# Ene Reactions of Allenes. Part 3.[1] Reactions of Electron-deficient Azo-compounds with Acyclic Allenes and Alkenes

By **Chan Boo Lee** and **David R. Taylor**,* Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

2,4-Dimethylpenta-2,3-diene and 3-methylbuta-1,2-diene undergo rapid ene insertion reactions with diethyl azodiformate at 70—80 °C to give diethyl 1-isopropenyl-2-methylprop-1-enylbicarbamate and diethyl 2-methyl-1-methyleneallylbicarbamate at rates, relative to 2,3-dimethylbut-2-ene, of 4.7 and 0.6 respectively. 2,3-Dimethylbut-2-ene and 2,3-dimethylbut-1-ene react with diethyl azodiformate under these conditions to yield, respectively, diethyl 1,1,2-trimethylallylbicarbamate and a 70 : 30 mixture of diethyl 3-methyl-2-methylenebutylbicarbamate and diethyl 2,3-dimethylbut-2-enylbicarbamate, at rates, relative to hex-1-ene, of 3.2 and 1.2. The only ene adduct isolated from the hex-1-ene reaction was the E-isomer of diethyl hex-2-enylbicarbamate. 2,4-Dimethylpenta-2,3-diene reacts with 4-phenyl-1,2,4-triazoline-3,5-dione at −25 °C to give, via initial rearrangement to 2,4-dimethylpenta-1,3-diene, the Diels–Alder adduct 1,2,3,6-tetrahydro-3,3,5-trimethylpyridazine-1,2-N-phenyldicarboximide. 2,3-Dimethylbut-2-ene reacts with the triazolinedione at 0 °C to give a 76% yield of the expected ene adduct 1-(4-phenyl-1,1,2-trimethylallyl)-1,2,4-triazolidine-3,5-dione.

ALKYLALLENES are highly reactive substrates in Alder's ene reaction [2] by virtue of the energetically favourable bond reorganisation which such reactions entail [e.g., equation (i), X=Y = RC≡CR, RN=NR, or $R_2C=O$].
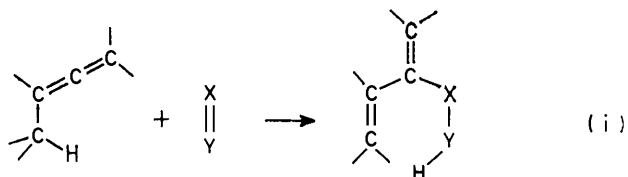
During an ongoing study of such reactions, we observed an interesting difference in behaviour between a tetra-alkylallene, $Me_2C\dot{:}C\dot{:}CMe_2$, and the unsymmetrical 1,1-dialkylallene, $Me_2C\dot{:}C\dot{:}CH_2$. The former, which offers two identical termini for ene reactions each with access to six hydrogen atoms, was expected to be the more reactive of the two towards enophiles, but only the less substituted allene gave ene adducts when treated with the powerful enophiles hexafluoroacetone [3] and 1,3-dichlorotetrafluoroacetone.[4] The 1 : 1 adducts isolated from the corresponding reactions of 2,4-dimethylpenta-2,3-diene were mainly (>90%) Diels–Alder cycloadducts (1), apparently formed via an initial isomerisation of the allene to 2,4-dimethylpenta-1,3-diene [equation (ii)].

At the time the difference in behaviour was attributed to the greater susceptibility of the more alkylated allene to prototropic rearrangement.[5] However, a report has appeared which suggests that steric hindrance may lead to unexpectedly low reactivity in the ene reactions of tetra-alkylethylenes,[6] so we have tested the alternative explanation that rearrangement predominates with the
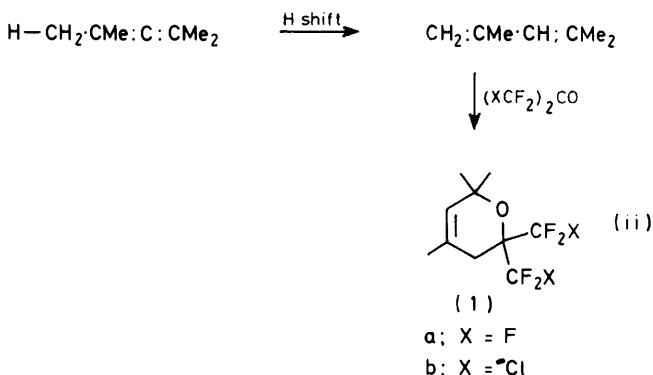
tetra-alkylallene because of steric inhibition of the ene reaction. As enophiles we chose the reactive azo-compounds diethyl azodiformate and 4-phenyl-1,2,4-triazoline-3,5-dione (2) (PTAD), partly because such

[1] Part 2, H.-A. Chia, B. E. Kirk, and D. R. Taylor, *J.C.S. Perkin I*, 1974, 1209.

[2] H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 556.

[3] D. R. Taylor and D. B. Wright, *J.C.S. Perkin I*, 1973, 956.

[4] R. J. J. Newman and D. R. Taylor, unpublished.

[5] T. L. Jacobs and P. Prempree, *J. Amer. Chem. Soc.*, 1967, **89**, 6177.

[6] G. T. Knight, M. J. R. Loadman, B. Saville, and J. Wildgoose, *J.C.S. Chem. Comm.*, 1974, 193.

compounds were used in earlier studies of relative reactivities of isomeric butenes, pentenes, and hexenes,[6,7] but also because only a single meagre report of such reactions of simple acyclic allenes had appeared previously,[8] in spite of the high probability that ene reactions would occur readily.

2,4-Dimethylpenta-2,3-diene–Diethyl Azodiformate Reaction.—The hoped-for ene reaction occurred with
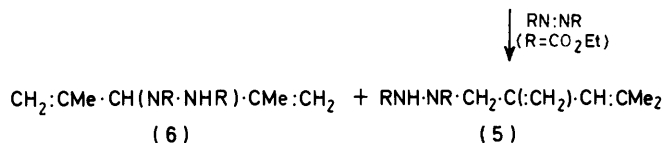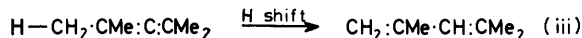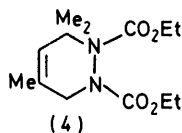

(2)
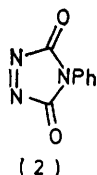
evolution of heat when diethyl azodiformate was mixed with either an excess of the allene or with a solution of an equimolar proportion of the allene. Diethyl 1-isopropenyl-2-methylprop-1-enylbicarbamate (3) was the sole product detected, and examination of the recovered excess of allene showed that no rearrangement had occurred.

The u.v. spectrum of (3) indicated weak conjugation

$$Me_2C:C:CMe \cdot CH_2-H \xrightarrow[(R=CO_2Et)]{RN:NR, 70\ ^\circ C} Me_2C:C(NR \cdot NHR) \cdot CMe:CH_2 \quad (94\%)$$

(3)
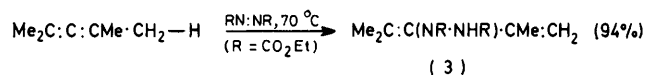
[$\lambda_{max.}$ (EtOH) 217 nm (ε 8 370)] and its i.r. spectrum suggested both $CH_2:CMe-$ ($\nu_{max.}$ 1 640 and 900 cm^{-1}) and $-NH \cdot CO-$ groupings ($\nu_{max.}$ 3 300 and 1 700 cm^{-1}). Besides showing that two different ethoxy-groups were present, the ^1H n.m.r. spectrum confirmed the NH (τ 2.6, shifting to 1.2 with added $CF_3 \cdot CO_2H$) and the $CH_2:CMe \cdot CX:CMe_2$

(4)

$$H-CH_2 \cdot CMe:C:CMe_2 \xrightarrow{\text{H shift}} CH_2:CMe \cdot CH:CMe_2 \quad \text{(iii)}$$

$$\downarrow \begin{array}{c} RN:NR \\ (R=CO_2Et) \end{array}$$

$$CH_2:CMe \cdot CH(NR \cdot NHR) \cdot CMe:CH_2 + RNH \cdot NR \cdot CH_2 \cdot C(:CH_2) \cdot CH:CMe_2$$
(6)   (5)

groupings. The spectroscopic data exclude a reaction pathway involving rearrangement followed by Diels–Alder cycloaddition to give (4), and also exclude rearrangement followed by an ene reaction [equation (iii)] of the isomeric penta-1,3-diene, previously reported to give a 3.5 : 1 mixture of (5) and (6) [liquids with $\lambda_{max.}$ (EtOH) 232 nm].[9]

Low pressure catalytic hydrogenation of (3) resulted in the uptake of only 1 mol. equiv. of hydrogen, giving

[7] W. A. Thaler and B. Franzus, *J. Org. Chem.*, 1964, **29**, 2226.
[8] See in ref. 2, ref. 51*d*.
[9] B. T. Gillis and P. E. Beck, *J. Org. Chem.*, 1963, **28**, 3177.

almost quantitatively a bicarbamate (7) the spectra of which show that there is no vinylic proton on the remaining carbon–carbon double bond ($\nu_{max.}$ 1 650 cm^{-1}). This bond is evidently too crowded to be reduced under such mild conditions. Further evidence of the steric hindrance within (7) is provided by the ^1H n.m.r. spectrum, in which the high-field six-proton portion of the isopropyl resonance appears as two overlapping doublets even at 50 °C. This signal collapses to two singlets when the

$$(3) \xrightarrow{H_2, 1\ atm, Pd-C} Me_2C:C(CHMe_aMe_b) \cdot N(CO_2Et) \cdot NH \cdot CO_2Et \quad (95\%)$$

(7)

CH resonance is irradiated. The methyl groups must be non-equivalent as a result of hindered rotation, a phenomenon known to be associated with bicarbamates[10] and also manifested by the 2,3-dimethylbut-2-ene adduct (see below).
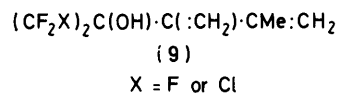
3-Methylbuta-1,2-diene–Diethyl Azodiformate Reaction. —A similarly ready reaction occurred when the dialkylallene and diethyl azodiformate were kept at 80 °C,

$$CH_2:C:CMe \cdot CH_2-H \xrightarrow[(R=CO_2Et)]{RN:NR, 80\ ^\circ C} CH_2:C(NR \cdot NHR) \cdot CMe:CH_2 \quad (71\%)$$

(8)
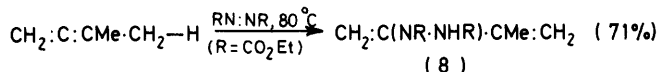
although the product (8), a high-boiling liquid which polymerises readily, was isolated in lower yield.

The spectroscopic data for (8) are similar to those of (3) except that a second $:CH_2$ group replaces the isopropylidene portion. The vinylic region of the ^1H n.m.r. spectrum shows a striking resemblance to those of the ene adducts (9) isolated from reactions between this allene and polyfluoro-ketones.[3,4]

Diethyl Azodiformate–Olefin Reactions.—Consideration of suitable olefins for use in relative rate studies with these two allenes led to the selection of 2,3-dimethylbut-2-ene, which also bears twelve allylic hydrogen atoms.

$$(CF_2X)_2C(OH) \cdot C(:CH_2) \cdot CMe:CH_2$$

(9)

X = F or Cl

Surprisingly, the reactions of this olefin with diethyl azodiformate and PTAD do not appear to have been reported previously, although the azodiformate reaction has been investigated elsewhere.[11] Since the dimethylbut-2-ene rearranges readily to the isomeric but-1-ene, we also studied the reaction of that olefin with diethyl azodiformate, and to assess their relative reactivities we compared both with hex-1-ene, a comparison which entailed the isolation and identification of the ene adduct of hex-1-ene.
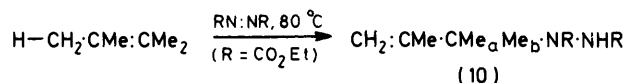
The reaction between the azodiformate and 2,3-dimethylbut-2-ene was essentially complete within 48 h at 80 °C. Distillation of the crude product yielded 92% of

[10] See for example A. H. Levin, J. Lipowitz, and T. Cohen, *Tetrahedron Letters*, 1965, 1241; E. Koerner von Gustorf, D. V. White, and J. Leitich, *ibid.*, 1969, 3109; for a review see Y. Shvo, ' The Chemistry of the Hydrazo, Azo, and Azoxy Groups,' ed. S. Patai, Interscience, New York, 1975, p. 1017.
[11] G. T. Knight and M. Porter, personal communication.

the expected adduct (10): there was no indication that isomerisation was occurring, and neither of the two adducts obtained from 2,3-dimethylbut-1-ene was detected.

An interesting feature of the ^{1}H n.m.r. spectrum of (10) is the appearance of three 3-proton singlets, the
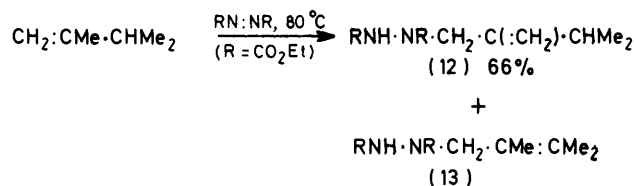
$$H-CH_2 \cdot CMe{:}CMe_2 \xrightarrow[\text{(R = CO$_2$Et)}]{\text{RN:NR, 80 °C}} CH_2{:}CMe \cdot CMe_a Me_b \cdot NR \cdot NHR$$
(10)

most deshielded of which (τ 8.28) is ascribed to :CMe. The other two (τ 8.49 and 8.68) are presumed to be due to non-equivalent methyl groups locked in different magnetic environments by restricted rotation about the $Me_2C{-}N$ bond.[10] Significantly, this phenomenon does not arise in the adduct of this olefin with PTAD, in which the triazolidine ring ensures that both carbonyl groups lie on the same side of the hydrazo-function. In (7) and in (10) the planar E-configuration for the bicarbamoyl group (11) allows only restricted motion in the alkenyl substituent. Indeed, space-filling molecular models suggest that rotations about the $Me_2C{-}N$ bond

(11) R =
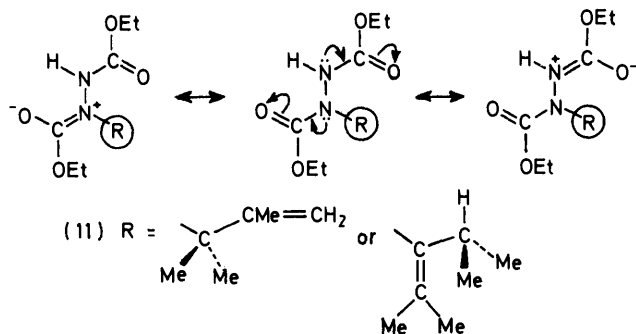
in (10) is prevented even with an orthogonal arrangement about the N–N bond in the bicarbamoyl function.

The reaction between the dimethylbut-1-ene and diethyl azodiformate gave a 91% yield of *ca.* 70 : 30 mixture of two isomers, identified without separation as (12) and (13). Non-equivalence was not detected in the ^{1}H n.m.r. spectrum of the mixture; models show that the congestion is relieved by the interposing of a methylene group between the bicarbamoyl and alkylidene functions.
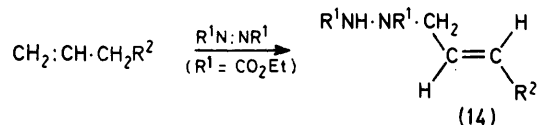
Preferential reaction of the primary CH bond to give

$$CH_2{:}CMe \cdot CHMe_2 \xrightarrow[\text{(R = CO$_2$Et)}]{\text{RN:NR, 80 °C}} RNH \cdot NR \cdot CH_2 \cdot C({:}CH_2) \cdot CHMe_2$$
(12) 66%

+

$$RNH \cdot NR \cdot CH_2 \cdot CMe{:}CMe_2$$
(13)

(12), as opposed to reaction at the weaker tertiary CH bond giving (13), is a well documented feature of the ene reaction, widely interpreted as an indication of steric hindrance in the transition state for tertiary abstraction.[2,7] A high degree of stereoselectivity was also apparent in the reaction of hex-1-ene with the azodifor-

mate, which gave an adduct in 85% yield identified as (14; $R^2 = Pr^n$) on spectroscopic grounds. Although the formation of a small proportion of the Z-isomer cannot be excluded, the E-isomer ($^3J_{trans}$ 20 Hz) predominates, and to a greater extent than in the corresponding reaction of but-1-ene,[7] which gave an 83 : 17 mixture of the analogous E- (14; $R^2 = Me$) and Z-isomers.

Competition Reactions involving Diethyl Azodiformate.— A simple procedure adequate for a semiquantitative

$$CH_2{:}CH \cdot CH_2R^2 \xrightarrow[\text{(R^1 = CO$_2$Et)}]{R^1N{:}NR^1} R^1NH \cdot NR^1 \cdot CH_2 \quad \underset{H}{\overset{H}{\diagdown}}C{=}C\underset{R^2}{\overset{H}{\diagup}}$$
(14)

evaluation of trends in reactivity was adopted.[7] Equimolar proportions of the two unsaturated hydrocarbons to be compared were mixed in large excess with an internal standard. After measuring the initial concentrations the azodiformate was added and the mixture kept at 80 °C for 24 h. Finally the mixture was rapidly chilled to $-78°$ and kept frozen until the final composition was to be determined by g.l.c. analysis. All g.l.c. determinations were performed in triplicate on a temperature-programmed capillary column which ensured complete resolution of all the components.

The relative reactivities so measured are shown in the Table, in which two main features are apparent. The tetra-alkylallene is roughly eight times more reactive than the dialkylallene, and roughly five times more reactive than the correspondingly substituted ethylene. The relative reactivity we find for 2,3-dimethylbut-2-ene with respect to hex-1-ene is at odds with that reported for these two olefins (0.73) in ene reactions with alkyl (phenylcarbamoylazo)formates such as PhNH·CO·N: N·CO$_2$Et,[6] but it is not surprising that the different azo-compounds have differing steric requirements.

We conclude that steric inhibition of the ene reaction

Relative reactivities towards diethyl azodiformate of allenes and alkenes

A	B	k_A/k_B
$Me_2C{:}C{:}CMe_2$	$Me_2C{:}CMe_2$	4.7 ± 0.5
$Me_2C{:}C{:}CH_2$	$Me_2C{:}CMe_2$	0.59 ± 0.05
$Me_2C{:}CMe_2$	$CH_2{:}CH \cdot CH_2Pr^n$	3.2 ± 0.4
$CH_2{:}CMe \cdot CHMe_2$	$CH_2{:}CH \cdot CH_2Pr^n$	1.16 ± 0.15

between these alkylallenes and azodiformates is not significant, possibly owing to the extended, more open, nature of the allenic bond as compared with an olefin. The contrast in behaviour of these two allenes towards fluoro-ketones must, as originally proposed, be due to faster prototropic rearrangement by the more alkylated allene.

Alkylallene–Phenyltriazolinedione   Reactions.—The powerful enophilicity of 4-phenyltriazolinedione (PTAD) has been exploited successfully by Pasto and his co-workers [12] in reactions with cyclopropylideneallenes,

[12] D. J. Pasto and A. F.-T. Chen, *J. Amer. Chem. Soc.*, 1971, **93**, 1563; D. J. Pasto and J. K. Borchardt, *ibid.*, 1974, **96**, 6220, 6994.

but no reports exist of its reactions with acyclic allenes. A very fast reaction occurs when PTAD and 2,3-dimethylpenta-2,3-diene are mixed at 0 °C in dichloromethane, and the colour of PTAD soon fades completely. Disappointingly, the 1 : 1 adduct proved to be (15), also obtained in high yield by a separate experiment in which

H—CH$_2$·CMe : C :CMe$_2$ ⟶ [CH$_2$:CMe·CH:CMe$_2$]

↓ PTAD

(15)
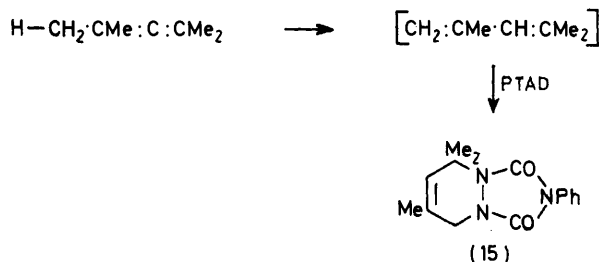
the conjugated hydrocarbon 2,4-dimethylpenta-1,3-diene was treated with PTAD, and evidently a Diels–Alder adduct.

The spectroscopic evidence for structure (15) is conclusive, especially the [1]H n.m.r. spectrum (no NH, 5 aryl, 1 vinyl, 5 allyl, and 6 terminal protons) which agrees with data reported for analogous PTAD adducts of 1,3-dienes.[13-15] The factor which promotes the rapid rearrangement of the allene in this instance is not known. Chlorinated solvents such as sym-tetrachloroethane which can liberate traces of hydrogen chloride on heating have been shown to initiate the rearrangement,[1] but the PTAD reaction took the same course when a slurry of finely powdered PTAD was stirred in an excess of the allene at −25 °C (no reaction occurred at −78 °C). The

(16)

a; R = Ph

b; R = Me
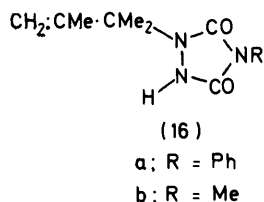
reaction between PTAD and 3-methylbuta-1,2-diene was even less satisfactory: no characterisable product was isolated.

By contrast, the phenyltriazolinedione reacted smoothly with 2,3-dimethylbut-2-ene in dichloromethane at 0 °C, and within 2 h gave the expected ene adduct (16a) in 76% yield. There was no indication that a prior rearrangement of the olefin had occurred, and the spectroscopic data agree well with data reported for the ene adduct of PTAD and cyclohexene[15] and the ene adduct (16b) obtained from the reaction of the dimethylbutene with 4-methyltriazolinedione.[16]

EXPERIMENTAL

Pure products were identified by i.r. (Perkin-Elmer models 137 with NaCl and 257 with grating optics), n.m.r. (Perkin-

Elmer R10 or Hitachi–Perkin-Elmer R20, at 60 MHz, or Varian HA-100 at 100 MHz; Perkin-Elmer R32 at 90 MHz for variable temperature and double resonance experiments; 10—20% solutions in CCl$_4$ unless otherwise indicated; Me$_4$Si internal standard), u.v. (Hilger and Watts Ultrascan SP 700), and mass spectrometry (A.E.I. MS902 with A.E.I. DS10 data acquisition system). Analytical g.l.c. was carried out with Perkin-Elmer F11 (flame ionisation detector with 50 m capillary wall-coated columns) and Pye-Unicam 104 (twin flame ionisation detectors with 4.5 mm i.d. packed columns) chromatographs; area determinations were made using a Kent Chromalog Mark 2 integrator, or by manual methods. Refractive indices were obtained on an Abbé refractometer.

2,4-Dimethylpenta-2,3-diene and 3-methylbuta-1,2-diene were prepared from the lactone dimer of dimethylketen and 3-chloro-3-methylbut-1-yne, respectively, as described previously.[17] 2,3-Dimethylbut-2-ene and 2,3-dimethylbut-1-ene were isolated by precise fractionation (100 cm Haage spinning-band column) of the products of dehydration (conc. H$_2$SO$_4$) of either 2,3-dimethylbutan-2-ol (54% and 11 yields, respectively), or 3,3-dimethylbutan-2-ol (60 and 8% yield).[18] Hex-1-ene was obtained commercially and redistilled prior to use. 2,4-Dimethylpenta-1,3-diene was obtained by prototropic rearrangement of 2,4-dimethylpenta-2,3-diene.[1] Diethyl azodiformate was prepared (81%) by oxidation (Cl$_2$) of the corresponding hydrazine and redistilled until pure (b.p. 110—112° at 16 mmHg; lit.[19] 107—111° at 15 mmHg). 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) was best prepared (77% yield) by oxidation (fuming HNO$_3$) of 4-phenyl-1,2,4-triazolidine-3,5-dione in dichloromethane at −15 °C,[20] and was purified by sublimation at 60 °C in vacuo until of satisfactory purity [m.p. 165—170° (decomp.); lit.,[21] 165—175°]. When pure it could be stored at −5 °C for 2 months without decomposition.

Reaction of 2,4-Dimethylpenta-2,3-diene with Diethyl Azodiformate.—Diethyl azodiformate (50 mmol) was slowly added to an excess of the pentadiene (156 mmol), and gentle reflux was permitted as an exothermic reaction occurred; the mixture was finally refluxed for 1 h, and the excess of dimethylpentadiene (105 mmol) was removed and shown (i.r., g.l.c.) not to have undergone rearrangement to 2,4-dimethylpenta-1,3-diene. The white residue was recrystallised [light petroleum (b.p. 60—80 °C)] to give diethyl 1-isopropenyl-2-methylprop-1-enylbicarbamate (3) (12.7 g, 47 mmol; 94% based on azodiformate), m.p. 81—82° (Found: C, 57.9; H, 8.3; N, 11.2%; M^+, 270.1581. C$_{13}$H$_{22}$N$_2$O$_4$ requires C, 57.7; H, 8.1; N, 10.4%; M, 270.1579), $\nu_{max.}$ (mulls) 3 300m (NH str.), 3 000m, 2 950sh, 1 750 and 1 700s (C:O str.), 1 670sh, 1 640w (C:C str.), 1 525m, 1 450m, 1 400m, 1 380s, 1 330s, 1 270s, 1 240s, 1 180m, 1 100m, 1 065s, 1 025m, 990w, 900m (:CH def.), 810w, 780w, 765w, and 725w cm^{-1}, $\lambda_{max.}$ (EtOH) 217 nm (ε 8 730), τ (60 MHz) 2.62br (s, NH; shifted to 1.25 with CF$_3$·CO$_2$H), 4.94 and 5.17 (m, :CH$_2$), 5.88 and 5.94 (overlapping q, OCH$_2$Me × 2), 8.24—8.26 (s, MeC: × 3), and 8.78 (t, O·CH$_2$Me × 2).

[13] J. Sauer and B. Schröder, Chem. Ber., 1967, 100, 678.
[14] B. T. Gillis and J. D. Hagarty, J. Org. Chem., 1967, 32, 330.
[15] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, J. Chem. Soc. (C), 1967, 1905.
[16] W. H. Pirkle and J. C. Stickler, Chem. Comm., 1967, 760.

[17] D. R. Taylor, M. R. Warburton, and D. B. Wright, J. Chem. Soc. (C), 1971, 385.
[18] S. R. Sandler and W. Karo, ' Organic Functional Group Preparations,' Academic Press, New York, 1968, p. 34.
[19] N. Rabjohn, Org. Synth., 1955, 3, 375.
[20] M. Furdik, S. Mikulasek, M. Livar, and S. Priehradny, Chem. Zvesti, 1967, 21, 427 (Chem. Abs., 1967, 67, 116858).
[21] R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, Org. Synth., 1971, 51, 121.

The outcome of the reaction was the same when the di-methylpenta-2,3-diene was treated with an equimolar proportion of the azodiformate in gently refluxing n-hexane.

Reaction of 3-Methylbuta-1,2-diene with Diethyl Azodiformate.—The methylbutadiene (70.6 mmol), diethyl azodiformate (35 mmol), and Terpene B polymerisation inhibitor (0.1 g), kept at 80 °C for 60 h in a sealed Pyrex tube (300 cm³), gave 3-methylbuta-1,2-diene (35.6 mmol) and a viscous oil which was distilled (15 cm Vigreux column) to give *diethyl 2-methyl-1-methyleneallylbicarbamate* (8) (6.0 g, 24.8 mmol, 71% based on azodiformate) as a liquid, b.p. 112—113° at 0.5 mmHg (Found: C, 51.9; H, 7.2; N, 10.7%; M^+, 242.1273. $C_{11}H_{18}N_2O_4$ requires C, 54.5; H, 7.4; N, 11.6%; M, 242.1266), $\nu_{max.}$ (film) 3 290m (NH str.), 2 940m, 2 900sh, 1 750 and 1 720vs (C:O str.), 1 650 and 1 640m (C:C str.), 1 370vs, 1 290vs, 1 245s, 1 220vs, 1 175m, 1 130m, 1 090s, 1 060s, 1 020w, 900w (CH def.), 855w, 840w, and 755w cm⁻¹, $\lambda_{max.}$ (EtOH) 221.5 nm (ε 7 865), $\lambda_{max.}$ (hexane) 219.5 nm (ε 8 590), τ (100 MHz) 2.45br (s, NH), 4.60 and 4.82 (apparent s, NC:CH₂), 4.88 and 5.06 (apparent s, MeC:CH₂), 5.82 and 5.89 (overlapping q, OCH₂Me × 2), 8.12 (m, MeC:CH₂), and 8.55—8.82 (overlapping t, OCH₂Me × 2). The adduct rapidly decolourised bromine in CCl₄. When left at ambient temperature in a stoppered flask for 14 days it was converted into a sticky uncharacterised gum.

Reaction of 2,3-Dimethylbut-2-ene with Diethyl Azodiformate.—The dimethylbut-2-ene (60 mmol) and diethyl azodiformate (30 mmol), kept in a sealed Pyrex tube (300 cm³) at 80 °C for 48 h, gave 2,3-dimethylbut-2-ene (28 mmol) and a viscous liquid which was distilled to give *diethyl 1,1,2-trimethylallylbicarbamate* (10) (7.1 g, 27.5 mmol, 92% based on azodiformate), b.p. 164° at 2.5 mmHg (Found: C, 55.8; H, 8.5; N, 10.9%; M, 258. $C_{12}H_{22}N_2O_4$ requires C, 55.8; H, 8.5; N, 10.8%; M, 258), n_D^{23} 1.464 8, $\nu_{max.}$ (film) 3 280cm (NH str.), 3 050w (: CH str.), 2 950s, 2 900sh, 1 750 and 1 710vs (C:O str.), 1 640w (C:C str.), 1 520m, 1 460m, 1 440m, 1 400m, 1 370vs, 1 340vs, 1 320sh, 1 240vs, 1 180m, 1 165m, 1 095vs, 1 080sh, 1 055s, 1 020w, 890w (:CH def.), 845w, 785w, and 765w cm⁻¹, τ (100 MHz) 2.84br (s, NH; at 0 °C, 90 MHz, appears as two unequal s), 5.20 and 5.33 (s, :CH₂), 5.88 and 5.95 (overlapping q, OCH₂Me × 2), 8.28 (s, MeC:), 8.49 and 8.68 (s, NCMe_aMe_b; the 8.68 s coincides with the low-field member of the 8.74 triplet, but at 90 MHz is fully resolved when the 8.74—8.80 triplets are collapsed by irradiation of the 5.88—5.95 signal), and 8.74 and 8.80 (overlapping t, OCH₂Me × 2). The yield was unaffected when the reaction was conducted by refluxing equimolar proportions of the reagents in n-hexane; no di-adduct was detected.

Reaction of 2,3-Dimethylbut-1-ene with Diethyl Azodiformate.—The dimethylbut-1-ene (75 mmol) and diethyl azodiformate (38.5 mmol), kept at 80 °C for 72 h in a sealed Pyrex tube (300 cm⁻³), gave 2,3-dimethylbut-1-ene (36 mmol) and a liquid which was distilled to give a fraction, b.p. 118—120° at 0.1 mmHg (9.05 g) (Found: C, 55.5; H, 8.4; N, 10.9%. Calc. for $C_{12}H_{22}N_2O_4$: C, 55.8; H, 8.5; N, 10.8%), shown by g.l.c. (2 m SE30 at 240 °C) and 100 MHz ¹H n.m.r. spectroscopy to consist of a 72 : 28 mixture of diethyl 3-methyl-2-methylenebutylbicarbamate (12) (estimated 6.5 g, 25 mmol, 66%) [τ 2.49br (NH), 5.20 (apparent s, : CH₂), 5.91 (q, OCH₂ Me × 2), ca. 6.0 (CH₂N; underlies line 3 of the OCH₂ quartet), 7.77 (sept, CHMe₂), 8.80 (t, OCH₂Me × 2), and 8.99 (d, CHMe₂)] and diethyl 2,3-dimethylbut-2-enylbicarbamate (13) (estimated 2.5 g, 9.8 mmol, 26%) [τ 2.62 (NH), 5.93 (q, OCH₂Me × 2), 6.0 (CH₂N),

8.37 (s, MeC: × 3), and 8.80 (OCH₂Me × 2)]. The relative intensities of the well-resolved :CH₂ and MeC: signals were used for integration-based determination of composition.

Reaction of Hex-1-ene with Diethyl Azodiformate.—Hex-1-ene (188 mmol) and diethyl azodiformate (104 mmol), refluxed without stirring for 72 h, gave hex-1-ene (78 mmol) and a viscous oil which was distilled (10 cm Vigreux column) to give *diethyl (E)-hex-2-enylbicarbamate* (14) (22.8 g, 88.4 mmol, 85% based on azodiformate) as a liquid, b.p. 140° at 0.1 mmHg (Found: C, 55.0; H, 8.4; N, 10.6%; M^+, 258. $C_{12}H_{22}N_2O_4$ requires C, 55.8; H, 8.5; N, 10.9%; M, 258), $\nu_{max.}$ (film) 3 300s (NH str.), 2 970s, 2 940s, 2 880m, 1 740 and 1 710vs (C:O str.), 1 650m (C:C str.), 1 450vs, 1 375vs, 1 265vs, 1 210vs, 1 180s, 1 150m, 1 120m, 1 100s, 1 060vs, 1 030m, 970s, (CH def.), 880w, 860w, 785m, and 760m cm⁻¹, τ (100 MHz) 2.75br (NH), 4.46 (downfield portion of ABX₂, d of t, :CH·CH₂N, ³J_{trans} 20 Hz), 4.60 (high-field portion of ABX₂, d of t, :CHPrⁿ), 5.91 (q, OCH₂Me × 2), 6.05 (d, NCH₂CH), 8.02 (d of t, CH₂CH₂CH:), 8.62 (m, MeCH₂CH₂), 8.77 (overlaps the 8.62 m; t, OCH₂Me × 2), and 9.12 (t, MeCH₂CH₂).

Hydrogenation of Diethyl 1-Isopropenyl-2-methylprop-1-enylbicarbamate (3).—A conventional atmospheric pressure hydrogenation manifold was used. The bicarbamate (3) (525 mg, 1.9 mmol) in ethanol (10 cm³) was stirred with 5% palladium–charcoal (2 mg) while hydrogen was admitted. After 5 h, when hydrogen uptake had slowed, gas absorbed measured 47.5 cm³ (2 mmol); the mixture was filtered and the filtrate evaporated to give a residue which was recrystallised from light petroleum (b.p. 60—80°) to yield *diethyl 1-isopropenyl-2-methylpropylbicarbamate* (0.495 g, 1.8 mmol, 95%) as a white solid (Found: C, 57.1; H, 9.2; N, 10.0%; M^+, 272.1731. $C_{13}H_{24}N_2O_4$ requires C, 57.3; H, 8.8; N, 10.3%; M, 272.1735), m.p. 82—83°, $\nu_{max.}$ (mull) 3 230s (NH str.), 2 950m, 2 850sh, 1 750 and 1 690vs (C:O str.), 1 650w (C:C str.), 1 530m, 1 410w, 1 370m, 1 355w, 1 330m, 1 320m, 1 290w, 1 245w, 1 230s, 1 185w, 1 170w, 1 110w, 1 085w, 1 060s, 1 025w, 980w, 925w, 785w, and 765w cm⁻¹, τ (100 MHz) 2.78br (s, NH), 5.90 (q, OCH₂Me × 2), 7.15 (apparent sept, CHMe_aMe_b), 8.28 and 8.33 (s, Me₂C:), 8.76 and 8.78 (overlapping t, OCH₂Me × 2), and 8.93 and 9.00 [apparent but unsymmetrical t, even at 50 °C (90 MHz), interpreted as two doublets, J_d 7.0 and 6.8 Hz, respectively, Me_aCHMe_b; at 50 °C (90 MHz), when the 7.15 signal is irradiated, these appear as two singlets, τ 8.92 and 8.98].

Reaction of 2,4-Dimethylpenta-2,3-diene with 4-Phenyl-1,2,4-triazoline-3,5-dione.—(a) *At 0 °C in dichloromethane.* The dimethylpenta-2,3-diene (6.3 mmol), 4-PTAD (6.3 mmol) and Terpene B (0.2 g) were mixed in dichloromethane (20 cm³) under nitrogen at 0 °C. The red colour of PTAD had faded after 5 min; after 1 h the solvent was removed (rotary evaporator) and the residue sublimed *in vacuo* to give white crystals of 1,2,3,6-tetrahydro-3,3,5-trimethylpyridazine-1,2-N-phenyldicarboximide (15) (1.45 g, 5.4 mmol, 86% based on PTAD), m.p. 98—99° (from CCl₄) (Found: C, 66.4; H, 6.5; N, 15.5%; M^+, 271.1321. $C_{15}H_{17}N_3O_2$ requires C, 66.4; H, 6.3; N, 15.5%; M, 271.1319), $\nu_{max.}$ (mull) at 3 050m, 1 990w, 1 760s, 1 700vs (C:O str.), 1 650 (C:C str.), 1 490m, 1 450m, 1 400m, 1 310w, 1 135w, 1 120w, 1 090w, 965w, 895w (:CH def.), 800 w, 765w, 732w, and 696w cm⁻¹, τ (100 MHz; 20% in CDCl₃) 2.65 (m, Ph), 4.68 (m, :CH), 6.03 (s, CH₂N), 8.18 (m, MeC:), and 8.45 (s, Me₂C·N).

(b) *At —25 °C in an excess of pentadiene.* The dimethyl-pentadiene (73 mmol), PTAD (1.8 mmol), and Terpene B

(0.2 g) were kept at −78 °C for 2 h; no colour change occurred. After 1 h at −25 °C the colour of PTAD had faded from the stirred slurry; the excess of penta-2,3-diene was removed *in vacuo* leaving a residue which was sublimed to give (15) (88%), identified by mixed m.p.

Reaction of 2,4-Dimethylpenta-1,3-diene with 4-Phenyl-1,2,4-triazoline-3,5-dione.—The dimethylpenta-1,3-diene (5.2 mmol) and PTAD (4.6 mmol) were stirred in dichloromethane (10 cm³) at 25 °C for 3 h. Solvent was removed *in vacuo* and the residue sublimed to give (15) (1.1 g, 4.1 mmol, 89% based on PTAD), spectroscopically identical with the material obtained from PTAD and the dimethylpenta-2,3-diene.

Reaction of 3-Methylbuta-1,2-diene with 4-Phenyl-1,2,4-triazoline-3,5-dione.—3-Methylbuta-1,2-diene (6 mmol), PTAD (6 mmol), and Terpene B (0.2 g) were stirred in dichloromethane (15 cm³) at 0 °C for 2 h. The colour of PTAD faded; solvent was removed *in vacuo*, but the sticky grey residue (1.4 g) insoluble in pentane, benzene, and ethanol, was not characterised further.

Reaction of 2,3-Dimethylbut-2-ene with 4-Phenyl-1,2,4-triazoline-3,5-dione.—2,3-Dimethylbut-2-ene (4.2 mmol), PTAD (4.2 mmol), and dichloromethane (15 cm³) were stirred at 0 °C until the solution was colourless (2 h). Solvent was removed *in vacuo* and the residue (0.9 g) sublimed *in vacuo* at 80 °C to give white sublimate identified as 4-*phenyl*-1-(1,1,2-*trimethylallyl*)-1,2,4-*triazolidine*-3,5-*dione* (16a) (0.83 g, 3.2 mmol, 76%) (Found: C, 64.7; H, 6.9; N, 16.1%; M^+, 259. $C_{14}H_{17}N_3O_2$ requires C, 64.9; H, 6.6; N,

16.2%); M, 259), m.p. 127.5—128.5°, $\nu_{max.}$ (mull) 3 200w (NH str.), 3 090m, 3 000sh, 2 890w, 1 771m, 1 720s (C:O str.), 1 650w (C:C str.), 1 490m, 1 430s, 1 380w, 1 360w, 1 245w, 1 210w, 1 170w, 1 125w, 1 020w, 910w, 895m, 870w, 775m, 730w, 720w, and 687m cm⁻¹, τ (100 MHz) 1.60br (s, NH), 2.58 (m, Ph), 5.02 and 5.05 (s, :CH₂), 8.20 (s, :CMe), and 8.42 (s, N·CMe₂). The triazolidinedione (16a) was also obtained in 85% yield by recrystallisation [light petroleum (b.p. 40—60 °C)] of the precipitate formed when 2,3-dimethylbut-2-ene (60 mmol) and a deficiency of PTAD (7 mmol) were stirred at 0 °C for 2 h.

Competition Reactions.—The two unsaturated hydrocarbons for comparison (30 mmol of each) and n-pentane or n-hexane (30 mmol) as internal standard were thoroughly mixed and a sample was removed for g.l.c. analysis. Diethyl azodiformate (3 mmol) and Terpene B (0.2 g) were then added, the reactor (10 cm³) was frozen, degassed, and sealed, and the reactor and contents were rapidly brought to 80 (±0.5) °C and left for 24 h. The reactor was rapidly chilled to −78 °C and so stored until ready for g.l.c. analysis. Triplicate g.l.c. analyses (50 m Apiezon L wall-coated capillary programmed from 50 to 100 °C at 10 °C min⁻¹) were performed on initial and final samples, and relative reactivities (see Table) were determined from the expression $k_A/k_B = \log (A_i/A_f) − \log (B_i/B_f)$. The initial (A_i, B_i) and final (A_f, B_f) concentrations were determined from the corresponding peak area ratios (reactant : internal standard).