Cycloadditions. Part III.¹ Steric Effects in the Addition of 2-Diazopropane to Conjugated Allenic Esters and Nitriles

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Esters of buta-2,3-dienoic acid and its methyl-substituted analogues react with 2-diazopropane at the more electrophilic ($\alpha\beta$) double-bond, but the orientation of addition is dependent on the degree of substitution at the y-carbon atom. Allenes monosubstituted or unsubstituted at the y-position give 4-alkylidene-1-pyrazolines (i.e. the electronically preferred adducts). The initial adduct from methyl buta-2,3-dienoate isomerises under the reaction conditions to 3-methoxycarbonyl-5,5-dimethyl-4-methylene-2-pyrazoline, which reacts readily with a second molecule of 2-diazopropane to give a spiran. The orientation of addition is reversed with $\gamma\gamma$ -disubstituted allenic esters and nitriles, which give solely 3-isopropylidene-1-pyrazolines. The reversals are attributed to a highly unfavourable 'wedging' interaction in the transition states for normal addition to the $\gamma\gamma$ -dimethylallenes. The orientation in several other allene-diazoalkane cycloadditions is discussed.

The 3-isopropylidene-1-pyrazolines give good yields of isopropylidenecyclopropanes on photolysis.

In the 1,3-dipolar addition of diazoalkanes to $\alpha\beta$ unsaturated carbonyl compounds, the nucleophilic diazo-carbon atom generally bonds to the β -position,² though steric effects may reverse the orientation of addition to conjugated ethylenic³ and acetylenic^{1,4} esters. Similar reversals have been observed with $\alpha\beta$ unsaturated sulphones 5 and nitro-compounds.6 † We have studied analogous reactions of conjugated allenic esters and nitriles and found that, whilst in all cases 2-diazopropane adds, as expected,² to the more electrophilic $(\alpha\beta)$ double-bond, the orientation is dependent on the degree of substitution of the γ -carbon atom. The reactions have some additional interest, since allenediazoalkane cycloadditions have received scant attention.8,9

The allenic ethyl esters (Ib—e) and nitriles (If and g) in the Table were obtained by published methods,¹⁰⁻¹² modified where necessary. It was most convenient to work with the methyl ester (Ia) of buta-2,3-dienoic acid, since this readily available acid ¹³ is best esterified by treatment at -78° with diazomethane.¹⁴ At this temperature, dipolar addition of diazomethane is not detectable. The nitrile (Ig), like its lower homologue (If),¹² readily dimerised, giving several products (see Experimental section), both during its preparation and when set aside at room temperature. Cycloadditions were performed by treatment of the allenes with (usually

† Steric factors may however influence the reactivity of diazoalkane-dipolarophile systems without leading to a reversal of orientation."

¹ Part II, A. C. Day and R. N. Inwood, J. Chem. Soc. (C), 1969, 1065.

² R. Huisgen, R. Grashey, and J. Sauer, in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 826;
R. Huisgen, Angew. Chem. Internat. Edn., 1963, 2, 565, 633.
³ S. D. Andrews, A. C. Day, and A. N. McDonald, J. Chem.

S. D. Hallews, A. C. Day, and A. N. McDohald, J. Chem.
 Soc. (C), 1969, 787.
 4 R. Hüttel, J. Riedl, H. Martin, and K. Franke, Chem. Ber., 1960, 93, 1425; K. von Auwers and O. Ungemach, Ber., 1933, 66, 560.

1205. ⁵ W. E. Parham, F. D. Blake, and D. R. Theissen, J. Org. Chem., 1962, 27, 2415.

⁶ W. E. Parham, H. G. Braxton, and P. R. O'Connor, *J. Org. Chem.*, 1961, 26, 1805; W. E. Parham, C. Serres, and P. R. O'Connor, J. Amer. Chem. Soc., 1958, 80, 588.

⁷ A. Ledwith and D. Parry, J. Chem. Soc. (C), 1966, 1408; A. Ledwith and Yang Shih-Lin, J. Chem. Soc. (B), 1967, 83; R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, Angew. Chem., 1961, 73, 170.

large)	exces	ses	of et	hereal	2-di	azop	oropan	e ¹⁵	at	0°	for
12	days;	the	majo	r prod	lucts	are	listed	in	the	Tal	ble.

				Fable		
	Cycload	dition	of alle	enes (I) to 2-diazoprop	pane
			R ¹		R^3	
)C	=C=C((I)	
			R^{2}		X	
Allenes					Product	
(I)	X	\mathbb{R}^{1}	\mathbb{R}^2	\mathbb{R}^3	(%)	Orientation
a;	CO_2Me	\mathbf{H}	\mathbf{H}	\mathbf{H}	(V) (61) *	Normal
b;	CO_2Et	\mathbf{H}	\mathbf{H}	Me	(II) (98) *	Normal
c;		\mathbf{H}	Me	Me	(III) (96)	Normal
d;		Me	Me	\mathbf{H}	(XIII) (96)	Reverse
e;		Me	Me	Me	(XIII) (5)	Reverse
f;	CN	Me	Me	н	(XIII) (93)	Reverse
g;		Me	Me	Me	(XIII) (6) *	Reverse
		* For	other	produc	ts see Text.	

As predicted on electronic grounds, the allenes (Ib) and (Ic) gave with 2-diazopropane the 4-alkylidene-1-



pyrazolines (II) and (III), respectively. The adducts, which were obtained in high yield, had the spectroscopic features expected for such compounds, 8 in particular an absorption band at λ_{max} . 327 mµ (ϵ 150—200) characteristic of an isolated azo-group. Their n.m.r. spectra

⁸ S. D. Andrews and A. C. Day, J. Chem. Soc. (B), 1968, 1271; Chem. Comm., 1966, 667; A. C. Day and M. C. Whiting, J. Chem. Soc. (C), 1966, 464; Proc. Chem. Soc., 1964, 368.
 ⁹ (a) R. J. Crawford and D. M. Cameron, J. Amer. Chem. Soc.,

Soc. (C), 1966, 464; Proc. Chem. Soc., 1964, 368.
(a) R. J. Crawford and D. M. Cameron, J. Amer. Chem. Soc., 1966, 88, 2589; P. Dowd, ibid., p. 2587; W. Ried and H. Mengler, Annalem, 1964, 678, 95; S. Corsano, L. Capitò, and M. Bonamico, Ann. Chim. (Italy), 1958, 48, 140; I. A. D'yakonov, Zhur. obshchei Khim., 1945, 15, 473 (Chem. Abs., 1946, 40, 4718⁴); (b) T. Sanjiki, H. Kato, and M. Ohta, Chem. Comm., 1968, 496.
H.-J. Bestmann and H. Hartung, Chem. Ber., 1966, 59, 1198; Angew. Chem. Internat. Edn., 1963, 2, 214.
G. R. Harvey and K. W. Ratts, J. Org. Chem., 1966, 31, 3907; cf. W. S. Wadsworth, jun. and W. D. Emmons, J. Amer. Chem. Soc., 1961, 83, 1733.
P. M. Greaves, S. R. Landor, and D. R. J. Laws, Chem.

¹² P. M. Greaves, S. R. Landor, and D. R. J. Laws, Chem. Comm., 1965, 321; J. Chem. Soc. (C), 1968, 291.
 ¹³ G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, J. Chem. Soc., 1954, 3197.
 ¹⁴ R. J. Bushby and G. H. Whitham, unpublished work.
 ¹⁵ A. C. D. D. D. D. M. Sock, M. M. So

A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, J. Chem. Soc. (C), 1966, 467; S. D. Andrews, A. C. Day, P. Raymond, and M. C. Whiting, Org. Synth., to be published.

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showed the presence of *exo*-methylene and -ethylidene groupings, respectively.

Methyl buta-2,3-dienoate (Ia) likewise reacted with 2-diazopropane in the electronically preferred sense; but, in this case, the product was not the 1-pyrazoline (IV), but the isomeric 2-pyrazoline (V). This was presumably



formed by tautomerisation of the 1-pyrazoline in the reaction medium: solutions of 2-diazopropane always contain its decomposition product, acetone azine,15 which could function as an effective basic catalyst for the conversion of (IV) into (V). (cf. The cycloaddition of 2-diazopropane to conjugated ethylenic esters bearing an α-hydrogen atom.³) Structure (V) followed from the intense absorption at λ_{max} , 223 and 330 mµ (ϵ 9000 and 10,000, respectively) and the presence of exo-methylene, gem-dimethyl, and NH in the i.r. and n.m.r. spectra. Compound (V) itself was unstable in the reaction solution [the known¹ 3*H*-pyrazole (VI; λ_{max} 245 mµ, ε 4250) being tentatively identified as one of its decomposition products by the appearance of a peak at ca. 250 m μ in aged solutions], and could be isolated in good yield only when the reaction mixtures were rapidly evaporated and recrystallised. It could be converted efficiently (85%)into the 3H-pyrazole (VI) by slow distillation at 0.01 mm. from glass wool. The three tautomers (IV), (V), and (VI) are probably related through the common, conjugate base (VII), isomers (V) and (VI) being respectively the products of kinetically and thermodynamically controlled protonation.

The yield of 61% quoted in the Table for the 4methylene-2-pyrazoline (V) refers to the reaction of methyl butadienoate and 2-diazopropane in equimolecular proportions. With an excess of diazoalkane, the major product (90%) was a 2:1 adduct $C_{11}H_{18}N_4O_2$. In an independent experiment it was shown that the methylenepyrazoline (V) could be converted into the same 2:1 adduct (78%) by treatment with 2-diazopropane. Since the *exo*-double-bond in (V) is activated by conjugation with C=N, the most likely structure for the 2:1 adduct is the spiran (VIII). The n.m.r.



spectrum was consistent with the spiran structure, indicating four C-methyl groups (singlets at $\tau 8.83$, 8.78, 8.64, and 8.37), methylene ($\tau 8.64$ and 7.99, J_{AB} 14 c./sec.), NH, and CO₂Me. In the i.r. spectrum, which confirmed the presence of NH, the carbonyl stretching

frequency (1715 cm.⁻¹) was similar to that found for 3-methoxycarbonyl-2-pyrazolines.³ As with simple 1-pyrazolines,³ the highest peak in the mass spectrum corresponded to the loss of one molecule of nitrogen (M - 28 = 210).

The spiran (VIII) is evidently formed from methyl butadienoate *via* the 2-pyrazoline (V), and not by direct cycloaddition of 2-diazopropane to the 4-methylene-1-pyrazoline (IV) followed by $\Delta^1 \longrightarrow \Delta^2$ tautomerisation, since the isolated *exo*-double-bond in (IV) should be relatively unreactive. A measure of the low reactivity of (IV) to cycloaddition is provided by its homologue (II). Though the allene (Ib) was treated with a large excess of diazoalkane, only a trace (0.7%) of a 2 : 1 adduct (IX) was formed along with the 1 : 1 adduct (II) (98\%). The 4-methylene-1-pyrazolines (II) and (IV) would not be expected to differ significantly in reactivity at the *exo*-double bond.

The n.m.r. spectrum of the spiro-compound (IX) contained an ethyl triplet and five *C*-methyl singlets in the range τ 8.84—8.57, an ethyl quartet at τ 8.54, and a doublet (*J* 13 c./sec.) at τ 8.37 for one proton of the cyclic methylene group. The second methylene doublet was obscured by the methyl signals. The two isolated azo-groups gave an n,π^* -absorption band at λ_{\max} . 327 m μ , the extinction coefficient being *ca*. twice as large as for a single azo-group, and in the mass spectrum the highest peak occurred at m/e 210 (M — 56, *i.e.* loss of 2N₂).

The spiran (VIII) from methyl butadienoate showed anomalous spectroscopic behaviour in the u.v. region. The N=N and NH·N=C·CO₂Me groups had λ_{max} 348 (ɛ 2600) and 300 mµ (ɛ 9100), respectively, i.e., some 20 mm longer than λ_{max} for the same chromophores in 1-pyrazolines (325–330 mµ, ε ca. 200) and, for example, 5,5-dimethyl-3-methoxycarbonyl-2-pyrazoline (276 mµ, ϵ 11,200).³ Also, the azo-band at 348 mµ was more than 10 times as strong as in the simple models. Large redshifts have been observed in the spectra of ketone dimethylhydrazones (X), where the steric interaction between \mathbb{R}^2 and $\mathbb{M}e$ forces the molecule to adopt a nonplanar conformation; 16 * this effect cannot be operative, however, with the spiran (VIII), since the C-N-N=C moiety in a pyrazoline ring is necessarily planar or nearly so. Furthermore, the spiran (IX), which differs little in strain etc. from (VIII) and should therefore provide a closer model for the N=N group in (VIII) than do monocyclic 1-pyrazolines, shows azoabsorption of unexceptional λ_{max} and extinction coefficient. It is probable that the anomalies in the spectrum of the spiran (VIII) are due to interaction between the N=N and C=N orbitals [cf. formula (XI)].

¹⁶ J. A. Barltrop and M. Conlong, J. Chem. Soc. (B), 1967, 1081.

^{*} Cf. also the dimethylhydrazone of methyl pyruvate (λ_{max} . 310 m μ , ε 2980). The n.m.r. spectrum of this compound (see Experimental section) also supports the nonplanar conformation with equivalent N-methyl groups, though the possibility that free rotation averages the environments of the methyl groups has not yet been eliminated.

(XI)

The n,π^* -transitions of certain $\beta\gamma$ -unsaturated ketones show similar enhancements of intensity, but without wavelength shift,¹⁷ and the effect has been discussed theoretically.¹⁸ The spectroscopic behaviour of (VIII) and related spirans, which is of some interest in this

Me

(X)

connection and also in relation to spiroconjugation,¹⁹ will be discussed in detail elsewhere.

ring

А

(XII)

ring

В

Some interaction might have been expected between the azo-groups in the spiran (IX) since, as shown in formula (XII), the π^* -orbital in ring B has the right symmetry for overlap with both the π - and the π^* -orbital in ring A. However, the distance between the chromophores may be too great for appreciable overlap in this case.

In contrast to the allenes so far discussed, the $\gamma\gamma$ disubstituted allenes (Id—g) in the Table reacted with 2-diazopropane at the $\alpha\beta$ -ethylenic bond in the reverse sense, giving 3-alkylidenepyrazolines (XIII) and no detectable analogues of compounds (II) and (V). The 3-alkylidenepyrazolines had absorption at λ_{max} 255—258 (ε 10,000) and 350—357 m μ (ε ca. 300) (from solvent shifts, π,π^* and n,π^* , respectively) for the vinylazogrouping, in good agreement with the spectra of acyclic analogues ²⁰ and 3H-pyrazoles.²¹ [The cisoid 3Hpyrazoles, however, show a much weaker π,π^* -transition (ε ca. 2000).] The n.m.r. spectra were consistent with structures (XIII), and with compounds (XIIId and f)



showed weak coupling (J 2 c./sec.) between the methine proton and the isopropylidene group. The structures of the adducts were confirmed by photolysis ($\lambda > 290 \text{ mµ}$),

¹⁷ R. C. Cookson and N. S. Wariyar, J. Chem. Soc., 1956, 2302;
R. C. Cookson and S. MacKenzie, Proc. Chem. Soc., 1961, 423;
W. B. Bennett and A. Burger, J. Amer. Chem. Soc., 1953, 75, 84;
R. B. Woodward and E. G. Kovach, *ibid.*, 1950, 72, 1009; but see S. Winstein, L. de Vries, and R. Orloski, *ibid.*, 1961, 83, 2020.
¹⁸ H. Labhart and G. Wagnière, Helv. Chim. Acta, 1959, 42, 2219.

which gave the isopropylidenecyclopropanes (XIV) as sole products. An attempt to convert the cyano-adduct (XIIIf) into the 3H-pyrazole (XV) with base gave, instead, the isopropenyl-2-pyrazoline (XVI); possibly the 3H-pyrazole (XV) is destabilised relative to the isomer (XVI) by steric interaction between the isopropyl and cyano-groups.

The tetrasubstituted allene (Ig) gave, in addition to the adduct (XIIIg), traces of the cyclopropane (XVII) (0.5%) and an unstable 1-pyrazoline (1.3%) which was convertible into the cyclopropane by photolysis. These compounds probably arose via 2,4-dimethylpenta-2,4dienonitrile, which could have been present as a trace impurity in the allene (Ig) or formed from the latter during the extended reaction times required for an appreciable yield of the adduct (XIIIg). Addition of 2-diazopropane to the terminal double-bond in 2,4dimethylpenta-2,4-dienonitrile is understandable since this is the less-hindered site for cycloaddition.



The reversal of orientation to the $\gamma\gamma$ -dimethylallenes (Id-g) is attributed to the very severe crowding which must occur in the transition states for normal addition (XVIII) to these compounds, an allenic γ -methyl group being effectively wedged between the two methyl groups of the diazoalkane. This wedging interaction is evidently large enough to control orientation, even with the tetrasubstituted allenes (Ie and g) where the transition states for reverse addition (XIX; R = Me, X =CO₂Et or CN) contain two eclipsing interactions. The eclipsing interactions in (XIX; R = Me) are, however, reflected in the very low reactivity of the tetrasubstituted allenes (Ie and g) to cycloaddition, only poor yields (5-6%) of the adducts (XIIe and g) being obtained after long reaction times with large excesses of reagent. Transition states of type (XVIII) are relatively uncongested for allenes (Ia and b) without γ -substituents, so electronic control of orientation prevails in these cases. A corollary is that the allenic ester (Ic) bearing a single γ -methyl groups should give a single adduct (as found),

¹⁹ H. E. Simmons and T. Fukunaga, J. Amer. Chem. Soc., 1967, 89, 5208; R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, p. 5215.

<sup>p. 5215.
²⁰ B. T. Gillis and J. D. Hagarty, J. Amer. Chem. Soc., 1965, 87, 4576.
²¹ A. C. Day and M. C. Whiting, J. Chem. Soc. (B), 1967, 991;</sup>

²¹ A. C. Day and M. C. Whiting, J. Chem. Soc. (B), 1967, 991; (C), 1966, 1719.

viz., the 4-alkylidene-1-pyrazoline formed by approach of 2-diazopropane trans to the γ -methyl group and therefore having the geometry (III). That the ethylidene group in this adduct actually has the stereochemistry shown in (III) remains to be proved.

Since our preliminary communication,²² diazomethane 90,23 and diazoethane 23 have been found to give normal adducts, analogous to (II), with the tetrasubstituted allene ester (Ie). Thus, the wedging interaction is severe enough to control orientation in these systems only if it involves three methyl groups. Recently, a steric reversal has been observed in the addition of diphenyldiazomethane to terminal allenes;²⁴ evidently the wedging effect becomes significant even for a hydrogen atom when the flanking groups are very bulky.

A search for analogous reversals in the reaction of ethyl 2-diazopropionate with allenic esters was unsuccessful, since this compound failed to react with the esters (Id and e) even after prolonged contact of the neat reactants. The unhindered ester (Ib), however, gave



an adduct of the expected structure (XX), the assignment of which followed from spectroscopic data (see Experimental section).

As previously reported,8 the propionoxy- and chloroallenes (XXI; $X = O \cdot COEt$) and (XXI; X = Cl) give 4-alkylidenepyrazolines (XXII) with 2-diazopropane. Similarly, the bromo-allene (XXI; X = Br) gives the analogous adduct (XXII; X = Br). The orientation in these three cases corresponds to the least hindered mode of cycloaddition. Tetramethylallene, which should on steric grounds give an adduct (XXIII), was unfortunately too unreactive to give any detectable product with 2-diazopropane.

A stereochemical argument similar to that advanced above has been applied in discussions of the dimerisation of ketens.25

The photolysis of the 4-alkylidene-1-pyrazolines described in this Paper will be discussed later; cf. the photolysis of (XXII; X = Cl and O·CO·Et).⁸

24 P. Battioni and Yen Vo-Quang, Compt. rend., 1968, 266, C, **13**10.

EXPERIMENTAL

General experimental procedures were as described in Part I.³ except that ' light petroleum ' refers to the fraction of b.p. 30-40° (AnalaR). For preparative t.l.c., 1-mm. layers of silica gel (Merck $HF_{254 + 366}$) were used on 20 \times 100cm. plates; the plates were developed by multiple elution as indicated and the components were detected by u.v. and isolated by Soxhlet extraction with ether. Unless otherwise stated, n.m.r. spectra were obtained with an instrument operating at 60 Mc./sec.

Methyl Buta-2,3-dienoate (Ia).-Buta-2,3-dienoic acid 13 (10 g.) in ether (200 ml.) was treated at -78° with an excess of ethereal diazomethane. After 15 min., the excess of reagent was destroyed with acetic acid and the solution was washed successively with 2n-sodium carbonate solution and brine; it was then dried and distilled to give the ester (9.4 g., 80%), b.p. $50^{\circ}/33$ mm., $n_{D}^{20\cdot5}$ 1.4640 (lit.,²⁶ b.p. 48- $49^{\circ}/26$ mm., n_{D}^{25} 1.4635); n.m.r. τ 6.32 (3H, s, OMe), 4.85 (2H, d, J 6 c./sec., CH₂), and 4.45 (1H, t, J 6 c./sec., CH).

Ethyl 2-Methylbuta-2,3-dienoate (Ib).—This was prepared by Bestmann's procedure, ¹⁰ except that dichloromethane was used as solvent. The ester (48%) had b.p. $42-44^{\circ}/9$ mm. (lit.,¹⁰ 52°/11 mm.), n_D^{20} 1.4648 (Found: C, 66.4; H, 7.8. Calc. for $C_7H_{10}O_2$: C, 66.6; H, 8.0%); n.m.r., τ 8.74 (3H, t, J 7 c./sec., CH₃ of Et), 8.16 [3H, t, J 3 c./sec., C(2)-Me], 5.86 (2H, q, J 7 c./sec., CH₂ of Et), and 5.03 (2H, q, J 3 c./sec., CH₂=).

Ethyl 2-Methylpenta-2,3-dienoate (Ic).-Ethyl triphenylphosphoranylpropionate 27 (24.2 g.) and propionyl chloride (3.08 g., freshly redistilled) were heated under reflux in dichloromethane (100 ml.) for 45 hr. After evaporation of the solvent, the residue was extracted twice with light petroleum, and the extracts were evaporated. The oil (2.8 g.), which was shown by its n.m.r. spectrum to contain ca. 10% of propionic anhydride, was shaken for 5 min. with sodium hydrogen carbonate (2 g.), water (50 ml.), and ethanol (50 ml.). Re-isolation with light petroleum followed by distillation gave ethyl 2-methylpenta-2, 3-dienoate (2.1 g., 45%), b.p. 53—55°/10 mm., n_D^{20} 1.4632 (Found: C, 68.6; H, 8.6. $C_8H_{12}O_2$ requires C, 68.5; H, 8.6%); n.m.r. τ 8.74 (3H, t, J 7 c./sec., CH₃ of Et), 8.24 [3H; d, J 7 c./sec., C(5)-H₃], 8·19 [3H, d, J 3 c./sec., C(2)-Me], 5·88 [2H, q, J 7 c./sec., CH₂ of Et], and 4.68 [1H, m, C(4)-H].

Ethyl 2,4-Dimethylpenta-2,3-dienoate (Ie).-Triethyl phosphonopropionate ²⁸ (12 g.) was added dropwise to a stirred suspension of sodium hydride (2.4 g. of a 50% oil dispersion) in dimethoxyethane (50 ml., dried by reflux over CaH₂), the temperature being kept below 30° during the addition. When evolution of hydrogen ceased (1 hr.), the stirred solution was cooled to -30° and was treated with a cold (initially -78°) solution of dimethylketen ²⁹ (ca. 4 g.) in dry dimethoxyethane (ca. 80 ml.). The mixture was warmed to 50° during 1 hr., and was then cooled and poured into water (ca. 1 l.). The allene (1.3 g., 17%), isolated by extraction with light petroleum and distilled, had b.p. 47—48°/2 mm. (lit., ¹⁰ 66—67°/11 mm.), n_D^{20} 1.4600 (Found: C, 70.3; H, 9.2. Calc. for $C_9H_{14}O_3$: C, 70.1; H, 9.15%);

²⁶ J. J. Drysdale, H. B. Stevenson, and W. H. Sharkey, J. Amer. Chem. Soc., 1959, 81, 4908. ²⁷ O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser,

and P. Zeller, *Helv. Chim. Acta*, 1957, 40, 1242.
 ²⁸ A. E. Arbuzov and I. I. Razumov, *J. Russ. phys.-chem. Soc.*, 1929, 61, 623 (*Chem. Abs.*, 1929, 23, 4444).
 ²⁹ C. W. Smith and D. G. Norton, *Org. Synth.*, 1963, Coll.

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²² S. D. Andrews and A. C. Day, Chem. Comm., 1967, 902.

²³ A. C. Day and P. Hindle, unpublished work.

²⁵ R. B. Woodward and G. Small, jun., *J. Amer. Chem. Soc.*, 1950, **72**, 1297; D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, ibid., 1965, 87, 5191.

n.m.r., τ 8.75 (3H, t, J 7 c./sec., CH3 of Et), 8.23 (9H, s, C-Me), and 5.90 (2H, q, J 7 c./sec., CH₂ of Et).

Attempts to prepare this compound by the reaction of isobutyryl chloride with ethyl triphenylphosphoranylpropionate in dichloromethane were unsuccessful. (With tetrahydrofuran as solvent, Bestmann and Hartung¹⁰ obtained the compound in 42% yield from these starting materials.)

Ethyl 4-Methylpenta-2,3-dienoate (Id).-Triethyl phosphonoacetate³⁰ (11 g.) and dimethylketen (ca. 4 g.) gave, under the conditions described in the preceding experiment, the allene (1.8 g., 26%), b.p. 47–48°/3 mm., $n_{\rm D}^{20}$ 1.4600 (lit.,³¹ b.p. 99—102°/60 mm., n_D^{18} 1·4580) (Found: C, 68·8; H. 8.7. Calc. for C₈H₁₂O₂: C, 68.5; H, 8.6%); n.m.r., τ 8.75 (3H, t, J 7 c./sec., CH₃ of Et), 8.21 (6H, d, J 3 c./sec., CMe₂), 5.91 (2H, q, J 7 c./sec., CH₂ of Et), and 4.70 [1H, septet, J 3 c./sec., C(2)-H].

4-Methylpent-2-yn-4-ol.—To a stirred solution of sodamide (from 52 g. of sodium metal) in liquid ammonia (21.) was added 2-(1',1'-dimethylpropynyloxy)tetrahydropyran³² (376 g.) during 30 min. The flask was cooled in an acetonesolid carbon dioxide bath and methyl iodide (320 g.) was added dropwise during 2 hr. The mixture was stirred for a further 3 hr., after which it was treated with ammonium chloride (40 g.). After evaporation of the ammonia, the solid was extracted with ether $(3 \times 100 \text{ ml.})$ and then dissolved in water (600 ml.). The aqueous solution was extracted with ether $(3 \times 150 \text{ ml.})$, and the combined ethereal solutions were dried and evaporated. A small sample of the oil was distilled to give 2-(1,1-dimethylbut-2ynyloxy)tetrahydropyran, b.p. 88°/15 mm. (Found: C, 72·15; H, 9.8. C₁₁H₁₈O₂ requires C, 72.5; H, 10.0%); n.m.r., τ 8.62 and 8.58 (6H, s, CMe₂ (nonequivalent)] and 8.18 (3H, s, MeC=). The tetrahydropyranyl protons gave broad absorptions at τ 8.25–8.55 (6H), 5.9–6.8 (2H), and 4.85– 5.1 (1H). The bulk of the crude tetrahydropyranyl ether was shaken vigorously with ether (500 ml.) and 2N-sulphuric acid (500 ml.) for 20 hr. The ethereal layer was dried and distilled to give 4-methylpent-2-yn-4-ol (174 g., 79%), b.p. 78°/100 mm. (lit., 33 b.p. 80-81°/100 mm.) (Found: C, 73.1; H, 10.1. Calc. for C₆H₁₀O: C, 73.4; H, 10.3%; n.m.r., $\tau 8.58$ (6H, s, CMe₂), 8.22 (3H, s, MeC=), and 6.32 (1H, s, OH).

Treatment of 3-methylbut-1-yn-3-ol with sodamide and methyl iodide in liquid ammonia gave solely 4-methoxy-4methylpent-2-yne, the product of CO-dimethylation [τ 8.65 (6H), 8.16 (3H), and 6.76 (3H)].

2,4-Dimethylpenta-2,3-dienonitrile (Ig).---A mixture of 4-methylpent-2-yn-4-ol (36 g.), copper(I) cyanide (50 g.), potassium cyanide (24 g.), copper bronze (0.4 g.), and hydroquinone (10 mg.) was treated with 47% hydrobromic acid (160 g.) and was then shaken at room temperature for 3 days. After addition of the mixture to water (300 ml.) and ether (300 ml.), the layers were separated, and the aqueous laver was extracted with ether. The combined ethereal solutions were dried and fractionally distilled to give the allenic nitrile (Ig) (15.0 g., 38%) b.p. 57-59°/14 mm. (Found: C, 78.8; H, 8.5; N, 12.6. C7H9N requires C, 78.5; H, 8.5; N, 13.1%); n.m.r., 7 8.19 and 8.13 (ratio 2:1).

After a small intermediate fraction (0.2 g.; b.p. $65-70^{\circ}/$ 14 mm.; Br: 34%), continued distillation gave a mixture

 G. M. Kosolapoff, J. Amer. Chem. Soc., 1946, 68, 1103.
 E. R. H. Jones, G. H. Whitham, and M. C. Whiting, J. Chem. Soc., 1957, 4628.

of allene dimers (20.1 g., 51%), b.p. 122-124°/14 mm., which gradually solidified. Preparative t.l.c. [ether-light petroleum (1:9), three elutions] of a portion (810 mg.) gave two fractions, (A) (560 mg.) and (B) (80 mg.). Fraction (A) had m.p. 51-53° (from hexane) (Found: C, 78.7; H, 8.3; N, 12.75. $C_{14}H_{18}N_2$ requires C, 78.5; H, 8.5; N, 13.1%); m/e 214; ν_{max} 2225m and 2210s cm.⁻¹ (C=N); λ_{max} 275 m μ $(\varepsilon 16,300);$ n.m.r., $\tau 8.70, 8.60, 8.53, 8.48, 8.10, 8.05, 8.03,$ and 7.95, the areas of the regions 8.48-8.70 and 7.95-8.10 being equal. This fraction, though crystalline, was probably a mixture of dimers. Fraction (B), probably a single allene dimer, had m.p. 75-77° (Found: C, 78.7; H, 8.5; N, 12.9%); m/e 214; ν_{max} 2235m cm.⁻¹ (C=N); λ_{max} 252 m μ (ϵ 31,400); n.m.r., τ 8.29 (6H, s), 8.16 (6H, $w_{\frac{1}{4}}$ 2 c./sec.), and 8.10 (6H, s).

The allenic nitrile gave a similar mixture of dimers when set aside at room temperature.

When hydrogenated in ether over 10% palladium charcoal, the allene (Ig) absorbed 1 mol. of hydrogen, to give 2,4-dimethylpent-2-enonitrile, b.p. 50-60° (bath)/12 mm. (Found: C, 76.4; H, 10.5; N, 13.0. $C_7H_{11}N$ requires C, 77.0; H, 10.2; N, 12.8%); v_{max} 2220 m(C=N) and 1645w cm.⁻¹ (C=C); n.m.r., τ 8.95 (6H, d, J 7 c./sec., CMe₂), 8.10 [3H, d, J 1.5 c./sec., C(2)-Me], 6.9-7.5 [1H, m, C(4)-H], and 4.08 [1H, d, (J 7 c/.sec.) of quartets (J 1.5 c./sec.), C(3)-H].

Cycloadditions with 2-Diazopropane.-Unless otherwise stated, the allenes were treated in the dark at 0° for 12-16 hr. with an excess of a ca. 15% solution of 2-diazopropane in ether.¹⁵ When multiple additions of the diazoalkane were required, they were made at 24 hr. intervals. Volatile materials were removed by distillation and the residues processed as indicated.

5,5-Dimethyl-3-methoxycarbonyl-4-methylene-2-pyrazoline (V).--Methyl buta-2,3-dienoate (2 g.) and 2-diazopropane (1.4 g.) in ether (150 ml.) gave, on recrystallisation from ether-light petroleum, the 4-methylene-2-pyrazoline (V) (2.1 g., 61%), m.p. 95-96° (Found: C, 57.1; H, 7.2; N, 16.7. $C_8H_{12}N_2O_2$ requires C, 57.1; H, 7.2; N, 16.7%); m/e 168; v_{max.} 3415m (NH), 1720 (CO₂Me), and 3010w, 1635w, and $\overline{895}$ m cm.⁻¹ (CH₂=); $\lambda_{max.}$ (EtOH) 223and 330 mµ (ε 9000 and 10,100); n.m.r. (CDCl₃), τ 8.69 (6H, s, CMe₂), 6.14 (3H, s, OMe), 5.04 and 4.11 (each 1H, s, CH₂=), and 3.4 (1H, broad, NH removed by $D_{0}O$).

The compound isomerised to 5-methoxycarbonyl-3,3,4trimethyl-3H-pyrazole (VI)¹ when the reaction mixtures were distilled. Efficient conversion (85%) into the 3Hpyrazole (VI) was achieved by slow distillation (b.p. 68°/ 0.01 mm.) from glass wool, the product being identical in all respects with an authentic sample.¹ The pyrazoline (V)was unstable in the reaction solutions, and from the occurrence of a peak at λ_{max} ca. 250 mµ in aged solutions, the 3H-pyrazole (VI) was identified tentatively as one of its decomposition products.

5,5-Dimethyl-3-methoxycarbonyl-2-pyrazoline-4-spiro-3'-(5',5'-dimethyl-1'-pyrazoline) (VIII).-(a) Methyl buta-2.3dienoate (196 mg.) and 2-diazopropane (6 g.) gave, on recrystallisation from ethanol, the spiro-pyrazoline (VIII) (430 mg., 90%), decomp. above 115° (Found: C, 55.3; H, 7.6; N, 23.65. C₁₁H₁₈N₄O₂ requires C, 55.4; H, 7.6; N, 23.5%); m/e 210 (M – 28; no molecular ion peak); v_{max} (CHCl₃) 3380w (N-H), 1715s (CO₂Me); ν_{max} (Nujol) 3240

 ³² D. N. Robertson, J. Org. Chem., 1960, 25, 931.
 ³³ A. I. Zakharova, Zhur. obshchei Khim., 1947, 17, 686 (Chem. Abs., 1948, 42, 1871f).

(broad, N–H), 1700s (CO₂Me), 1570w (N=N), and 1530mw cm.⁻¹ (C=N); λ_{max} (EtOH) 223, 300, and 348 mµ (ε 3380, 9100, and 2600); λ_{max} (benzene) 348 mµ (ε 2050); n.m.r. (100 Mc./sec., CDCl₃), τ 8·83, 8·78, 8·64, and 8·37 [each 3H, s, C(5)- and C(5')-Me₂], 8·64 and 7·99 (each *ca.* 1H, d, *J* 14 c./sec., C(4')-H₂], 6·23 (3H, s, OMe), and 3·6 (1H, broad, NH). Solutions of the compound decomposed rapidly in daylight; the photolysis products will be reported later.

(b) The methylenepyrazoline (V) (100 mg.), treated with an excess of diazopropane, gave, on recrystallisation from ethanol, the spiro-compound (VIII) (110 mg., 78%), identical in all respects with the product from (a).

Methyl Pyruvate 1,1-Dimethylhydrazone.—Methyl pyruvate ³⁴ (350 mg.) and 1,1-dimethylhydrazine (210 mg.) were warmed together briefly at 100°, then sodium hydroxide pellets were added. The mixture separated into two layers. The upper, organic phase was collected with ether, dried (sodium hydroxide), and distilled to give the 1,1-dimethyl-hydrazone (300 mg., 61%), b.p. 81°/15 mm., n_D^{21} 1.4810 (Found: C, 49.85; H, 8.2; N, 19.15. C₆H₁₂N₂O₂ requires C, 50.0; H, 8.4; N, 19.4%); λ_{max} , 310, shoulder at 210 mµ (ϵ 2980 and 5100); λ_{max} , (EtOH) 305, shoulder at 213 mµ (ϵ 4270 and 4550); n.m.r. (CDCl₃), τ 7.97 (3H, s, C-Me), 7.26 (6H, s, NMe₂), and 6.29 (3H, s, OMe).

3-Ethoxycarbonyl-4-methylene-3,5,5-trimethyl-1-pyrazoline (II).—Ethyl 2-methylbuta-2,3-dienoate (1.5 g.) and 2diazopropane (2 × 6 g.) gave, on distillation, the 4methylene-1-pyrazoline (II) (2.29 g., 98%), b.p. 71—73°/0·15 mm., n_D^{20} 1.4530 (Found: C, 61·2; H, 8·1; N, 14·3. C₁₀H₁₆N₂O₂ requires C, 61·2; H, 8·2; N, 14·3%); m/e 168 (M — 28; no molecular ion peak); ν_{max} 3080w, 1660w, and 870m (CH₂=), 1550w, (N=N), and 1750s cm.⁻¹ (CO₂Et); λ_{max} . 328 mµ (ε 190); λ_{max} . (EtOH) 326 mµ (ε 165); n.m.r., τ 8·85 (3H, t, J 7 c./sec., CH₃ of Et), 8·67 [6H, slightly broadened singlet, C(5)-Me₂], 8·50 [3H, s, C(3)-Me], 5·95 (2H, q, J 7 c./sec., CH₂ of Et), and 5·17 and 4·97 (each one H, s, CH₂=). The crystalline residue from distillation of the pyrazoline was recrystallised from hexane to give 3-ethoxycarbonyl-3,5,5-trimethyl-1-pyrazoline-4-spiro-3'-

(5',5'-dimethyl-1'-pyrazoline) (IX) (22 mg., 0.7%) as needles m.p. 89—90° (Found: C, 58·4; H, 8·3; N, 21·0. $C_{13}H_{22}N_4$ -O₂ requires C, 58·6; H, 8·3; N, 21·0%); m/e 210 (M – 56, *i.e.*, loss of 2N₂; no molecular ion peak); v_{max} 1730s (CO₂Et) and 1570w cm.⁻¹ (N=N); λ_{max} (EtOH) 327 mµ (ε 400); n.m.r. (100 Mc./sec.), five CH₃ signals (τ 8·84, 8·73, 8·70, 8·58, and 8·57) overlapping an ethyl triplet and one doublet of an AB pattern, and signals at τ 8·37 [d, J 13 c./sec., one of the C(4')-protons] and 5·84 (q, J 7 c./sec., CH₂ of Et).

3-Ethoxycarbonyl-4-ethylidene-3,5,5-trimethyl-1-pyrazoline (III).-Ethyl 2-methylpenta-2,3-dienoate (1.3 g.) and 2-diazopropane $(2 \times 6 \text{ g.})$ gave an oil (1.93 g.), a portion (1.74 g.) of which was separated by t.l.c. [ether-light petroleum (1:9), 2 elutions] into two components. The first, the 4-ethylidene-1-pyrazoline (III) (1.703 g., 96%), had b.p. 66-67°/0·1 mm., n_D²⁰ 1·4605 (Found: C, 62·8; H, 8·7; N, 13.0. $C_{11}H_{18}N_2O_2$ requires C, 62.8; H, 8.6; N, 13.3%); m/e 182 (M - 28; no molecular ion peak); v_{max} 3040w (CH=), 1750s (CO₂Et), and 1560w cm.⁻¹ (N=N); λ_{max} 327 mµ (ε 174); λ_{max} (EtOH) 325 mµ (ε 151); n.m.r. (100 Mc./ sec.), τ 8.76 (3H, t, J 7 c./sec., CH₃ of Et), 8.63 and 8.60 [each 3H, s, C(5)-Me2], 8.40 [3H, s, C(3)-Me], 8.35 (3H, d, J 7 c./sec., MeC=), 5.85 (2H, q, J 7 c./sec., CH₂ of Et), and 4.63 (1H, q, J 7 c./sec., CH=). The second component (<5 mg.), an oil which rapidly darkened, had m/e 210 (weak) and 182 (strong).

3,3-Dimethyl-4-ethoxycarbonyl-5-isopropylidene-1-pyrazoline (XIIId).—Ethyl 4-methylpenta-2,3-dienoate (0·4 g.) and 2-diazopropane (12 g.) gave, on distillation, the pyrazoline (XIIId) (0·575 g., 96%), b.p. 60—70° (bath)/0·1 mm., $n_{\rm D}^{20}$ 1·4795 (Found: C, 63·1; H, 8·7; N, 13·6. C₁₁H₁₈N₂O₂ requires C, 62·8; H, 8·6; N, 13·3%); m/e 210; $\nu_{\rm max}$ 1750s (CO₂Et), 1680w (C=C), and 1498w cm.⁻¹ (N=N); $\lambda_{\rm max}$ 255 and 350 mµ (ε 10,000 and 300); $\lambda_{\rm max}$ (EtOH) 259 and 344 mµ (ε 9500 and 320); n.m.r. τ 8·76 (3H, t, J 7 c./sec., CH₃ of Et), 8·70 [6H, slightly broadened singlet, C(3)-Me₂], 8·25 and 7·64 (each 3H, narrow multiplets, Me₂C=), 7·03 [one H, m, C(4)-H], and 5·91 (2H, q, J 7 c./sec., CH₂ of Et).

4-Ethoxycarbonyl-5-isopropylidene-3,3,4-trimethyl-1pyrazoline (XIIIe).—Ethyl 2,4-dimethylpenta-2,3-dienoate (2·3 g.) when treated with 2-diazopropane (3 × 12 g.) gave much unchanged allene ester. The residue (300 mg.) was subjected to t.l.c. [ether-light petroleum 1 : 9, 9 elutions] to give the pyrazoline (XIIIe) (170 mg., 5%), b.p. 65—75° (bath)/0·1 mm., n_D^{20} 1·4680 (Found: C, 64·3; H, 8·8; N, 12·7. C₁₂H₂₀N₂O₂ requires C, 64·25; H, 9·0; N, 12·5%); m/e 224; ν_{max} 1730s (CO₂Et), 1670w (C=C), and 1500w cm.⁻¹ (N=N); λ_{max} 258 and 355 mµ (ε 10,000 and 275, respectively); n.m.r., τ 8·95, 8·87, and 8·61 (each *ca.* 3H, s, ring methyls), 8·76 (*ca.* 3H, t, J 7 c./sec., CH₃ of Et), 8·26 and 7·65 (each 3H, s, Me₂C=), and 5·92 (2H, q, J 7 c./sec., CH₂ of Et).

4-Cyano-3,3-dimethyl-5-isopropylidene-1-pyrazoline (XIIIf).—4-Methylpenta-2,3-dienonitrile (If) ¹² (3 g.) and 2-diazopropane (2 × 12 g.) gave, on distillation, the pyrazoline (XIIIf) (4·9 g., 93%), b.p. 72—73°/0·1 mm., n_D^{20} 1·5002 (Found: C, 66·45; H, 7·7; N, 25·6. C₃H₁₃N₃ requires C, 66·2; H, 8·0; N, 25·75%); m/e 163; $\nu_{max.}$ 2240m (C=N), 1680m (C=C), and 1495m cm.⁻¹ (N=N); $\lambda_{max.}$ 252 and 353 m μ (ε 10,500 and 290); n.m.r., τ 8·63 and 8·47 [each 3H, s, C(3)-Me₂], 7·94 and 7·60 (each 3H, narrow multiplets, Me₂C=), and 6·90 [one H, m, C(4)-H].

4-Cyano-5,5-dimethyl-3-(1-methylvinyl)-2-pyrazoline (XVI). —The preceding compound (XIIIf) (305 mg.) was stirred for 3 hr. with a solution of potassium hydroxide (0.5 ml. of a saturated ethanolic solution) in ethanol (20 ml.). After dilution with water and isolation with ether, the oil (220 mg.) was separated by t.l.c. [ether-light petroleum (1:9), 10 elutions] into starting material (8 mg.) and the 2pyrazoline (XVI) (210 mg., 69%), $n_{\rm D}^{20}$ 1.4627 (Found: C, 66.1; H, 7.8; N, 25.85. C₉H₁₃N₃ requires C, 66.2; H, 8.0; N, 25.75%); m/e 163; $\nu_{\rm max}$ 3340s (N-H), 3095w, 1630m, and 890s (CH₂=), 2240m, (C=N), and 1560w cm.⁻¹ (C=N); $\lambda_{\rm max}$ 267 mµ (ε 12,400); n.m.r., τ 8.66 and 8.52 (each 3H, s, C(5)-Me₂], 7.98 (3H, narrow multiplet, MeC=), 6.43 [1H, $w_{\frac{1}{2}}$ 2 c./sec., C(4)-H], and 4.72 (2H, $w_{\frac{1}{2}}$ 3 c./sec., CH₂=).

Reaction of 2-Diazopropane with 2,4-Dimethylpenta-2,3dienonitrile (Ig).—The cyano-allene (2 g.) was treated with 2-diazopropane (4×6 g., 30% ethereal solution). Distillation gave much unchanged cyano-allene. The residue (1·3 g.) was separated by t.l.c. [ether-light petroleum (1:9), 5 elutions] into five components.

The first component (44 mg.), a very unstable oil, had b.p. 50—60° (bath)/0·1 mm. (Found: C, 55·4; H, 6·7. $C_{10}H_{14}$ -BrN requires C, 52·6; H, 6·2%); m/e 229 and 227 (contains Br); ν_{max} 2210 cm.⁻¹ (C=N); n.m.r., signals at τ 9·1(m), 8·84(s), 8·72(s), 8·60(s), and 7·95(s) of roughly equal intensity. Presumably this compound is, or derives from, an impurity in the starting material.

³⁴ F. Arndt, M. Ozansoy, and H. Üstünyar, Rev. Fac. Sci. Univ. Istanbul, 1939, **4**, 83 (Chem. Abs., 1939, **33**, 6246⁸).

second component, 1-(2-cyanoprop-1-enyl)-1,2,2-The trimethylcyclopropene (XVII) (15 mg., 0.54%), had b.p. 50-60° (bath)/0·1 mm. (Found: C, 80·6; H, 9·9; N, 9·5. C₁₀H₁₅N requires C, 80.5; H, 10.1; N, 9.4%); m/e 149; ν_{max} , 3060w and 1630w (C=C), and 2200m cm.⁻¹ (C=N); $\lambda_{\text{max.}}^{\text{max.}}$ 220 mµ (ϵ 1290); n.m.r., τ 9.48 and 9.25 [each 1H, d, $\int 5 \text{ c./sec., C(3)-H}_2$], 8.96 and 8.83 [each 3H, s, C(2)-Me₂], 8.72 [3H, s, C(1)-Me], 8.07 (3H, unsymm. d, J ca. 1.5 c./sec., MeC=), and 3.85 (1H, m, vinyl-H).

The third component, an oil (5 mg.), had m/e 214, corresponding to a dimer of the cyano-allene.

The fourth component, 4-cyano-5-isopropylidene-3,3,4trimethyl-1-pyrazoline (XIIIg) (210 mg., 6.2%) had m.p. 34-35° (ex hexane) (Found: C, 66.9; H, 8.4; N, 24.0. $C_{10}H_{15}N_3$ requires C, 67.8; H, 8.5; N, 23.7%); m/e 177; $v_{max.}$ 2240m (C=N), 1670m (C=C), and 1490m cm.⁻¹ (N=N); $\lambda_{\rm max}$ 255 and 357 mµ (ϵ 8500 and 266, respectively); n.m.r., τ 8.79, 8.74, and 8.44 (each 3H, s, ring methyls), and 7.82 and 7.58 [each 3H, s (slightly broadened at high resolution), Me₂C=].

The fifth component (100 mg.) was contaminated with the preceding compound; t.l.c. as described above gave an oil (43 mg., 1·3%) [possibly 3-(2-cyanoprop-1-enyl)-3,5,5trimethyl-1-pyrazoline] which was too unstable to be distilled (Found: C, 66.9; H, 8.4; N, 22.1. C₁₀H₁₅N₃ requires C, 67.8; H, 8.5; N, 23.7%); m/e 177, 149 $(M - N_2)$; $\nu_{max.}$ 2210m (C=N) and 1550w cm $^{-1}$ (N=N); $\lambda_{max.}$ 328 mµ; n.m.r., 7 8.70, 8.67, and 8.36 (each 3H, s, ring-methyls), 7.85 (3H, broadened, MeC=), and 3.5 (1H, m, vinyl-H) and several peaks due to impurities. A similar sample (100 mg.) from a subsequent preparation was photolysed ($\lambda > 290 \text{ m}\mu$) in light petroleum (40 ml.). The product (56 mg., 67%) was shown by its n.m.r. spectrum to be the cyanopropenylcyclopropane (XVII) described above.

Photolysis of 3-Alkylidene-1-pyrazolines.—The compounds (XIII) (200-500 mg.) in light petroleum (30-60 ml.) were photolysed (Pyrex filter) under nitrogen with a mediumpressure, mercury-arc immersion lamp at room temperature. The products (XIV) were isolated by distillation.

1,1-Dimethyl-2-ethoxycarbonyl-3-isopropylidenecyclopropane (XIVd; 88%) had b.p. 80-90° (bath)/15 mm., $n_{\rm D}^{20}$ 1.4503 (Found: C, 72.7; H, 9.9. Calc. for C₁₁H₁₈O₂: C, 72.5; H, 10.0%; spectroscopic data (i.r. and n.m.r.) were closely similar to those reported by Meinwald et al.³⁵ $\label{eq:2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-isopropylidene-1,1,2-trimethylcyclo-2-Ethoxycarbonyl-3-Ethoxycarbon$

propane (XIVe) (91%) had b.p. 85-95° (bath)/15 mm., n_D²⁰ 1.4510 (Found: C, 73.2; H, 10.3. C₁₂H₂₀O₂ requires C, 73.4; H, 10.3%); m/e 196; n.m.r., τ 8.84(s), 8.80(s), 8.79 (t, J 7 c./sec.) and 8.71(s) [12H, C(1)-, C(2)-, and ethyl-CH₃ groups], 8.28 and 8.24 (each 3H, s, Me₂C=), and 5.95 (2H, q, J 7 c./sec., CH_{2} of Et).

2-Cyano-1,1-dimethyl-3-isopropylidenecyclopropane (XIVf) (84%) had b.p. 80—90° (bath)/15 mm., n_D^{20} 1.4560 (Found:

³⁵ J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, J. Org. Chem., 1965, **30**, 1039. ³⁶ S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, J. Chem. Soc. (C) 1002

J. Chem. Soc. (C), 1966, 1223.

C, 80.0; H, 9.7; N, 10.2. C₉H₁₃N requires C, 79.95; H, 9.7; N, 10.4%); m/e 135; v_{max} 2235s cm.⁻¹ (C=N); n.m.r., τ 8.73 and 8.62 [each 3H, s, $\overline{\rm C(1)}\text{-}{\rm Me_2}],$ 8.36 [1H, m, J 1.5 c./sec., C(2)-H], and 8.15 (6H, broadened, Me₂C=).

2-Cyano-3-isopropylidene-1,1,2-trimethylcyclopropane (XIVg) (71%) had b.p. 85-95° (bath)/15 mm., $n_{\rm D}^{20}$ 1.4640 (Found: C, 80.8; H, 9.9; N, 9.3. C₁₀H₁₅N requires C, 80.5; H, 10.1; N, 9.4%); m/e 149; v_{max} 2225s cm.⁻¹ (C=N); n.m.r. (CS₂), τ 8.79 (3H, s) and 8.63 (6H, s) (ring methyls), and 8.18 and 8.16 (6H, s, Me₂C=); n.m.r. (benzene), singlets of equal intensity at τ 9.18, 8.92, 8.70, 8.53, and 8.44.

4-Bromomethylene-3,3,5,5-tetramethyl-1-pyrazoline (XXII; X = Br).—1-Bromo-3-methylbuta-1,2-diene (XXI; X =Br) 36 (20 g.) and 2-diazopropane (2 \times 12 g.) gave, on evaporation and recrystallisation from hexane, the 1pyrazoline (XXII; X = Br) (8.3 g., 28%), m.p. 84-85° (Found: C, 44·4; H, 5·8; Br, 37·2; N, 13·25. C₈H₁₃BrN₂ requires C, 44.3; H, 6.0; Br, 36.8; N, 12.9%); m/e 218 and 216 (weak), m/e 190 and 188 (strong, M-28); $v_{\rm max}$ 3060w and 1650m (C=C) and 1550w cm. $^{-1}$ (N=N); λ_{max} 327 mµ (ϵ 245); λ_{max} (EtOH) 325 mµ (ϵ 195); n.m.r., τ 8.60 and 8.43 (each 6H, ring methyls) and 4.03 (1H, vinyl-H).

3,5-(Diethoxycarbonyl-3,5-dimethyl-4-methylene-1-pyrazoline (XX).-Ethyl 2-methylbuta-2,3-dienoate (0.205 g.) and ethyl 2-diazopropionate 37 (0.25 g.) were kept in the dark at 20° for 1 week. Distillation then gave the *pyrazoline* (XX) (282 mg., 68%), b.p. 95-105° (bath)/0.5 mm. (Found: C, 56.5; H, 7.1; N, 10.8. C₁₂H₁₈N₂O₄ requires C, 56.7; H, 7.1; N, 11.0%); m/e 226 (M - 28; no molecular ion peak); v_{max} 1740s (C=O), 1550w (N=N), and 870m cm⁻¹ ($\hat{C}H_2$ =); 327 mµ (ε 162); n.m.r., τ 8.75 (6H, t, J 7 c./sec., CH₃ of Et), 8.38 [6H, s, C(3)- and C(5)-Me], 5.85 (4H, q, J 7 c./sec., CH₂ of Et), and 4.80 (2H, s, CH₂=).

The allenic esters (Id) and (Ie) failed to react with ethyl 2-diazopropionate even after prolonged reaction times. The sole product (32%) when ester (Id) was kept at 40° for 5 days with the diazo-ester was a decomposition product of the latter, 3,5-diethoxycarbonyl-5-methyl-2-pyrazoline (the adduct of diazopropionic ester and its decomposition product, ethyl acrylate), which had b.p. 100-110° (bath)/ 0.1 mm. (Found: C, 52.6; H, 7.0; N, 11.8. C₁₀H₁₆N₂O₄ requires C, 52.6; H, 7.1; N, 12.3%); m/e 228; v_{max} 3360m (N-H), 1745s (5-CO₂Et), 1715s (3-CO₂Et), and 1580w cm.⁻¹ (C=N); λ_{max} 270 mµ (ϵ 6300); n.m.r., τ 8.91 and 8.88 (6H, overlapping triplets, J 7 c./sec., CH3 of Et), 8.50 [3H, s, C(5)-Me], 7·33 [1H, d, J 17 c./sec., C(4)-H], 6·60 [1H, d, J17 c./sec., C(4)-H], 5.81 (4H, overlapping quartets, J 7 c./sec., CH_2 of Et), and 3.60 (1H, broad, NH, removed by D_2O). This compound was also detected by n.m.r. in aged samples of ethyl diazopropionate.

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³⁷ T. Curtius and E. Müller, Ber., 1904, 37, 1261; cf. N. E. Searle, Org. Synth., 1963, Coll. Vol. 4, 424.