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ADDITION-CYCLIZATION OF VINYLDIAZOMETHANE WITH UNSATURATED COMPOUNDS[1]

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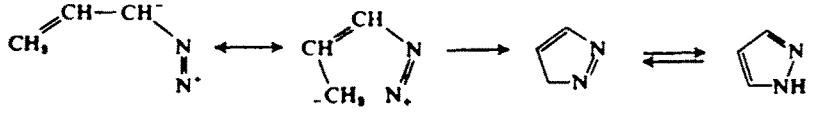
Abstract—Addition-cyclization of vinyldiazomethane with various olefins has been investigated. The products consisted of vinylpyrazolines, cyclopropanes and dienes. From methyl acrylate, a small amount of cyclopentenylcarboxylate was also obtained, the formation of which was interpreted as being due to the 1,5-dipolar structure of vinyldiazomethane. Generalized mechanisms concerned with addition-cyclization of vinyldiazomethane and with decomposition of intermediates have been presented, the latter involves a competition of carbanion- and hydride-attack on the carbonium ion moiety.

INTRODUCTION

ALTHOUGH experimental data has been accumulated on the addition-cyclizations of 1,3-dipolar reagents with unsaturated compounds,[2] the addition-cyclization reaction of vinyldiazomethane has been investigated only in preliminary form.[1,3]

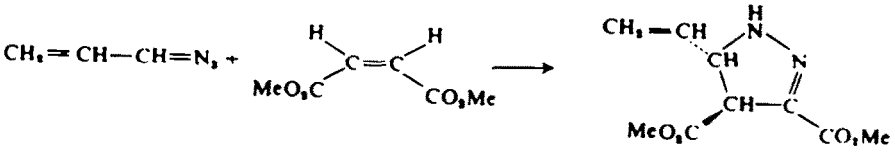
Vinyldiazomethane was reported to cyclize readily to pyrazole,[4] presumably through a 1,5-dipolar structure. In the addition reaction of vinyldiazomethane with fumarate or maleate, however, *only* 1,3-addition products were obtained.[1,3]



If other olefins (especially electronically asymmetric olefins) were used, vinyldiazomethane often gave non-nitrogenous products, cyclopropanes and olefins as well as 5-membered heterocyclic compounds. And, from acrylate, a small amount of a product (originating from 1,5-dipolar addition) was obtained. In this article, these results are discussed on the basis of mechanism.

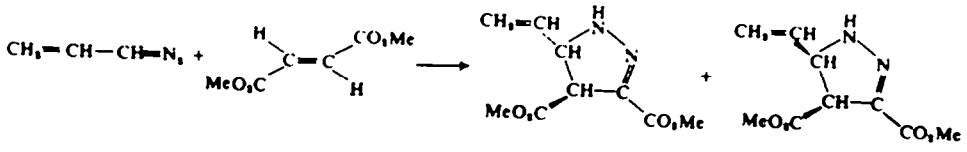
RESULTS AND DISCUSSION

Addition to maleate and fumarate. Dimethyl maleate and dimethyl fumarate are typical examples of 1,3-dipolar addition of vinyldizaomethane, giving vinylpyrazolinecarboxylates (I and II) without any appreciable decomposition.



I

[1] I. Tabushi, K. Takagi and R. Oda, *Tetrahedron Letters* 2075 (1964).
[2] see R. Huisgen, *Angew Chem.* 75, 604 (1963), a review and recent papers by Huisgen.
[3] I. Tabushi, K. Takagi and R. Oda, *J. Chem. Soc. Japan, Pure Chemistry Section* 85, 701 (1964).
[4] C. D. Hund and S. C. Lui, *J. Am. Chem. Soc.* 57, 2656 (1935).



I (30%) II (70%)

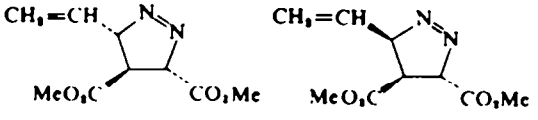
The structural proofs of I and II were obtained by UV, IR and NMR spectra, elementary analysis and chemical behaviour involving hydrogenation and conversion to the known pyrazole-3,5-dicarboxylic acid through 5-vinylpyrazoline-3-carboxylic acid.[1,3] Position of unsaturation in the ring was assigned as shown in the above scheme, because C=N was found to conjugate with carboxylate and not with the vinyl group. The relation was evident from the IR absorption corresponding to C=N which did not change appreciably on hydrogenation of the vinyl group (ν_{max}, ca. 1550 cm^{-1} for both compounds) and from UV absorptions cited below.

Dimethyl *cis*-5-vinyl-3,4-pyrazoline- dicarboxylate	Corresponding 5-ethyl derivative
λ_{max} = 294 mμ	λ_{max} = 302 mμ
ε_{max} = 9,390	ε_{max} = 10,300

Very close λ values (and also close ε values) in UV absorptions of vinyl and of ethyl derivatives are in accord with an unconjugated vinyl group.[5]

The stereochemistry of the products I and II was based on the spectral data and on the assumption that the *cis, cis*-stereoisomer was much less stable than the *cis, trans*-isomer in the formation of initial adducts, pyrazoline-1.[6]

Thus, maleate gave only *trans* (as for 4- and 5-substituents) pyrazoline derived from *cis, trans*-pyrazoline-1[7], but fumarate gave both *trans*- and *cis*-pyrazoline-2, derived from 3,4-*trans*-3,5-*cis* (Ia) and 3,4-*trans*-3,5-*trans*-pyrazoline (IIa), respectively. Compounds Ia and IIa have corresponding 1,3- and 1,2-steric interactions, and



Ia IIa

since these interactions seem to be of a similar order of magnitude, they enable the formation of both stereoisomers. Further discussion on the mechanism of the addition to fumarate and maleate is given later. (*vide infra*).

[5] The configurations were temporarily determined as 3-vinyl-pyrazoline-4,5-dicarboxylates but further study indicated that this structure was not correct. Comparison of the UV and IR spectral data in this literature gives, about 40 mμ lower wavelength-shift of λ_{max} in UV and about 10 cm^{-1} higher wave number-shift of C=N band in IR spectra than expected when the C—C—C—N system goes to C—C—C—N. Absence of such a remarkable shift in both UV and IR spectra during hydrogenation of vinyl indicates that no conjugation exists between vinyl and C=N. Besides the presence of two types of ester carbonyls is evident from IR spectra (strong absorption at 1730 anp 1690 cm^{-1}, the first is sharp and the latter is somewhat broad which seems to correspond to the conjugated carbonyl). The observation is also in accord with the above assignment of unconjugated vinyl.

[6] Previous assignments[1] of *cis* and *trans* were based on 3-vinyl (conjugated with C=N of the ring) so that these are not correct.

[7] Only a trace of *cis*-stereoisomer (from a 3,4-*cis*-3,5-*cis* isomer) was detected by IR spectra but this was not enough to be determined quantitatively.

Addition on various acceptor olefins. A considerable amount of de-nitrogenated products (cyclopropanes and olefins) were often obtained when various electron acceptor olefins were used and Table 1 shows the products obtained together with the available data on unsubstituted diazomethane in the literature. Consequently, the following generalization can be drawn:

(1) 5-Vinylpyrazolines are generally less stable than the corresponding 5-unsubstituted pyrazolines. The trend is evident on comparing the decomposition temperatures of both groups of compounds.

(a) In the reaction of vinyldiazomethane with some olefins, considerable amounts of non-nitrogenous products are formed.

(2) Pyrazolines from electronically asymmetric olefins give more olefinic products than those from less asymmetric olefins. (i.e. pyrazolines from less asym. olefins give more cyclopropane derivatives)

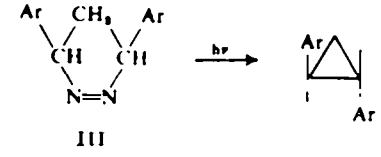
(a) 1,1-Disubstituted acceptor olefins give less stable pyrazoline, and when both substituents are electron withdrawing, olefinic products (non-nitrogenous) are given exclusively.

(3) 5-Vinylpyrazolines give more cyclopropane derivatives than the corresponding 5-unsubstituted pyrazolines.

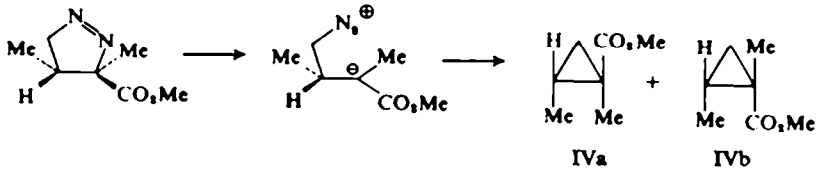
Based on the above generalization, the mechanism of addition-cylization as well as that of initial de-nitrogenation (not by thermal decomposition of pyrazoline) is discussed later.

There are two important suggestions in the literature on the mechanism of decomposition of pyrazoline. One, the free radical mechanism based on ESR spectra of the low temperature (77°K) photolysis of 3,5-diaryl-Δ^1-pyrazoline (III)[8] and the other, the ionic mechanism based on the stereochemistry of the products[9] (mainly C_3—C_4 rotation during the addition) and based on distribution of stereoisomers of cyclopropane products IVa and IVb from *cis* and *trans* methyl 3,4-dimethyl-Δ-^{1} pyrazoline-3-carboxylate.

In addition, a concerted mechanism has been presented.[10]



III



IVa IVb

[8] C. G. Overberger and J. Anselme, *J. Am. Chem. Soc.* **86**, 658 (1964).

[9] T. V. von Auken and K. L. Reinhart, *J. Am. Chem. Soc.* **84**, 3736 (1962).

[10] eg, Both of C—N bonds in pyrazoline or related compds were found to be ruptured (as a biradical) in a transition state. See, S. G. Cohen, R. Zand and C. Steel, *J. Am. Chem. Soc.* **83**, 2895 (1961). cf. R. J. Crawford, R. J. Dummel and A. Mishra, *ibid.* **87**, 3023 (1965) and D. E. McGeer *et al.*, *Canad. J. Chem.* **43**, 1407 (1965).

TABLE 1

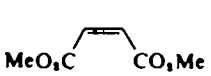
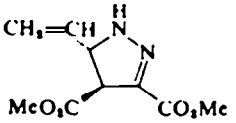
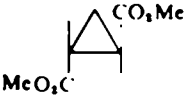
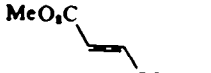
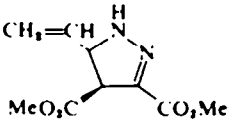
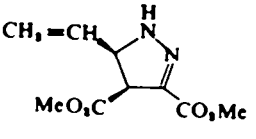
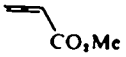
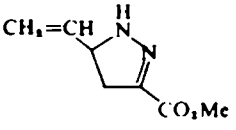
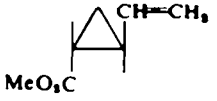
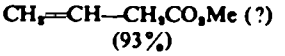
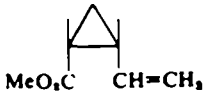
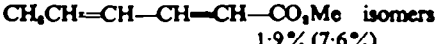
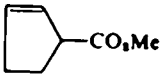
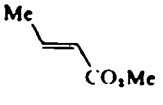
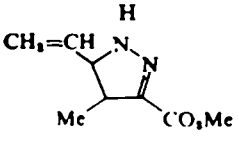
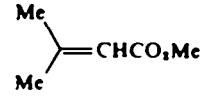
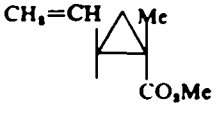
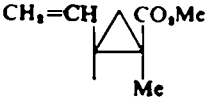
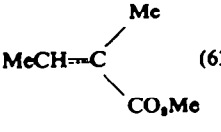
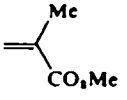
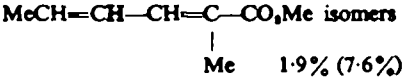
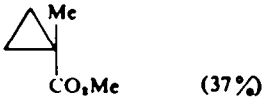
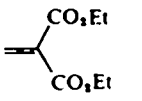
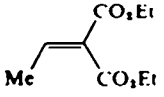
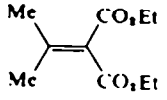
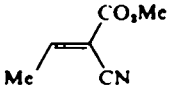
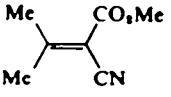
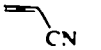
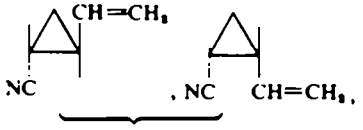
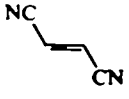
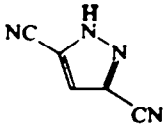
Starting olefin	Products from vinyldiazomethane, yield based on nitrosourethane,[a] dec temp observed by us		Products from diazomethane after dec (reported)
		35%(100%)[b] [120°]	180°  (33%)
		 21% (70%)[b] [122°]	 (2%)
	9% (30%) [120°]		 (65%)
	 14% (55%) [90°]	 2·3% (9·2%)	[150°]  (93%)
	 1·9% (7·6%)		
	 1·9% (7·6%)		
		0·2% (0·8%)	
		12% (48%) [140°]	140°  (100%)
			100°  (63%)
	17% (68%)	4·4% (18%)	
	 1·9% (7·6%)		 (37%)

TABLE 1 (*contd.*)

Starting olefin	Products from vinyldiazomethane, yield based on nitrosourethane,[a] dec temp observed by us	Products from diazomethane after dec (reported)
	CH_3—CH=CH—CH=C$(CO_2Et)_2$ and isomers 24% (96%)	
		[60°  (100%)
		room temp.
		 (100%)
	 olefins 20% (80%)	112° or above
	 4·1% (16%)	

[a] The yield based on a nitrosourethane, a precursor of vinyldiazomethane. The yield of vinyldiazomethane from the nitrosourethane is ca. 25% determined by esterification of benzoic acid.[c] The calculated yields of adducts based on vinyldiazomethane are given in parentheses.

[b] The yield of the adduct was better than that estimated by esterification presumably because very fast reaction (or complex formation) of vinyldiazomethane with maleate or fumarate.

[c] K. Auwers and F. König, *Liebigs Ann.* **496**, 252 (1932).

[d] W. G. Young, L. J. Andrews, S. L. Lindenbaum and S. J. Cristol, *J. Am. Chem. Soc.* **66**, 810 (1944).

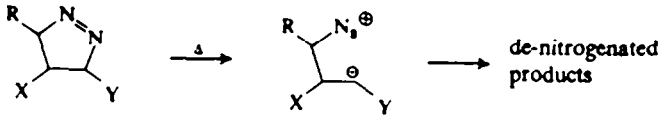
[e] S. M. Gurvich and A. P. Terentév, *Chem. Abstr.* **49**, 1048 (1955).

The free radical mechanism seems to be applicable only to limited cases with a less polar substituent and Auken's mechanism is not adequate to explain the effect of a 5-substituent of pyrazoline. Neither mechanism accounts for the ratio of olefinic products to cyclopropanes.

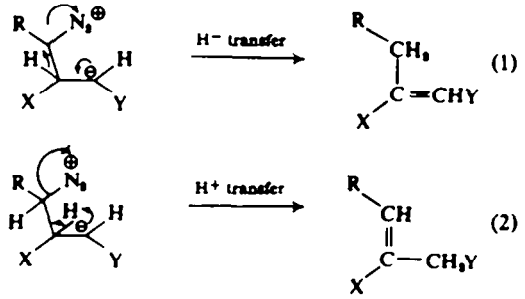
Substituent effect on the decomposition of pyrazoline. 1-Pyrazoline is generally assumed (and often proved) as the starting species of thermal decomposition or of photolysis even for stable 2-pyrazoline. Therefore, consideration of the decomposition mechanism should be made on 1-pyrazoline.

For 1-pyrazoline (V) when Y is a strong electron-withdrawing group, initial

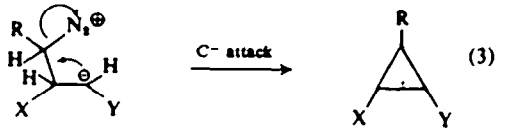
heterolytic cleavage to VI seems to be more important than biradical cleavage. As nearly all the adducts of diazomethanes and electron accepting olefins give 1-pyrazoline the ionic cleavage (whether it is concerted or not) should be the more important.



The products generally consist of olefins and cyclopropanes. The former can be derived through either H^- transfer reaction (1) or proton transfer reaction (2).



However, since the electron-withdrawing ability of Y is greater than that of X (by considering the orientation in initial addition step), a contribution of the mechanism (2) should be much smaller compared with that of (1) and/or (3), especially in the



cases considered. The mechanism (3) corresponds to nucleophilic attack of carbanion to form a cyclopropane derivative. Support for the above mechanism is found in the observed results:

In general, principal olefinic products were terminal olefins attached with an electron-withdrawing group on the end C atom, in accord with the expected products from the mechanism (1). Competition between reaction (1) and (3) is controlled by the following factors.

(a) *Electron deficiency on* C_5. This would accelerate both (1) and (3), but the rate of (1) should be accelerated more than that of (3), because the very unstable $C_5^{\oplus}$ (or $C_5^{\delta+}$) can not exist long enough for bond-making with C_3.[10a]

(b) *Availability of* H *on* C_4 *as a hydride ion.* Electron donating group X makes H on C_4 more available as hydride ion, thus favouring reaction (1). X does not seem to have much influence on reaction (3).

(c) *Nucleophilicity of* C_3. This again would accelerate both (1) and (3). But very reactive carbanion $C_3^{\ominus}$ (or $C_3^{\delta-}$) can attack C_5 prior to the formation of carbonium ion from C_5 so that this effect would affect (3) rather than (1).

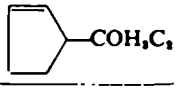
[10a] If electron deficiency at C_5 is serious, then heterolytic cleavage of C_5—N should be retarded and no effective carbanion is available. Even in this stage, hydride ion can interact with electron deficient center, $C_5^{\delta+}$.

Effect of substituent of C_3, C_4 and C_5 position on the product ratio can be interpreted by factors (a), (b) and (c). From (a) Electron-donating R increases cyclopropanes and decreases olefins; from (b) Electron-donating X (on C_4) increases olefin; from (c) Strong electron-withdrawing Y (on C_3) increases olefin and weak electron-withdrawing Y increases cyclopropane. These interpretations are in good agreement with observations (2) (2a) and (3) on page 3.

A decomposition rate of 2-pyrazoline is dependent on the isomerization rate from 2-pyrazoline to 1-pyrazoline, as well as on the stability of the ionic transition state (whether it is concerted or not). A 5-vinyl group accelerates the isomerization rate by its inductive effect on N—H and also it stabilizes the ionic intermediate (this must be a main effect) by an allylic conjugation with the carbonium ion. Observed result (1) can be interpreted by these factors.

The decomposition of 3,3-disubstituted-5-H (or vinyl)-pyrazoline (observation (2a)) may be correlated with an absence of isomerization from 1-pyrazoline to 2-pyrazoline.

TABLE 2. SOLVENT EFFECT ON ISOMER DISTRIBUTION IN THE ADDITION OF VINYLDIAZOMETHANE ON METHYL ACRYLATE

Solvent	Product (% on nitrosourethane)		de-N_2 Product composition (%)			
	Pyrazoline	de-N_2	*cis*Δ	*trans*Δ	olefins	
CH_2Cl_2	0	33·0	34	36	29	1
$(C_2H_5)_2O$	13·6	6·4	30	36	30	4
CH_3NO_2	7·7	10·8	17	56	27	0
Pyrolysis of pyrazoline			34	39	27	0

Formation de-nitrogenated products. On the basis of the decomposition data of pyrazoline, complex reaction products from diazomethanes and electrophilic olefins result from the partial decomposition of the initial adducts, pyrazolines. Vinyldiazomethane, especially, gives less stable pyrazolines so that even in mild condition, decomposition of pyrazolines is important.

However, an alternative may exist to give de-nitrogenated products directly from an ionic intermediate and not through pyrazoline. Methyl acrylate, for example, gives a considerable amount of de-nitrogenated products even in conditions where the corresponding pyrazoline is sufficiently stable (decomposition temp 90°).

Table 2 shows the effect of solvents on the product distribution in the reaction of methyl acrylate in order to determine if the alternative mechanism is important.

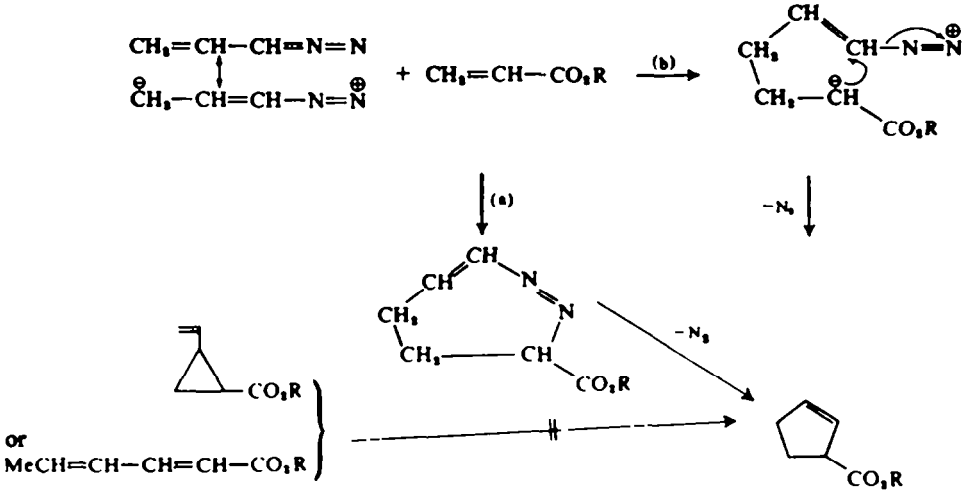
Cyclopentenecarboxylate probably arises from ionic intermediate through 1,5-type addition (*vide infra*) and *cis* to *trans* ratio of cyclopropanes varies in a very polar solvent (nitromethane). These two observations indicate that the decomposition through ionic intermediate is, at least, operative, which reflects the solvent effect on product distribution. Obviously, the decomposition and cyclization are competing and through very similar transition states because, in methylene chloride, no pyrazoline was obtained but product distribution was very similar to that from pyrolysis of pyrazoline.[11]

[11] This observation also shows that de-nitrogenation in methylene chloride mainly through pyrazoline

Stability of the ionic intermediate depends on a substituent (Table 1) as well as solvent. For example, fumarate and maleate gave no de-nitrogenated product during the addition reaction, and they gave pyrazoline in a practically quantitative yield. This behaviour can be interpreted by substituent effects on stability of pyrazolines (*loc. cit.*) and by stability of the ionic intermediate. The latter may be correlated with concerted addition of acceptor olefins of symmetric electron-density by means of multi-center complex.

A possibility of participation of 1,5-*dipolar structure.* The possibility of participation of the 1,5-addition mechanism was observed only in the case of methyl acrylate. Among the products already discussed (namely, pyrazoline, cyclopropanes and olefins) a small amount of cyclopentenecarboxylate was obtained. This cyclized product can only be explained by the addition of carbanion at C_5 either through mechanism (a) or (b), because the possibility of isomerization from other products was excluded by the following: First, 5-vinyl-3-pyrazolinecarboxylate did not give cyclopentenecarboxylate on heating but gave vinylcyclopropanes and olefins. Second, 2-vinylcyclopropanecarboxylates or hexadienoates remained unchanged on further heating at a decomposition temperature.

This is the first instance of intermolecular addition involving an 1,5-dipolar structure.



EXPERIMENTAL

Vinyldiazomethane. Allylamine was prepared from allylisothiocyanate[13] and the former was converted to N-nitrosoallylurethane through allylurethane.[13,14] As N-nitrosoallylurethane was not stable enough to be purified by distillation or any other common purification procedure, it was used without further purification. Nitrosation was repeated until no more absorption of NH(streching) was observed in IR spectra. (Twice nitrosation was found practically satisfactory.)

Vinyldiazomethane was prepared by means of Hund's procedure[4] with some minor modifications.[5] Preparation and purification of vinyldiazomethane were conducted in the cold and dark, and

[13] M. T. Leffler, *Organic Syntheses* Coll. Vol. 2, 24 (1943).

[14] cf. preparation of N-nitrosomethylurethane, W. W. Hartman, R. Phillips, *Organic Syntheses* Coll. Vol. 2, 464 (1943).

[14] cf. preparation of N-nitrosomethylurea, F. Arndt, *Organic Syntheses* Coll. Vol. 2, 461 (1943).

used as an ethereal soln immediately after purification. Vinyldiazomethane had characteristic absorptions at 2080 cm^{-1} (diazo group) and 1610 cm^{-1} (C=C) in an IR spectrum.

Reaction of vinyldiazomethane with methyl maleate. See the previous paper[9] (including the detn of adduct structure and also following paper.[16]

Reaction of vinyldiazomethane with methyl fumarate. Into an ethereal soln of vinyldiazomethane (from 0·2 mole of the nitroso compound), 11 g (0·052 mole) dimethyl fumarate (powder) was added in small portions at room temp in the dark until the red color of the diazo compound almost disappeared. A crude mixture of *cis*- and *trans*-dimethyl-5-vinyl-Δ^2-pyrazoline -3,4-dicarboxylate (16.2 g) was obtained on distillation of the solvent. Recrystallization of the crude mixture from benzene (15 ml) gave 4·6 g of the *cis*-isomer (m.p. 122°). It decomposed at m.p. ν_{max}, 3240 cm^{-1} (NH), 1730 and 1690 cm^{-1} (C=O), 1635 cm^{-1} (C=C), 1550 cm^{-1} (C=N), 995, 945 and 935 cm^{-1} (the former and one of the latter two, C=CH_2).

UV spectrum (95% EtOH): λ_{max} at 294 mμ (ε_{max} = 9390). (Found: C, 50·84; H, 5·84; N, 13·53 $C_9H_{12}O_4N_2$ requires: C, 50·94; H, 5·70; N, 13·24%.)

The filtrate, after distilling off the solvent gave crystalline *trans* isomer on standing for a week. After recrystallization from a small amount of benzene, the *trans* isomer weighed 2·5 g (m.p. 56·57°). This ester was identical with dimethyl *trans*-5-vinyl-Δ^2-pyrazoline-3,4-dicarboxylate (no m.p. depression on mixing) obtained from dimethyl maleate.[9]

In order to determine the approximate ratio of *cis*- to *trans*-vinylpyrazolinedicarboxylates in the crude mixture, absorption at 935 and 946 cm^{-1} of the *cis* isomer was used (best in Nujor). A comparison of an IR spectrum of the crude mixture with those of calibrated mixtures of known ratio of isolated *cis* and *trans* isomers, a ratio of *cis* 7 : *trans* 3 was obtained.

Hydrogenation and hydrolysis of cis-5-*vinyl*-3,4-*pyrazoline*-Δ^2-*dicarboxylate.* Hydrogenation was carried out in EtOH with Pd-C catalyst. The 5-vinyl compound absorbed 1·02 mole H, giving the 5-ethyl compound which was recrystallized from benzene, m.p. 110° (dec temp, 165°). γ_{max}, 3250 cm^{-1} (NH), 1730 and 1690 cm^{-1} (C=O), 1540 cm^{-1} (C=N). λ_{max} at 302 mμ, (ε_{max} = 10,300 in 99·5% EtOH). (Found: C, 50·52; H, 6·59; N, 13·16 $C_9H_{14}O_4N_2$ requires: C, 50·46; H, 6·59; N, 13·08%.)

Hydrolysis of the *cis* ester was performed with alcoholic NaOHaq (50/50 vol%). On acidification followed by extraction with ether, a white powder was obtained. After recrystallization from water, it melted at 183° (2 g from 4·5 g of ester). The acid was identical with 5-vinyl-Δ^2-pyrazoline 3,4-dicarboxylic acid obtained from the *trans* isomer[9] (from the addition of dimethyl maleate) (no m.p. depression on mixing).

Reaction of vinyldiazomethane with methyl acrylate. Into an ethereal soln of vinyldiazomethane (from 0·1 mole of the nitroso compound), 8·6 g (0·1 mole) methyl acrylate containing 1 wt % of N-phenyl-β-naphthylamine (as an inhibitor to polymerization of acrylate) was added and the mixture was stirred for 1 hr at room temp until a red color of vinyldiazomethane completely disappeared. After distilling off the solvent and methyl acrylate at reduced press, a colorless liquid was obtained with considerable evolution of N.[16] If distillation was performed below 80°, 0·8 g of distillate was obtained at 68–70° (35 mm Hg). Analysis showed that the distillate was a de-nitrogenation product. (Found: C, 66·65; H, 7·97 Calc. for $C_6H_{10}O_2$: C, 66·67; H, 7·94%.) IR spectrum, 1735 cm^{-1} (C=O), 1635 cm^{-1} (C=C), 1000, 920, 910 and 795 cm^{-1}. This liquid consisted of methyl esters of *cis*- and *trans*-2-vinylcyclopropanecarboxylic acid, methyl 2-cyclopentenecarboxylate and possible isomers of methyl hexadienoate-1. The composition was determined for saturated compounds obtained by hydrogenation of the mixture with authentic samples.[16] Further distillation of the residue gave 2·1 g of methyl 5-vinyl-Δ^2-pyrazoline-3-carboxylate. b.p. 115–117° (4 mmHg), n_D^{19} 1·5261. IR spectrum; 3280 cm^{-1} (NH), 1700 cm^{-1} (C=O), 1650 cm^{-1} (C=C), 1565 cm^{-1} (C=N), 1000 and 935 cm^{-1} (C=CH_2). λ_{max} at 294 mμ (ε_{max}, 8430 in 95% EtOH). (Found: C, 54·48; H, 6·89; N, 18·11, $C_7H_{10}O_2N_2$ requires: C, 54·53; H, 6·54; N, 18·17%.)

Similar procedures were adopted for the reactions in various solvents.

Methyl 5-vinyl-Δ^2-pyrazoline-3-carboxylate was pyrolyzed at 180–190° to give a mixture of de-nitrogenated products (b.p. 153–155°, 760 mm Hg) which were analysed by the procedure used for the initial de-nitrogenated products.

[16] Detailed description of the determination procedure is discussed in a separate paper,[16a] I. Tabushi, K. Takagi and R. Oda, *J. Chem. Soc. Japan, Pure Chemistry Section* in press.

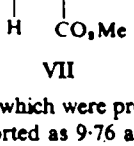
[16] Even at room temp, a gentle evolution of N was observed and NMR of the crude product showed the presence of olefin and cyclopropane.

Structural determination of methyl 5-vinyl-Δ^2-pyrazoline -3-carboxylate was accomplished by transformation of the ester to the known pyrazole-3,5-dicarboxylic acid.[18a]

Reaction of vinyldiazomethane with methyl methacrylate. Vinyldiazomethane (from 0·1 mole of the nitroso compound, ethereal soln) and 20·2 g methyl methacrylate (0·2 mole) were kept for 2 hr in the presence of N-phenyl-β-naphthylamine (1 wt%) as described in the reaction of acrylate. After distilling off the solvent and the recovered methyl methacrylate, 3·3 g of de-nitrogenated product (a mixture) was obtained at 70° (25 mm Hg). n_D^{24} = 1·4608, IR spectrum; 1730 cm^{-1} (C=O), 1640 cm^{-1} (C=C), 995, 910 and 905 cm^{-1} (C=CH$_2$). (Found: C, 68·18; H, 8·60 $C_8H_{12}O_2$, requires: 68·54; H, 8·63%.)

The distillate absorbed 1·08 mole H per mole on hydrogenation with Pd-C catalyst, giving a mixture of saturated compounds. IR spectrum (1640, 995, 910 and 905 disappeared) and NMR spectrum (complex absorptions at τ = ca. 4·6 disappeared) of the products showed that hydrogenation was complete and VPC (column, apiezone-L) showed that the saturated mixture consisted of 4 components in a relative intensity of 13:14:72:2. The main product (the third peak) was isolated by preparative VPC. This was identified as methyl *cis*-1-methyl-2-ethylcyclopropane-1-carboxylate (VII) by means of its NMR and IR spectra. NMR: τ 6·47, singlet (ester Me), 8·79, singlet (1-Me), 9·02, triplet (ethyl Me), complex absorption ranging 8·5–9·1 (ethyl CH$_2$ + ring H), 9·67, doublet (ring H), and these peaks were in expected ratio.

The NMR spectrum is in good agreement with methyl *cis*-1,2-dimethylcyclopropane-1-carboxylate



VII

(VIII) rather than *trans* isomer IX, both of which were prepared and identified.[9] τ Values of ring H in NMR spectra of VIII and IX were reported as 9·76 and ca. 9·3,[17] respectively. Methyl *trans*-1-methyl-2-ethyl-cyclopropane-1-carboxylate was similarly identified.

A mixture of stereoisomeric methyl X-methylhexa-Y, Z-diene-1-carboxylates could not be separated because of poor yield and poor separation by VPC, but VPC and a NMR spectrum of the crude mixture suggested the presence of dienocarboxylates.

Reaction of vinyldiazomethane with diethyl methylenemalonate. Vinyldiazomethane (from 0·1 mole of the nitroso compound, ether soln) and 5·1 g of diethyl methylenemalonate (0·03 mole) reacted in the presence of N-phenyl-β-naphthylamine by the procedure described.

The reaction was very rapid at room temp with gentle heat evolution and with a vigorous evolution of N. After complete disappearance of the red color of vinyldiazomethane, distillation of the products gave 5·1 g of a mixture of isomeric diethyl X,Y,-pentadiene-1,1-dicarboxylates. b.p. 86–88° (4·0 mm Hg), yield 24%. n_D^{25}, 1·4621. IR spectrum; 1750, 1735 and 1720 cm^{-1} (C=O), 1670 and 1650 cm^{-1} (C=C), 1000, 970, 930 and 850 cm^{-1} (olefin).

UV spectrum showed a λ_{max} at 220 mμ (ε_{max} = 6190 in 99·5% EtOH). (Found: C, 61·95; H, 7·85 $C_{11}H_{16}O_4$ requires: C,62·25; H, 7·60%.)

On hydrogenation, the mixture absorbed 2·18 moles H per mole, giving a saturated ester. Absorptions at 1670, 1645, 1000, 970, 930 and 850 cm^{-1} in IR spectrum were not observed in the saturated ester.

The saturated ester was identified as diethyl pentane-1,1-dicarboxylate by comparison with an authentic sample. The NMR spectrum of the ester showed the following absorptions: τ, 9·05, triplet (ϵ-CH$_3$), 8·5–9.0, complex (γ- and δ-CH$_2$), 8·70, triplet (ester CH$_3$), 8·11, quartet (β-CH$_2$), 6·73, triplet (α-CH) and 5·73, quartet (ester CH$_2$) in expected intensities.

Diene-esters were not isolated but the major compound appeared to be diethyl 1,3-pentadiene-1,1-dicarboxylate since absorptions of NMR spectrum of the mixture at τ; 4·9 (olefinic H), 5·93 (ester CH$_2$), ca. 8·5 (Me), 8·77 and 8·80 (ester Me) in an approximate ratio 3:4:3:6, agreed with the expected ratio for the 1,3-diene ester (by considering that the diene ester should not have alkyl branch as ascertained with the hydrogenated ester).

[17] This approximate estimation was made on the chart reported previously.[9]

Abnormally low λ_{max} and ϵ_{max} values of the diene ester in the UV absorption may be due to the fact that the diene has very poor coplanarity because of steric interaction of substituents.

Reaction of vinyldiazomethane with methyl crotonate. Vinyldiazomethane (from 0·1 mole of the nitroso compound, as an ethereal soln) and 28 g of methyl crotonate (0·28 mole) were stirred at room temp for 10 hr until the red color disappeared. Distillation gave 1·3 g of pyrazole (from self cyclization 19%) and 0·3 g of methyl 4-methyl-5-vinyl-Δ^3-pyrazoline-3-carboxylate (1·7%); b.p. 96–97° (3·5 mm Hg) and deco temp, 140°. n_D^{21}, 1·5200. IR spectrum; 3300 cm^{-1} (NH), 1710 cm^{-1} (C=O), 1650 cm^{-1} (C=C), 1550 cm^{-1} (C—N), 990 and 925 cm^{-1} (C—CH_3). The UV spectrum showed λ_{max} at 298 mμ (ϵ_{max}, 8970 in 99·5% EtOH). (Found: C, 57·35; H, 7·44; N, 16·31 $C_8H_{12}O_2N_2$ requires: C 57·13; H, 7·19; N, 16·66%.)

Formation of a considerable amount of pyrazole indicates that self-cyclization was faster than the desired addition reaction on crotonate. In order to enhance the relative rate of the addition reaction (presumably second order) to the self cyclization (presumably first order), 2·8 moles of the crotonate were used and the soln (ca. 500 ml after mixing) was condensed *in vacuo* to 150 ml, then the condensed soln was kept at room temp, yield of methyl 4-methyl-5-vinyl-Δ^3-pyrazoline-3-carboxylate by distillation increased by 11·9% and no appreciable amount of pyrazole was observed.

Reaction of vinyldiazomethane with acrylonitrile. Vinyldiazomethane and acrylonitrile gave mostly de-nitrogenated products and only a very small amount of 3-cycno-5-vinyl-Δ^3-pyrazoline was obtained. De-nitrogenated products consisted of 2 major products in a ratio of 92:8, the principal product being identified as the corresponding cyclopropane deriv.

3-Cyano-5-vinyl-Δ^3-pyrazoline was converted to the 3-cyanopyrazole-5-carboxylic acid by oxidative hydrolysis with alkaline permanganate in aqueous MeOH. The cyanocarboxylic acid was further converted to hyrazole-1,3-dicarboxylic acid by alkaline hydrolysis in the presence of H_2O_2, which was identical with the authentic sample prepared previously.[9] (See a separate paper for details.[16a])

Reaction of vinyldiazomethane with fumarontrile. Vinyldiazomethane and fumaronitrile gave a viscous liquid which was separated through an alumina column. From the red eluted soln, 3-cyano-5-vinylpyrazole was obtained in a low yield (this was presumably formed by elimination of HCN from the initial adduct, 5-vinyl-3,4-dicyanopyrazoline). Vinylcyanopyrazole was identified by conversion to pyrazoledicarboxylic acid as described above. (See a separate paper for details.[16a]) Analysis of 3-cyano-5-vinylpyrazole (m.p. 106–107°); (Found: C, 60·33; H, 4·51; N, 35·29 $C_6H_5N_3$ requires: C, 60·49; H, 4·23; N, 35·28%.)