Petrov and Nikishin.[8] *Triethylvinylsilane* was synthesized by the method outlined by Nagel and Post.[7]

4,4-Dimethyl-4-sila-1,7-heptylene dithioacetate and *4,4-diphenyl-4-sila-1,7-heptylene dithioacetate* were prepared by the addition of thiolacetic acid to the proper olefinic silane but were not isolated. They were not distilled but converted to their respective dimercaptans immediately upon synthesis.

4-Methyl-4-phenyl-4-sila-1,7-heptylene dithioacetate. This compound was prepared by treating 40.47 g. (0.20 mole) of methylphenyl-diallylsilane in 75 cc. of cyclohexane, in a 200 cc. three necked flask with the usual stirrer, dropping funnel, and adapter, with 30.4 g. (0.40 mole) of redistilled thiolacetic acid in 25 cc. of cyclohexane, slowly added, with the temperature kept at about 65°. After two hours of refluxing, excess thiolacetic acid and cyclohexane were removed by distillation at reduced pressures. Above 200° at 1 mm. decomposition occurred. The pot material was dissolved in an equal volume of methyl alcohol, and the colored impurities removed by Norite. The organic products were then thrown out of solution by water, dried over anhydrous sodium sulfate, and analyzed, n_D^{25} 1.5480, d_4^{25} 1.0819. Purification was limited as distillation resulted in slight decomposition.

Anal. Calcd. for $C_{17}H_{26}O_2S_2Si$: Si, 7.91, M.R., 104.1. Found: Si, 8.21, 8.26, M.R., 102.9.

2,4,4-Trimethyl-4-silapentyl-1 thiolacetate. By a procedure similar to that used in the preceding preparation, this compound was prepared and isolated in 53% yield, b.p. 99°–100° (9 mm.), n_D^{25} 1.4664, d_4^{25} 0.9158.

Anal. Calcd. for $C_9H_{20}OSSi$: Si, 13.73, M.R., 61.28. Found: Si, 13.32, 13.50, M.R., 60.51.

3,3-Diethyl-3-silapentyl-1 thiolacetate. This compound was prepared as indicated above, yield 42%, b.p. 117°–119° (6.5 mm.) n_D^{25} 1.4779, d_4^{25} 0.9284. Infrared absorption occurred at 3.3, 5.8, 8.0, 11.8, and 14.3 μ.

Anal. Calcd. for $C_{10}H_{22}OSSi$: Si, 12.85, M.R., 66.91. Found: Si, 13.05, 13.11, 13.09, M.R., 66.57.

4,4-Dimethyl-4-silaheptylene-1,7 dimercaptan. As described for the thiolacetates, 75 cc. of purified cyclohexane and 33.6 g. (0.24 mole) of dimethyldiallylsilane were treated with 36.5 g. (0.48 mole) of redistilled thiolacetic acid at 55°. After two hours of refluxing, the mixture was hydrolyzed by the slow addition of 40 g. (1.0 mole) of sodium hydroxide in 100 cc. of distilled water and 40 cc. of 95% ethyl alcohol. The system was refluxed for 90 minutes, then neutralized with 6*N* hydrochloric acid. After cooling, the upper layer was separated and combined with two 50 cc. benzene extracts of the water layer. After drying over 10 g. of anhydrous sodium sulfate, the material was fractionated yielding 4,4-dimethyl-4-silaheptylene-1,7 dimercaptan, 25% yield, b.p. 119.0–119.5° (6 mm.), n_D^{25} 1.5034, d_4^{25} 0.9631. Infrared absorption was recorded at 3.3, 7.0, 8.0, 8.5, 10, 10.8, and 12–13 μ.

Anal. Calcd. for $C_8H_{20}S_2Si$: Si, 13.46, M.R., 64.24. Found: Si, 13.06, 13.51, M.R., 64.01.

4-Methyl-4-phenyl-4-silaheptylene-1,7 dimercaptan was prepared in the same manner, yield 25%, b.p. 161–162° (2.5 mm.), n_D^{25} 1.5580, d_4^{25} 1.0396. Infrared absorption appeared at 3.4, 6.9, 7.8, 8.7, 9.7, 12.2, 13, and 13.6 μ.

Anal. Calcd. for $C_{12}H_{22}S_2Si$: Si, 10.38, C, 57.7, H, 8.17, M.R., 84.07. Found: Si, 10.58, 10.66, C, 56.5, H, 7.69, M.R., 83.87.

2,4,4,6-Tetramethyl-4-silaheptylene-1,7 dimercaptan. This compound was also prepared as described above, 22% yield, b.p. 147–148° (8 mm.), n_D^{25} 1.5031 d_4^{25} 0.9534.

Anal. Calcd. for $C_{10}H_{24}S_2Si$: Si, 11.87, C, 50.79, H, 10.2, M.R., 73.50. Found: Si, 11.65, 11.73, C, 50.53, H, 9.6, M.R., 72.36.

2,4,4-Trimethyl-4-silapentyl-1-mercaptan. In a similar apparatus, 40.0 g. (0.19 mole) of 4,4-dimethyl-4-silapentyl-1 thiolacetate in 80 cc. of purified cyclohexane was treated with 24.0 g. (0.60 mole) of sodium hydroxide in 100 cc. of water and 50 cc. of ethyl alcohol at 45–50°. The mixture was refluxed for five hours, then cooled and acidified with 6N hydrochloric acid. The product was worked up as in the cases described above, giving a 9% yield, b.p. 69.5–70.5° (16 mm.), n_D^{25} 1.4576, d_4^{25} 0.8597. Infrared absorption was recorded at 3.3, 5.1, 6.1, 6.8, 7.0, 8.1, 9.4, 9.8, 11.4–12.7, 13.1, and 14.0 μ.

Anal. Calcd. for C_7H_8SSi: C, 51.79, H, 11.17, M.R., 51.88. Found: C, 51.70, H, 11.41, M.R., 51.48.

β-Triethylsilylethyl mercaptan. Similarly, this compound was prepared in 50% yield by the hydrolysis of the corresponding thiolacetate, b.p. 113° (23 mm.), n_D^{25} 1.4730, d_4^{25} 0.8789. Infrared absorption occurred at 3.3, 6.8, 7.0, 7.8, and 9.8 μ.

Anal. Calcd. for $C_8H_{20}SSi$: Si, 15.91, M.R., 56.52. Found: C, 15.94, 16.01, M.R., 56.30.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF BUFFALO
BUFFALO 14, N. Y.

---

[8] A. D. Petrov and S. I. Nikishin, *Izvest. Akad. Nauk, U.S.S.R., Otdel. Khim. Nauk*, 1128 (1952); *Chem. Abstr.*, **48**, 1247 (1954).

The γ-Ionones

E. T. THEIMER, W. T. SOMERVILLE, B. MITZNER, AND S. LEMBERG

Received May 12, 1961

The base catalyzed condensation of citral with acetone, followed by acid cyclization, leads to a mixture of α- and β-ionones[1]; the ratio of the isomers formed is related to the acid used.[2] Similarly, methyl ethyl ketone has been shown to condense with citral to form on cyclization the *n*-methylionones (α and β) and the isomethylionones (α and β).[3] The γ-isomers (exocyclic methylene) have not previously been reported as products of these reactions, nor have they hitherto been characterized.[4]

We wish to report the isolation and characterization of pure γ-ionone and γ-*n*-methylionone from commercial products.

The formation of the exocyclic methylene isomer is not unexpected, as the intermediate II, prob-

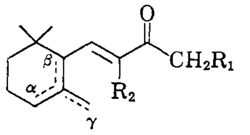
---

[1] F. Tiemann and P. Kruger, *Ber.*, **26**, 2693 (1893); F. Tiemann, *Ber.*, **31**, 2318 (1898); **32**, 827 (1899); **33**, 883 (1900).

[2] H. Hibbert and L. T. Cannon, *J. Am. Chem. Soc.*, 119 (1924); *Org. Syntheses*, **23**, 78 (1943).

[3] M. G. J. Beets and H. van Essen, *Rec. trav. chim.*, **77**, 1138 (1958), and references therein.

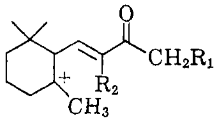
[4] Two reports of a derivative of γ-ionone have appeared: (a) B. Willhalm, V. Steiner, and H. Schinz, *Helv. Chim. Acta*, **41**, 1359 (1958) have reported the semicarbazone of this isomer (column chromatographed), originally thought to be present as a mixture of β- and γ-ionone. More recently, D. Szabo, *Chem. Abstr.*, **54**, 19748 (1960) has indicated the presence of γ-ionone in the phosphoric acid cyclization of pseudo ionone by conducting the cyclization in the presence of 2,4-dinitrophenylhydrazine. Thus far, our efforts to form derivatives of both pure new compounds reported here have led to viscous, intractable oils with semicarbazide, 2,4-dinitrophenylhydrazine and thiosemicarbazide, due to apparent product instability.



I

$R_1 = H, R_2 = H$; ionones, α, β, γ
$R_1 = CH_3, R_2 = H$; *n*-methylionones, α, β, γ
$R_1 = H, R_2 = CH_3$; isomethylionones, α, β, γ

ably formed during cyclization, is common to the three isomers anticipated.

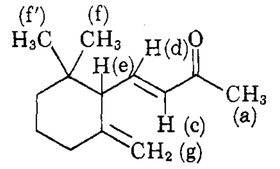


II

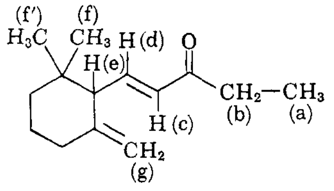
We have found that the gamma components codistill with their respective isomers and, therefore, even under the most stringent distillation techniques only partial isomeric enrichments are accomplished. The γ-ionone was isolated by vapor-phase chromatographic trapping from a mixture, the composition of which is described below.[5]

By vapor phase chromatographic analyses anomalous components have been observed, but not identified, in commercial methylionones. Enrichment of the component, which in vapor phase chromatography showed as a peak between α-*n*-methylionone and β-*n*-methylionone, was effected by fractionation of commercial α-isomethylionone[6] through a 4-foot protruded packed column (20:1 reflux ratio). Vapor phase chromatographic examination of the distilled fractions showed that α-isomethylionone had a retention time of thirty minutes and the unknown isomer (tentatively designated IV), thirty-four minutes.

The structures under discussion are particularly amenable to proton NMR analyses,[7] and the latter firmly support the proposed structures.



γ-Ionone
III



γ-*n*-Methylionone
IV

The NMR spectrum[10] of γ-ionone (III) shows a clearly resolved doublet at 7.49 p.p.m. (J = 10.2 c./s.) attributed to the tertiary hydrogen *e*, allylic to both double bonds. Signals at 5.32 and 5.53 p.p.m. are compatible with the hydrogen of the vinylidene methylene, *g*.

The positions of the *gem*-dimethyl group (9.14, 9.10 p.p.m.) and of the methyl group attached to the carbonyl (7.85 p.p.m.) as well as of the olefinic proton alpha to the carbonyl, τ = 4.05, (uncorrected, J = 15.2 c./s.), and the quartet of the olefinic proton beta to the carbonyl (τ = 3.41, 3.24, 3.14, and 2.98) conform to expectation.

The NMR spectrum of γ-*n*-methylionone (IV) suggests a doublet at 7.51 p.p.m. (J = 10.2 c./s.), again supporting the assignment of this signal to *e*. This doublet is partially obscured by the methylene protons, as shown below. The hydrogens of the vinylidine methylene occur at 5.50 and 5.27 p.p.m. The decision between the two possible structures, γ-*n*-methylionone and γ-isomethylionone, is resolved readily by observation of the following facts: (1) There are no methyl groups attached directly to a double bond and (2) the methylene group *b* appears as a quartet (τ = 7.69, 7.59, 7.56, 7.33). The adjacent methyl group, *a*, appears at 8.81 and 8.93 τ with a suggestion of a shoulder at 9.0 p.p.m., the latter signal being overlapped by the *gem*-dimethyl grouping; the compound is, therefore, γ-*n*-methylionone.

The corresponding γ-isomethylionone has not been isolated in pure form to date, but partial separation from the α-isomethyl isomer with which it is simultaneously eluted on vapor phase chromatography has been achieved.

It should be noted that the assignment of the tertiary hydrogen, *e*, is most critical if the interpretation is to be unequivocal. A study of α-ionone and α-*n*-methylionone shows the presence of this doublet, which is absent in the "beta" series. We shall record the results of this NMR study in a future publication.

EXPERIMENTAL

γ-Ionone. Vapor-phase chromatographic separation of the mixture (described in ref. 5) was accomplished by using a 10 ft. 1/4-in. column of silane-treated Celite (60–80 mesh) impregnated (10%) with Craig polyester succinate; the α-ionone had a retention time of 27 minutes and the gamma iso-

---

(5) This sample was kindly supplied by Dr. J. Bain of The Glidden Co., Jacksonville, Fla. Its composition was approximately 35% of the presumed γ-ionone and 65% α-ionone, as determined by vapor phase chromatography. The appearance of a terminal methylene absorption in the infrared ($\nu_{max.}^{liq.}$ 892 cm.$^{-1}$) was strong evidence for the gamma content.

(6) The commercial methylionones examined were rich (80%) in α-isomethylionone with smaller amounts of β-isomethylionone, α-*n*-methylionone, and β-*n*-methylionone.

(7) NMR spectra were measured on a Varian High Resolution Spectrometer, HR60. Samples were dissolved in carbon tetrachloride in 7–10% concentration (by volume). The magnetic field strength was 14,092 gauss and the oscillating frequency 60*M* c./s. Tetramethylsilane (1/4%) was used as the standard, as described by G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(8) G. Buchi and N. C. Yang, *Helv. Chim. Acta*, **38**, 1338 (1955).

PERTINENT NMR DATA

	Values						
	a	*b*	*c*	*d*	*e*	*f,f'*	*g*
III	7.85	—	4.18, 3.91	3.41, 3.24 3.14, 2.98	7.58, 7.41	9.14, 9.10	5.50, 5.27
IV	—	7.69, 7.59 7.46, 7.33	4.14, 3.89	3.37, 3.20 3.11, 2.93	7.61, 7.42	9.12, 9.08	5.49, 5.27

mer, 30 minutes; column temperature, 180°; flow rate 50 ml./min. at an inlet pressure of 46 p.s.i.

Unequivocal evidence for the ionone skeleton of IV was obtained by the following: On atmospheric hydrogenation with platinum oxide in glacial acetic acid, three mole equivalents of hydrogen were absorbed; chromic acid oxidation (12 hr.) of the tetrahydroionol thus formed gave, on work-up, a ketone whose semicarbazone melted at 172–174°. Admixture of the latter with the semicarbazone of authentic tetrahydroionone,[8] m.p. 175–177°, prepared from α-ionone, showed no melting point depression.

Anal.[9,10] Calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.53; H, 10.47; mol. wt., 192; n_D^{20} 1.5003; $\lambda_{max}^{C_2H_5OH}$ 226 mμ, ε 12,620. γ_{max}^{liq} 1682 cm.$^{-1}$ (conjugated carbonyl), 892 cm.$^{-1}$ (vinylidene methylene).

γ-n-Methylionone. Vapor phase chromatography trapping of the distillate richest in γ-*n*-methylionone gave the pure compound; for this purpose, a Celite packing, impregnated with Dow Corning Silicone No. 710 (25% w./w.) in a $^3/_{16}$-in. ten-foot column, with a flow rate of 50 ml./min. (inlet pressure of 26 p.s.i.) at 180°, was used. Support for the *n*-methylionone skeleton of IV was obtained as follows: On hydrogenation, as described above, three moles of hydrogen were absorbed; chromic acid oxidation of the *n*-methyltetrahydroionol gave a ketone whose semicarbazone melted at 116–118° after repeated recrystallizations. The melting point of the latter was undepressed upon admixture with the semicarbazone of authentic *n*-methyltetrahydroionone, m.p. 116–118°.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.81; H, 10.65; mol. wt., 206, n_D^{20} 1.4969; b.p. 76°/0.3 mm.; $\lambda_{max}^{C_2H_5OH}$ 227 mμ, ε 12,430. γ_{max}^{liq} 1682 cm.$^{-1}$ (conjugated carbonyl), 892 cm.$^{-1}$ (vinylidene methylene).

RESEARCH DEPARTMENT
INTERNATIONAL FLAVORS AND FRAGRANCES INC.
UNION BEACH, N. J.

---

(9) Microanalyses by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(10) Molecular weights were determined by the low-ionization, parent-ion technique on a Consolidated Electrodynamics Model 21-103C mass spectrometer. See, for example, F. H. Field and S. H. Hastings, *Anal. Chem.*, **28**, 1248 (1956).

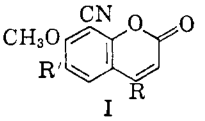
Cyanocoumarins

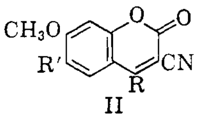
S. S. LELE, M. G. PATEL, AND SURESH SETHNA

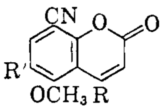
Received May 19, 1961

A few cyanocoumarins have been previously synthesized[1–5] but no attempt appears to have been made so far to prepare them by the Rosenmund-von Braun reaction on the halogenated coumarins or to study their hydrolysis. The present work deals with these aspects.

Methyl 7-methoxy-8-iodocoumarin-6-carboxylate, methyl 7-methoxy-8-iodo-4-methylcoumarin-6-carboxylate, and methyl 5-methoxy-8-iodo-4-methylcoumarin-6-carboxylate, when heated with anhydrous cuprous cyanide at temperatures mentioned in Table I, yielded the corresponding 8-cyano derivatives (Ia and b) and (IIIb). With hot 10% alkali the cyano group of these coumarins remained intact, but the esters were hydrolyzed to the corresponding carboxylic acids which on decarboxylation gave the cyanocoumarins (Ic and d) and (IIId), respectively, identical with those obtained by the Rosenmund-von Braun reaction on 7 - methoxy - 8 - iodocoumarin, 7 - methoxy - 8-iodo-4-methylcoumarin and 5-methoxy-8-iodo-4-methylcoumarin. These cyanocoumarins also remained unaffected on boiling with 10% potassium hydroxide solution.


I


II


III

	a	b	c	d	e
R =	H	CH_3	H	CH_3	CH_2COOCH_3
R′ =	$COOCH_3$	$COOCH_3$	H	H	H

7-Methoxy-3-iodocoumarin, 7-methoxy-3-iodo-4-methylcoumarin, and methyl 7-methoxy-3-iodo-4-methylcoumarin-6-carboxylate on similar reaction with anhydrous cuprous cyanide yielded the corresponding 3-cyano derivatives (IIc, d, and b). The cyanocoumarin (IIc) was previously prepared by Baker[3] by the condensation of 2-hydroxy-4-methoxybenzaldehyde with malononitrile in presence of piperidine. With hot 10% alkali these 3-cyanocoumarins yielded the corresponding coumarin-3-carboxylic acids.

Methyl 7-methoxy-8-iodocoumarin-4-acetate on a similar Rosenmund-von Braun reaction gave a mixture of 7-methoxy-8-cyano-4-methylcoumarin (Id) and methyl 7-methoxy-8-cyanocoumarin-4-acetate (Ie).

On hydrolysis with sulfuric acid (90% by volume)

---

(1) B. B. Dey and A. Kutti, *Proc. Indian Acad. Sci., India.* **6**, 641 (1940).

(2) C. H. Schroeder and K. P. Link, *J. Am. Chem. Soc.*, **75**, 1886 (1953).

(3) W. Baker and C. S. Howes, *J. Chem. Soc.*, 119 (1953).

(4) M. Crawford and J. W. Rasburn, *J. Chem. Soc.*, 2155 (1956).

(5) C. Wiener, C. H. Schroeder, and K. P. Link, *J. Am. Chem. Soc.*, **79**, 5301 (1957).