	12	12	1.28 (center line)
H_A	2	2.3	2.45
H_B or H_C	1	0.9	3.66 or 4.35
OCH_2 + H_B or H_C	5	4.8	4.09, 4.13

crude product indicated four components. The major component was eluted first on an acid-washed alumina column with methylene chloride as eluent. This compound (90% pure) was rechromatographed in the same manner to 95% purity (v.p.c.) and showed no N–H absorption according to infrared analysis. Of the other three minor components, one corresponded to ethyl hydrazodicarboxylate and the other two were not identified.

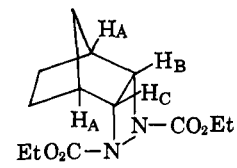
Anal. Calcd. for $C_{13}H_{20}N_2O_4$: C, 58.15; H, 7.51. Found: C, 58.32; H, 7.68.

N.m.r. was consistent with the structure **23** (see Table VIII). A cycloaddition product such as **24** would also be compatible with the observed n.m.r. if inversion of the carbethoxyl group were restricted. It is, however, likely that the inversion of these groups would be sufficiently free such that the bridgehead hydrogens would be equivalent and give a different n.m.r. spectrum from that observed.

Reaction with N-Benzylidenebutylamine.—N-Benzylidenebutylamine ($C_6H_5CH{=}NCH_2CH_2CH_2CH_3$) was prepared by azeotropic distillation of a benzene solution of *n*-butylamine and benzaldehyde (83.5% yield), b.p. 52–54° (0.2 mm.).



23



24

A sample of 16.1 g. of this imine (0.1 mole) and 4.33 g. (0.025 mole) of ethyl azodicarboxylate was placed in a 50-ml. bomb tube and heated for 45 hr. at 80°. The reaction mixture was then distilled at reduced pressure and 13.2 g. of unreacted imine recovered. The nonvolatile residue (6.2 g.) was a rather immobile liquid which was glassy when cold.

Anal. Calcd. for $C_{23}H_{35}O_8N_5$: C, 54.21; H, 6.92; N, 13.75; mol. wt., 509.6. Found: C, 53.90; H, 6.94; N, 13.86; mol. wt., 465. The analysis indicated the formation of a 2:1 azo ester–imine adduct in 97.7% yield. The n.m.r. of this product was consistent with structure **21**.

The ultraviolet spectrum of an acetonitrile solution showed a maximum at 244 mμ (ε 9410) as did the N-benzylidenebutylamine (ε 9075).

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The Reactions of Nitric Oxide with Tri- and Tetramethylethylene. The β-Nitroolefin and Nitrosite Rearrangements

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When the branched olefins trimethylethylene and tetramethylethylene were treated with nitric oxide at room temperature, reaction occurred smoothly to produce mixtures of nitroolefins (mainly) along with lesser quantities of nitrosites, dinitroalkanes, nitro alcohols, and cleavage products. The structures of most of the nitrated products were found to be analogous to those of the corresponding products derived from isobutylene or the unbranched olefins; *i.e.*, the nitro groups appeared at the less heavily substituted of the original olefinic carbons, and the other substituents or double bond termini appeared at the more heavily substituted position. In addition to these "normal" nitration products, "abnormal" allylic isomers of the β-nitroolefins appeared in considerable quantity, *e.g.*, 2-methyl-1-nitro-2-butene from trimethylethylene and 2,3-dimethyl-1-nitro-2-butene from tetramethylethylene. It was found that these arose from a remarkably facile, NO_2-catalyzed allylic rearrangement of the normal products, 2-methyl-3-nitro-1-butene and 2,3-dimethyl-3-nitro-1-butene, respectively. This rearrangement is believed to result from the addition of NO_2 to the β-nitroolefin to give a β,β′-dinitroalkyl radical which can then lose either β-nitro group to form either β-nitroolefin. It is suggested that similar eliminations of nitro groups from β-nitroalkyl radicals are also responsible for the thermal regeneration of olefins from certain nitrosites, the low kinetic chain lengths of nitroalkane chlorinations, and the very well-known NO_2-catalyzed *cis–trans* isomerization of olefins. It was long assumed that trimethylethylene nitrosite had an "abnormal" structure (secondary nitroso group, tertiary nitro) because upon treatment with alkalis or amines it yielded ketoximes, often with additional displacement of the nitro group by –OH, –NHR, etc. The present study confirmed the ketoxime formation, but showed that the original nitrosite actually had the "normal" structure (secondary nitro, tertiary nitroso) as required by the nitration mechanism. An intramolecular oxygen shift ("nitrosite rearrangement") is proposed in order to account for the ketoxime formation.

Most olefins react readily with nitric oxide containing catalytic traces of NO_2, thereby producing α- and β-nitroolefins, nitrosites, and a variety of other nitrated products. In the case of isobutylene, these products have been studied in detail and a mechanism proposed to account for the observed reaction behavior.[1] In this paper, we shall describe the products obtained from tri- and tetramethylethylene, and shall discuss two new rearrangements which were encountered during the course of these studies.

(1) J. F. Brown, Jr., *J. Am. Chem. Soc.*, **79**, 2480 (1957).

Experimental

Nitration of Tr methylethylene.—The olefin (385.5 g., 5.50 moles was charged into a 1-l. Parr reactor fitted with a stirrer, coo ing coils, and collection tank for the product gas s, and flushed with dry nitrogen. Nitric oxide (205.5 g., 6.85 mol s) under 50-p.s.i.g. pressure was added at a rate of 4.5 moles/hr. at 21°. The deep green liquid reaction product was subjected to a flash distillation in a falling film evaporator at 100° at 1 mm., and then further fractionated and analyzed by the general procedures[1] used for the isobutylene–nitric oxide reaction products. The indicated product composition is shown in Table I.

During the distillations, there was a considerable conversion of the nitrosite (VI) and presumably also of any N-(2-methyl-3-nitro-2-butyl)hydroxylamine present to regenerated trimethyl-