PART III. THE PREPARATION AND PYROLYSIS OF 4,5-DIMETHYL-3-CARBOMETHOXY- Δ^2 -PYRAZOLINE AND 3,5-DIMETHYL-3-CARBOMETHOXY- Δ^1 -PYRAZOLINE

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ABSTRACT

4,5-Dimethyl-3-carbomethoxy- Δ^2 -pyrazoline and 3,5-dimethyl-3-carbomethoxy- Δ^1 -pyrazoline have been synthesized and pyrolized neat and in the vapor phase. The product analysis from these and a related dimethyl-3-carbomethoxypyrazoline indicate that substituent effects of methyls in the ring are cumulative.

In an earlier study (1) it has been shown that of the methyl 3-carbomethoxypyrazolines studied the compound with methyl substitution at 3 gives a higher proportion of cyclopropane derivative in the product than was obtained from 3-carbomethoxy- Δ^2 -pyrazoline. However, substitution by methyl at position 5 has little effect on the proportion of cyclopropane derivative and substitution at position 4 gives a reduced proportion of cyclopropane product. It is of interest to see if these effects are cumulative and for this reason we have investigated the pyrolysis of the dimethyl-substituted 3-carbomethoxypyrazolines I and II.



4,5-Dimethyl-3-carbomethoxy- Δ^2 -pyrazoline (I) was prepared by the addition of diazoethane to methyl *trans*-crotonate. The stereochemistry in the pyrazoline was not determined but would be expected to be mainly with the methyls trans since these groups would be in close proximity in the transition state leading to the pyrazoline.

Pyrolysis of I (the pyrolysis of I has been reported (2) to give methyl 3-methyl-3pentenoate as the sole product) gave the products indicated in Chart I in the proportions listed in Table I. These products were isolated by vapor chromatography and identified on the basis of their physical and chemical properties. The cyclopropane derivatives having methyls cis and trans (IX and VIII) were characterized through a comparison with the physical properties and infrared spectra reported for these compounds by Doering (3). The unsaturated esters were readily identified from their n.m.r. and infrared spectra.

The α,β -unsaturated esters (IV and V) showed carbonyl absorption at 1702 cm⁻¹ and carbon–carbon double-bond absorption near 1645 cm⁻¹, and the n.m.r. spectra were in agreement with the structural assignments given by Wagner and Moore (4).

The β , γ -unsaturated esters (VI and VII) showed carbonyl absorption at 1725 cm⁻¹ and weak carbon–carbon double-bond absorption at 1665 cm⁻¹. The n.m.r. spectra were

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as expected for the isomeric methyl 3-methyl-3-pentenoates and excluded the possibility that one of these isomers was methyl 3-ethyl-3-butenoate. The stereochemistry of the β , γ -isomers was determined by the following sequence of steps.

Bromination of tiglic acid (methyl groups cis) under conditions to give trans bromination gave 2-methyl-2,3-dibromobutanoic acid. This acid was converted with thionyl chloride to the acid chloride and then by treatment with diazomethane to the diazoketone. Treatment of the dibromodiazoketone with silver oxide in methanol gave a mixture of brominated products. Reaction of this mixture with zinc gave a debrominated product from which was isolated methyl tiglate and the isomeric methyl 3-methyl-3-pentenoates in the ratio of 1:10. The major isomer was assigned the trans structure on the basis of earlier demonstrations of trans stereochemistry in the zinc debromination of 2,3-dibromobutane (5).

All of the unsaturated esters found in the product from the pyrazoline pyrolysis were also formed in the dehydration of methyl 3-methyl-3-hydroxypentanoate with phosphorus pentoxide by the procedure of Kon and Nargund (6). Under these conditions the β , γ -unsaturated esters formed 72% of the product (ref. 4 reports 61%). From the dehydration product there was isolated, in addition to the four unsaturated esters described above, a compound with infrared bands at 1725 and 1650 cm⁻¹ believed to be methyl 3-ethyl-3butenoate.

3,5-Dimethyl-3-carbomethoxy- Δ^1 -pyrazoline (II) was prepared by the addition of diazoethane to methyl methacrylate. The n.m.r. of this pyrazoline showed it to be a 60:40 mixture of the two possible isomers; however, it was not possible to determine which was present to the greater extent.

Pyrolysis of II gave the products indicated in Chart I in the proportions listed in Table I. These products were isolated and identified on the basis of their physical constants. The low yield of the unsaturated esters prevented complete identification of these esters and thus the structural assignments are tentative. The cyclopropane derivatives having the methyls cis and trans (XIV and XIII) were characterized by comparison of their physical properties with those obtained by van Auken and Rinehart (7, 8).

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The major unsaturated ester product showed infrared bands at 1700 and 1645 cm⁻¹ indicative of an α,β -unsaturated ester. The n.m.r. was consistent with the structure methyl 2-methyl-trans-2-pentenoate (X) since the methyl hydrogens at C₄ gave a value of 7.94 τ (compare 7.73 τ for methylene hydrogens trans to the carbomethoxy group in methyl trans-3-methyl-2-pentenoate and 7.45 τ for methylene hydrogens cis to the carbomethoxy group in methyl cis-3-methyl-2-pentenoate).

A second unsaturated ester which was isolated (infrared bands at 1705 and 1641 cm⁻¹) was tentatively assigned the structure methyl 2-methyl-*cis*-2-pentenoate (XI). Insufficient sample was obtained for an n.m.r. spectrum.

A final sample (infrared bands at 1725 and 967 cm⁻¹) was isolated but could not be completely characterized. However, the infrared spectrum suggests that it is methyl *trans*-2methyl-3-pentenoate (XII).

The product analyses reported in Table I when compared to the analyses of the products from the monomethyl pyrazolines (1) suggests that indeed the effects of methyl substitution are cumulative, although I yielded a higher proportion of cyclopropanes than might have been predicted. The product composition from a pyrolysis is somewhat influenced by the stereochemistry of the pyrazoline (see the results of van Auken and Rinehart given in Table I); however, in general it should now be possible to predict the usefulness of the pyrazoline method for synthesizing cyclopropane derivatives with a

CANADIAN JOURNAL OF CHEMISTRY. VOL. 41, 1963 CH₃CH₂ CH₃CH₂ CO₂CH₃ CH₃ CH₃ Η ++ĆН3 ĆН₃ CO₂CH₃ Н CH₂CO₂CH₃ H IV V I VI CH3 CH₃ CH₂CO₂CH₃ CH₃ + ++CH₃ CO₂CH₃ H CH: СНз CO₂CH₃ VII VIII IXCH₂CH₂ CH₃ CH₃CH₂ CO₂CH₃ CH: Η ++СН3 H CO₂CH₃ H H CHCO₂CH₃ ĊH₃ х XI XII Π + CH₃ + CH3 CH₃ Ć́Н₃ `CO₂CH₃ CO₂CH₃ XIV XIII CH₃ CO₂CH₃ CH₃ CH₂= CH₃ CH3 CHCO₂CH₃ ĊН3 XV XVI ш +CH₃ CH₃ CH3 ĆН, CO₂CH₃ ℃O₂CH₃ XIII XIV

Chart I

variety of alkyl substituents. A number of examples in the literature (9-14) fit in well with the general trends found in this work.

Vapor phase pyrolysis of I and II yielded a higher proportion of cyclopropane derivative than was obtained in the liquid phase, proving again that this is a useful modification of the pyrolysis procedure. It has been found that 20-mesh firebrick makes an excellent column packing for the pyrolysis of Δ^2 -pyrazolines in the vapor phase. Presumably there are sufficient acid sites on the firebrick to catalyze the tautomerism of the Δ^2 -pyrazoline into the pyrolizable Δ^1 -form.

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Pyrazoline I	Phase Liquid Vapor	Unsaturated esters					
		α,β		β,γ		Cyclopropanes	
		IV 25 15	V 26 14	${\scriptstyle \begin{array}{c} VI\\ 2\\ 2\end{array}}$	$\begin{array}{c} \text{VII} \\ 3 \\ 2 \end{array}$	VIII 27 43	IX 16 24
II	Liquid Vapor	$\begin{array}{c} X\\ 15\\ 2\end{array}$	$egin{array}{c} { m XI} \\ 10 \\ 3 \end{array}$	$\overset{\text{XII}}{\overset{3}{1}}$		XIII 27 42	$\begin{array}{c} \mathrm{XIV} \\ 45 \\ 53 \end{array}$
III (methyls cis)* III (methyls trans)*	Liquid Liquid	XV 66 33		$\operatorname{XVI}_{4}_{4}$		$\begin{array}{c} \mathrm{XIII} \\ 12 \\ 35 \end{array}$	XIV 18 28

TABLE I

Product compositions for the pyrolysis of dimethyl-3-carbomethoxypyrazolines

EXPERIMENTAL

Melting points and boiling points are uncorrected. Most boiling points were determined by the micro inverted capillary method. Infrared spectra were measured with a Perkin–Elmer Model 21 spectrometer using sodium chloride optics. The n.m.r. spectra were recorded on a 40 Mc/s Varian spectrophotometer with field stabilizer VK 3506, and the methylene chloride used as an external standard was observed to have a value of 4.60τ . The vapor chromatography unit was an Aerograph A-100-C.

4,5-Dimethyl-3-carbomethoxy- Δ^2 -pyrazoline

*Reference 8.

Methyl crotonate was reacted with diazoethane in ether prepared from ethyl nitrosourea. After distillation of the ether the product was distilled to give a yellow solid, m.p. $46-47^{\circ}$ and b.p. $101-102^{\circ}$ at 1.8 mm (lit. (15) b.p. 139–140 at 14 mm). The infrared spectrum showed bands at 3400, 1710, and 1557 cm⁻¹ characteristic of a 3-carbomethoxy- Δ^2 -pyrazoline (1, 16).

Pyrolysis of 4,5-Dimethyl-3-carbomethoxy- Δ^2 -pyrazoline

Pyrolyses in the liquid and vapor phase were carried out as reported earlier except that 20-mesh firebrick was used as the packing material in the vapor phase pyrolysis apparatus. The product compositions are reported in Table I. The product from the liquid phase pyrolysis (12 g, b.p. 140–165°, from 17 g of pyrazoline) was separated into five components using a dinonyl phthalate column, and one of these fractions was further separated into two components with a Ucon Polar column. The components were identified as indicated below, where boiling point, refractive index, retention time in the vapor chromatogram using a 10-ft dinonyl phthalate column of 0.25-in. diameter at 116° with a helium flow rate of 67 cc/min, and infrared bands for 5% solutions in chloroform are given.

Methyl trans-3-methyl-2-pentenoate: b.p. 160°, n_D^{25} 1.4424 (lit. (4) b.p. 79° at 50 mm, n_D^{20} 1.4446), 44.8 minutes, 1702 and 1647 cm⁻¹. The n.m.r. spectrum (0.5 ml per ml of carbon tetrachloride) showed vinyl hydrogen signals at 4.55 τ (singlet), ester methyl hydrogens at 6.36 τ (singlet), methylene hydrogens at 7.73 τ (quartet with $J \simeq 7$ c.p.s.), and alkyl methyl hydrogens at 7.70 τ (singlet) and 8.66 τ (triplet with $J \simeq 7$ c.p.s.).

Methyl cis-3-methyl-2-pentenoate: b.p. 151°, n_D^{23} 1.4409 (lit. (4) b.p. 74° at 50 mm, n_D^{20} 1.4420), 36.8 minutes (67.2 minutes on a 10-ft Ucon Polar column at 112° and a flow rate of 45 cc/min), 1702 and 1645 cm⁻¹. The n.m.r. spectrum (0.30 ml per ml of carbon tetrachloride) showed a vinyl hydrogen signal at 4.51 τ (singlet) and peaks for the ester methyl hydrogens at 6.46 τ (singlet), methylene hydrogens at 7.45 τ (quartet with $J \simeq 6.9$ c.p.s.), and alkyl methyl hydrogens at 8.22 τ (singlet) and 8.19 τ (triplet with $J \simeq 7$ c.p.s.).

Methyl *cis*-3-methyl-3-pentenoate: b.p. 148°, n_D^{20} 1.4321, 29.6 minutes, 1725 and 1665 (weak) cm⁻¹. Calc. for C₇H₁₂O₂: C, 65.49; H, 9.45. Found: C, 65.65; H, 9.41. The n.m.r. spectrum (0.33 ml per ml of carbon tetrachloride) showed vinyl hydrogen signals at 4.70 τ (multiplet), ester methyl hydrogens at 6.40 τ (singlet), methylene hydrogens at 7.07 τ (singlet), and methyl hydrogens at 8.29 τ (singlet) and 8.43 τ (doublet with $J \simeq 6.8$ c.p.s.). This ester was assigned the cis structure on the basis of the synthesis of the trans ester described below.

Methyl trans-3-methyl-3-pentenoate: b.p. 150°, n_D^{21} 1.4323, (lit. (17) b.p. 74° at 50 mm, n_D^{20} 1.4306), 33.6 minutes, 1725 and 1665 (weak) cm⁻¹. Calc. for C₇H₁₂O₂: C, 65.49; H, 9.45. Found: C, 65.43; H, 9.51. The n.m.r. spectrum (0.50 ml per ml of carbon tetrachloride) showed vinyl hydrogen signals at 4.67 τ (multiplet), ester methyl hydrogens at 6.41 τ (singlet), methylene hydrogens at 7.14 τ (singlet), and methyl hydrogens at 8.33 τ (singlet) and 8.42 τ (doublet with $J \simeq 7$ c.p.s.). The trans geometry of this ester was assigned on the basis of its synthesis from tiglic acid (see below).

Methyl trans-1,2-cyclopropane-3-carboxylate: b.p. 143°, n_{D²⁵} 1.4241 (lit. (3) b.p. 40-50 at 20 mm, n_{D²⁰}

1.4252), 26.0 minutes; infrared bands found at 1365, 1302, 1165, 1095, and 1055 cm⁻¹ are not found in the spectra of the other cyclopropane isomer (lit. (18) reports bands at 1363, 1302, 1164, 1093, and 1055 cm⁻¹ for this isomer). The n.m.r. spectrum (0.50 ml per ml of carbon tetrachloride) showed signals assigned to the ester methyl hydrogens at 6.49 τ (singlet) and the remaining hydrogens in a group at 9.05 τ .

Methyl cis-1,2-dimethyl-3-trans-carboxylate: b.p. 150° at 759 mm, n_D^{18} 1.4330 (lit. (3) n_D^{20} 1.4306), 36.8 minutes (70.8 minutes on a 10-ft Ucon Polar column at 112° and a flow rate of 45 cc/min); infrared bands found at 1325, 1125, 1085, and 1040 cm⁻¹ are not found in the spectra of the other cyclopropane isomer (lit. (18) reports bands at 1322, 1128, 1089, and 1040 cm⁻¹ for this isomer and 1378, 1158, 1115, 1093, and 1026 cm⁻¹ for methyl cis-1,2-dimethyl-3-cis-carboxylate). The n.m.r. spectrum (0.20 ml per ml of carbon tetrachloride) showed signals assigned to the ester methyl hydrogens at 6.42 τ (singlet) and the remaining hydrogens in a group at 8.9 τ .

Methyl trans-3-Methyl-3-pentenoate

Tiglic acid (30 g, 0.3 mole) in carbon tetrachloride was brominated with 48 g of bromine (0.3 mole) by the procedure of Buckles and Mock (19) to give 63 g (83%) of 2,3-dibromo-2-methylbutanoic acid, m.p. 85–88° (lit. (19) m.p. 82–88°).

2,3-Dibromo-2-methylbutanoyl chloride (62 g, 86%), b.p. 73–74° at 14 mm, was prepared by refluxing 39 g of thionyl chloride with 63 g of the acid. Calc. for $C_5H_7OBr_2Cl$: C, 21.54; H, 2.51. Found: C, 21.69; H, 2.38.

Methyl 2,3-dibromo-3-methylpentanoate.—2,3-Dibromo-2-methylbutanoyl chloride (36 g, 0.12 mole) was reacted with an ether solution containing 13 g of diazomethane at 0–5°. The solution was let stand for 12 hours and the ether distilled. Anhydrous methanol (200 ml) was added to the oily diazoketone and the solution stirred and warmed on a water bath. Silver oxide (50 g as a slurry in anhydrous methanol) was added in portions to the hot methanolic solution. After it was cooled the methanol solution was decanted from the silver residues, filtered through alumina to remove colloidal silver and silver salts, and distilled to give 13.6 g of a product, b.p. 62–64° at 2 mm. The n.m.r. spectra, the analysis, and the debromination results showed this to be a mixture of brominated esters. Calc. for $C_7H_{12}O_2Br_2$: C, 29.18; H, 4.20. Found: C, 36.39; H, 5.10. Further purification by V.P.C. was found not practical.

Methyl trans-3-methyl-3-pentenoate.—A mixture of 7 g of the brominated esters, 10 g of 20-mesh zinc, and 30 ml of water was stirred in the dark according to the procedure of Schubert et al. (5) for 20 hours. The product was extracted with ether and filtered. The ether solution was washed with water, dried over sodium sulphate, filtered, and distilled to give 2 g of product, b.p. 38-49° at 40 mm. Vapor chromatography of the product showed the presence of three components in the ratio of 11:1:10. The first component was identified as methyl tiglate, $n_{\rm D}^{28}$ 1.4346, b.p. 141° (lit. (20) b.p. 139.4–139.6°, $n_{\rm D}^{20}$ 1.4370). The infrared spectrum was identical with that of an authentic sample. The second component was shown by its V.P.C. retention time and infrared spectrum to be identical with the lower-boiling methyl 3-methyl-3-pentenoate. The third component, n_D^{25} 1.4308, b.p. 152°, had a V.P.C. retention time and infrared spectrum identical with those of the higher-boiling methyl 3-methyl-3-pentenoate. Because of the absence of methyl angelate in the debromination and the known stereochemical requirements of the debromination reaction (5), the higherboiling isomer of methyl 3-methyl-3-pentenoate was assigned the trans structure. The cis and trans esters show some differences in the fingerprint region of their infrared spectra. Particularly, there is a band at 1380 cm⁻¹ for the trans ester which is much stronger than any band near this region for the cis ester. For the trans ester below 1500 cm⁻¹ bands are found at 1433 (s), 1510 (w), 1380 (m), 1330 (m), 1296 (m), 1255 (s), 1220 (m), 1188 (m), 1150 (s), 1112 (vw), 1090 (w), 1035 (m), 1002 (m), and 957 (w) cm⁻¹ and for the cis ester at 1432 (s), 1420 (sh), 1372 (w), 1350 (vw), 1315 (m), 1285 (m), 1245 (s), 1192 (m), 1150 (s), 1175 (m), 1035 (w), and 1005 (m).

Methyl 3-Methyl-2- and -3-pentenoates from Methyl 3-Methyl-3-hydroxypentanoate

Methyl 3-methyl-3-hydroxypentanoate (28 g, 0.19 mole) prepared by the procedure of Kuhn *et al.* (21) was refluxed in 125 ml of benzene with 3 g of phosphorus pentoxide for 5 hours (6). Distillation gave 17 g (70%) of a methyl 3-methylpentenoate mixture, b.p. $145-160^{\circ}$.

Separation of the mixture by vapor chromatography on a dinonyl phthalate column gave:

Methyl trans-3-methyl-2-pentenoate: b.p. 160° , n_D^{25} 1.4425, 19%Methyl cis-3-methyl-2-pentenoate: b.p. 150° , n_D^{17} 1.4431, 9%Methyl cis-3-methyl-3-pentenoate: b.p. 148° , n_D^{25} 1.4307, 26%Methyl trans-3-methyl-3-pentenoate: b.p. 150° , n_D^{25} 1.4302, 38%

Methyl 3-ethyl-3-butenoate (?): b.p. 146°, n_D^{23} 1.4261. Infrared bands at 1725, 1650, 1420, and 897 cm⁻¹ indicate this to be a $\beta_{,\gamma}$ -unsaturated ester with a terminal double bond; however, insufficient sample was obtained for analysis.

3,5-Dimethyl-3-carbomethoxy- Δ^1 -pyrazoline

Methyl methacrylate was reacted with diazoethane in ether and the product distilled to give a colorless liquid, b.p. 54° at 0.5 mm. Calc. for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.75; H, 7.91;

N, 18.11. The n.m.r. spectrum showed this to be a mixture of the two possible isomers (C_{δ} -methyl cis or trans to the carbomethoxy group) with peaks at 4.28, 4.34 τ (ester methyl), 8.53, 8.51 τ (doublet for C₅methyl), 8.64, 8.39 τ (C₃-methyl), and 5.45 τ (multiplet), 7.69 τ (multiplet), and 9.26 τ (multiplet) for the various ring protons. The proportion of these isomers was 3:2 as determined by integration of the peaks. Where two signals are reported the larger signal is given first. It is felt that this data is not sufficient to permit designation of the isomer present in the larger amount as cis or trans.

Pyrolysis of 3,5-Dimethyl-3-carbomethoxy Δ^1 -pyrazoline

Pyrolysis in the liquid phase was vigorous at 120°. In the gas phase the pyrolysis was carried out using a packing of glass beads and a pressure of 5 mm (1). The product compositions are reported in Table I. The product from the liquid phase pyrolysis (8 g from 11 g of pyrazoline) was separated into five components using a dinonyl phthalate column. The components were identified or partially identified as indicated below, where boiling point, refractive index, retention time in the vapor chromatogram using a 10-ft dinonyl phthalate column of 0.25-in. diameter at 98° with a helium flow rate of 55 cc/min, and infrared bands for 5%solutions in chloroform are given.

Methyl trans(?)-2-methyl-2-pentenoate: b.p. 156°, nD²⁴ 1.4394, 58 minutes, 1700 and 1645 cm⁻¹. Calc. for C7H12O2: C, 65.49; H, 9.45. Found: C, 65.27; H, 9.45. The n.m.r. spectrum (0.05 ml per ml of carbon tetrachloride) had a triplet signal in the olefin region at 3.48 τ with $J \simeq 7.5$ c.p.s. Other peaks were due to ester methyl hydrogens at 6.41 τ (singlet), methylene hydrogens at 7.94 τ (multiplet), and alkyl methyl hydrogens at 8.26 τ (singlet) and 9.04 τ (triplet with $J \simeq 7.2$ c.p.s.).

Methyl cis(?)-2-methyl-2-pentenoate: b.p. 143°, n_D²⁴ 1.4351, 36 minutes, 1705 and 1641 cm⁻¹. Calc. for C7H12O2: C, 65.49; H, 9.45. Found: C, 65.23; H, 9.46.

In addition there was a minor component at 31.6 minutes with b.p. 139°, n_D^{23} 1.4229, and infrared bands at 1725 and 967 $\rm cm^{-1}$. The position of the carbonyl band and the absence of carbon-carbon double-bond stretch indicate that this is a symmetric non-conjugated unsaturated ester. The presence of the characteristic band at 967 cm⁻¹ for trans olefins suggests that this is methyl trans-2-methyl-3-pentenoate.

Methyl cis-1,2-dimethyl cyclopropane-1-carboxylate: b.p. 145°, n_D²⁰ 1.4314 (lit. (7) n_D²⁵ 1.4289), 39.6 minutes, 1720 cm⁻¹. The infrared and n.m.r. spectra were identical with those obtained by Rinehart and van Auken (8).

Methyl trans-1,2-dimethylcyclopropane-1-carboxylate: b.p. 136°, n_D²⁷ 1.4220 (lit. (7) n_D²⁵ 1.4218), 26.4 minutes, 1720 cm⁻¹. The infrared and n.m.r. spectra were identical with those obtained by Rinehart and van Auken (8).

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REFERENCES

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF SOUTH CAROLINA on 11/24/14 For personal use only.

- N. D. E. MCGREER, W. WAI, and G. CARMICHAEL. Can. J. Chem. 38, 2410 (1960).
 K. VON AUWERS and F. KONIG. Ann. 496, 252 (1932).
 W. VON E. DOERING and T. MOLE. Tetrahedron, 10, 65 (1960).
 R. B. WAGNER and J. A. MOORE. J. Am. Chem. Soc. 72, 974 (1950).
 W. M. SCHUBERT, B. S. RABINOVITCH, W. R. LARSON, and V. A. SIMS. J. Am. Chem. Soc. 74, 4590 (1952). H. O. HOUSE and R. S. RO. J. Am. Chem. Soc. 80, 182 (1958).
 G. A. R. KON and K. S. NARGUND. J. Chem. Soc. 2461 (1932).
 K. L. RINEHART, JR. and T. V. VAN AUKEN. J. Am. Chem. Soc. 82, 5251 (1960).
 K. L. RINEHART, JR. and T. V. VAN AUKEN. Personal communication.
 D. GOTKIS and J. B. CLOKE. J. Am. Chem. Soc. 56, 2710 (1934).
 W. G. YOUNG, L. J. ANDREWS, S. L. LINDENBAUM, and S. J. CRISTOL. J. Am. Chem. Soc. 66, 810 (1944).

- (1944). (1944).
 11. P. C. GUHA and D. K. SANKARAN. Ber. 71, 2673 (1938).
 12. H. L. SLATES and N. L. WENDER. J. Am. Chem. Soc. 81, 5472 (1959).
 13. K. KOCSIS, P. G. FERRINI, D. ARIGONI, and O. JEGER. Helv. Chim Acta, 43, 2178 (1960).
 14. G. NOMINE and D. BERTIN. Bull. Soc. Chim. France, 82, 550 (1960).
 15. K. VON AUWERS and E. CAVER. Ann. 470, 284 (1929).
 16. J. A. MOORE. J. Org. Chem. 20, 1607 (1955).
 17. R. B. WAGNER and J. A. MOORE. J. Am. Chem. Soc. 71, 3214 (1949).
 18. W. VON E. DOERING and T. MOLE. Personal communication.
 19. R. E. BUCKLES and G. V. MOCK. J. Org. Chem. 15, 680 (1950).
 20. M. NASTER and A. GAVRILOFF. Bull. Soc. Chim. Belges, 42, 519 (1933).
 21. R. KUHN, F. KOHLER, and L. KOHLER. J. Physiol. Chem. 247, 197 (1937).