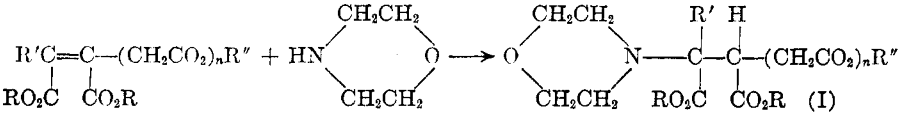
TABLE I

PREPARATION OF MORPHOLINO ESTERS



(I)

No.	Olefinic ester used R	R′	R″	n	Distillation data Temp., °C.	Press. μ	Rate DPM[a]	Yield, %	Sapon. equiv. Calcd.	Found
Ia	CH_3	H	CH_3	1	[b]	..	...	95	...	...
Ib	C_2H_5	H	C_2H_5	1	128[c]	15	64	75	115	120
Ic	n-C_4H_9	H	n-C_4H_9	1	155[c]	30	75	94	169	143
Id	$CH_2{=}CHCH_2$	H	$CH_2{=}CHCH_2$	1	150	45	100	68	127	136
Ie	n-C_4H_9	H	H	0	130	75	100	66	157	157
If	n-C_4H_9	CH_3	H	0	135	40	100	68	...	...

[a] Drops per minute. [b] Melting point, 81°. [c] The hydrochloride was obtained by passing anhydrous hydrogen chloride through a petroleum ether solution, m.p. Ib·HCl, 130–131°; m.p. Ic·HCl, 78–79°.

TABLE II

ANALYTICAL RESULTS FOR MORPHOLINO ESTERS (I)

No.	R	R′	R″	n	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Ia	CH_3	H	CH_3	1	$C_{13}H_{21}NO_7$	51.48	51.94	6.93	6.98	4.62	4.59
Ib	C_2H_5	H	C_2H_5	1	$C_{16}H_{27}NO_7$	55.65	55.95	7.83	7.84	4.05	4.03
Ic	n-C_4H_9	H	n-C_4H_9	1	$C_{22}H_{39}NO_7$	61.54	61.69	9.09	9.14	3.01	3.01
Id	$CH_2{=}CHCH_2$	H	$CH_2{=}CHCH_2$	1	$C_{19}H_{27}NO_7$	59.84	57.93	7.09	6.96	3.60	3.59
Ie	n-C_4H_9	H	H	0	$C_{16}H_{29}NO_5$	60.95	60.90	9.21	9.36	4.30	4.29
If	n-C_4H_9	CH_3	H	0	$C_{17}H_{31}NO_5$	62.00	61.77	9.42	9.42	4.26	4.22

itaconate, and dibutyl citraconate were prepared according to the method of Roberts, *et al.*[2]

General Procedure for Syntheses of Morpholinotricarballylates (I).—($R = R''$; $R' = H$; $n = 1$). A homogeneous solution formed from the ester and a 10% molar excess of morpholine was heated in a stoppered flask on the steam cone (*ca.* 90°) for 15 hr. The solution darkened slightly and increased in viscosity. Excess morpholine was removed by distillation at 15 mm. and the reaction mixture distilled under high vacuum rejecting a 5% forerun. Yields are reported on the fractionally distilled product. The infrared spectra of the compounds showed *tert*-C—H bending (1330 cm.$^{-1}$).

Di-*n*-butyl Morpholinosuccinate (Ie). Method I.—One hundred grams (1.15 moles) of morpholine was slowly added to 228 g. (1.00 mole) of di-*n*-butyl maleate maintaining a temperature of 30° with the aid of an ice bath. The flask was stoppered and the reaction mixture was heated for 15 hr. at 90°. The dark brown product was taken up in an equal volume of petroleum ether, washed three times with distilled water, dried over anhydrous sodium sulfate, and the solvent removed. The morpholino ester was purified by fractionally distilling at high vacuum.

Method II.—A mixture of 228 g. (1.00 mole) of di-*n*-butyl fumarate and 100 g. (1.15 moles) of morpholine was heated on the steam bath, 90°, for 15 hr. in a stoppered flask. Isolation of the purified product was the same as described above. The distilled products prepared by methods I and II had identical infrared spectra.

Di-*n*-butyl α-morpholinopyrotartrate (If). Method I.—A mixture of 50 g. (0.21 mole) di-*n*-butyl citraconate and 20 g. (0.23 mole) of morpholine was heated at 90° for 15 hr. After removal of excess morpholine under reduced pressure, the reaction mixture was distilled under high vacuum.

Method II.—A homogeneous mixture of 242 g. (1.00 mole) of di-*n*-butyl itaconate and 100 g. (1.15 moles) of morpholine was heated, 90°, for 15 hr. and the product was purified in the same manner as described above. The distilled products prepared by methods I and II had identical infrared spectra.

α-Morpholinotricarballylic Acid Hydrochloride.—Sixty grams (0.14 mole) of tri-*n*-butyl morpholinotricarballylate (Ic) was hydrolyzed by refluxing in 200 ml. of 6 *N* hydrochloric acid for several hours using a Dean-Stark trap for removal of the released butanol. Thirty grams of butanol (required, 31 g.) was removed after which the solution was reduced to half volume. The crystals which formed on storage of the solution over solid sodium hydroxide for 3 days were filtered off and recrystallized from glacial acetic acid. Thirty-one grams representing a 75% yield of α-morpholinotricarballylic acid hydrochloride was obtained, 150–151° dec. Neut. equiv.: calcd. 74.4; found 75.0.

Acknowledgment.—The authors are indebted to Mr. R. T. O'Connor for running the spectra of some of the above compounds and to Mr. L. E. Brown for the microanalyses reported herein.

γ-Isomethylionone

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Received January 18, 1962

The isolation and characterization of pure γ-ionone and γ-*n*-methylionone have been reported recently.[1]

We now wish to report the separation and isolation in pure form of the remaining member of this series, the exocyclic γ-isomethylionone, I.

We present here its isolation and proof of structure.

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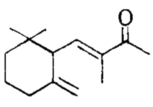
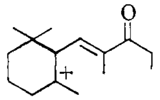
(1) Ernst T. Theimer, Willard T. Somerville, Bernard M. Mitzner, and Seymour Lemberg, *J. Org. Chem.*, **27**, 635 (1962).



I

I is undoubtedly formed during the cyclization from the intermediate carbonium ion, II.

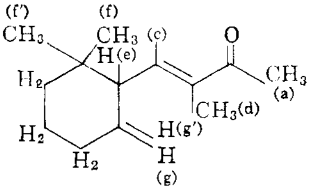


II

It has been our experience that even with the most exacting distillation techniques, γ-isomethylionone is not completely separable from the alpha and beta isomers derived from II.

The isolation of I was accomplished by preparative vapor phase chromatography. I and its alpha iso isomer were found to be separable on a polar column.

The n.m.r. spectrum of I firmly supports the proposed structure and has the following analysis.[2]



TAU VALUES

a	c	d	e	f and f^1		g and g^1	
7.83	3.38	8.38	7.17	9.16	9.10	5.56	5.32

($J_{c,e}$ = 9.6 c.p.s.) ($J_{e,c}$ = 10.8 c.p.s.)

This work completes the characterization of all the ionones, *n*-methylionones and isomethylionones derivable from the corresponding carbonium ion precursors.

Experimental

Commercial methylionone[3] was chromatographed through a 9-ft. 1/2-in. o.d. column packed with 15% Carbowax 20M on 60/80 mesh silane treated Celite at 170°, 120 ml. of helium per minute carrier gas, 10 p.s.i. inlet pressure. Numerous repetitive chromatograms were required, collecting only the "tail" portion of the α-isomethyl peak (the major constituent).

The collected trappings were retrapped *via* the same column. At this point n.m.r. showed approximately 10% β-isomethylionone remaining.

The latter was eliminated by trapping from a nonpolar column. (A 10-ft. 1/4-in. o.d. column, packed with Dow Corning 710 on 60/80 mesh Chromosorb, column temperature 150°, 50 ml./min. carrier gas, and 30 p.s.i. helium inlet pressure.) A complete separation of I was thus obtained.

The pure I obtained, b.p. 76°/0.3 mm., had a molecular weight of 206, as determined by the mass spectrometer[4] and analyzed as follows[5]: Calcd. C, 81.50; H, 10.75; found C, 81.78; H, 10.75; isooctane 228; ε 13,380; infrared, 1680 cm.$^{-1}$ (conjugated carbonyl); 892 cm.$^{-1}$ (vinylidene methylene).

I in glacial acetic acid with Adams platinum oxide catalyst, at atmospheric pressure, absorbed 3.0 moles of hydrogen. Chromic acid oxidation of the tetrahydroisomethylionol thus formed, gave on work-up a ketone whose semicarbazone had a m.p. of 168–171° after several recrystallizations from ethanol. Admixture with the semicarbazone of tetrahydroisomethylionone[6] showed no melting point depression.

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[2] N.m.r. 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 Mc./s. Tetramethylsilane (1/4%) was used as the standard, as described by G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[3] A number of commercially available methylionones rich in α-isomethylionone were examined. All contained small amounts of I.

[4] 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).

[5] Microanalyses by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

[6] Pure tetrahydroisomethylionone was prepared by hydrogenating pure α-isomethylionone using Adams' catalyst (3 mole equivalents of hydrogen were absorbed). The resulting tetrahydroionol was subjected to chromic acid oxidation in order to obtain the tetrahydroisomethylionone.

Conversion of Dihydroquercetin to Eriodictyol

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Received March 6, 1962

In the original paper[1] on the isolation of dihydroquercetin (3,3′,4′,5,7-pentahydroxyflavanone) from Douglas-fir heartwood, the conversion of this substance to eriodictyol (3′,4′,5,7-tetrahydroxyflavanone) in good yield was described. This was accomplished by reducing it in alcoholic solution with zinc dust and concentrated hydrochloric acid. Wheeler[2] confirmed the reaction, and then Hergert and Kurth[3] prepared eriodictyol in this manner. Wender,[4] however, made several unsuccessful attempts to use the method and finally resorted to other means for preparing eriodictyol. Later Murray[5] reported failure.

The author secured a sample of Murray's starting material (exact history unknown) and confirmed Murray's results. This dihydroquercetin had the previously described[1] melting point and color reactions but had a specific rotation of only +11° (*c*, 4 in equal volumes of acetone and water) instead of +46°. It was presumed to have been largely racemized, possibly by the use of an alkaline isolation method. This alone could not explain the failure to yield eriodictyol since, in the original work, racemic dihydroquercetin was shown to

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[1] J. C. Pew, *J. Am. Chem. Soc.*, **70**, 3031 (1948).

[2] L. M. Wheeler, private communication, 1949.

[3] H. L. Hergert and E. F. Kurth, *J. Am. Chem. Soc.*, **75**, 1622 (1953).

[4] S. L. Wender, private communication, 1953.

[5] C. W. Murray, private communication, 1956.