

Reaction of 3,3'-Di(2-chloroallyl)hexestrol with 3 *N* Potassium Hydroxide in 1-Butanol.—To 25 ml. of a 3 *N* potassium hydroxide solution in 1-butanol, 1.25 g. of 3,3'-di(2-chloroallyl)hexestrol was added, and the mixture refluxed for 2 hr. The crystals, which separated on cooling, were collected on a filter, washed with 1-butanol, and recrystallized from glacial acetic acid. The yield of I was 0.8 g., m.p. 201°. The analysis was in accord with the proposed structure of I.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.19; H, 7.57. Found: C, 83.10; H, 7.59.

3,4-Bis[5(2-methylbenzofuranyl)]hexane (I) from 3,3'-Diallylhexestrol Diacetate.—To 10.85 g. of 3,3'-diallylhexestrol diacetate,⁷ dissolved in 50 ml. of chloroform, a solution of 8.0 g. of bromine in 50 ml. of chloroform was added at 0°. The solvent was evaporated and the residue was crystallized from a mixture of ether and alcohol. To 1.88 g. of this crystallizate, a solution of 3 g. of potassium hydroxide in 100 ml. of ethanol was added and the mixture refluxed for 2 hr. The solution was concentrated, diluted with water, and acidified. The resulting precipitate was extracted with ether, the solvent evaporated, and the residue crystallized from glacial acetic acid. The product, m.p. 201–202°, was shown to be identical with that obtained from the treatment of 3,3'-di(2-chloroallyl)hexestrol with 3 *N* potassium hydroxide in 1-butanol solution by its melting point and infrared and ultraviolet absorption spectra.

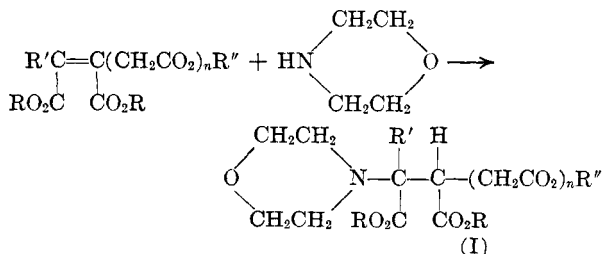
Morpholinotricarballylates and Related Compounds

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During our search for new plasticizers from aconitic esters² our attention was turned to some of the amine addition products of these esters. Amines^{3a} and ammonia^{3b} have been treated with aconitic acid esters, but no mention of the preparation of morpholinotricarballylates has been reported. Morpholine reacts readily with aconitic acid esters, without solvent, under relatively moderate conditions using but a slight excess of the morpholine. The reaction is shown below.



(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

(2) E. J. Roberts, L. F. Martin, F. C. Magne and R. R. Mod, *Rubber World*, **130**, 801 (1954).

(3)(a) S. Ruhemann and K. C. Browning, *J. Chem. Soc.*, **73**, 723 (1898); (b) J. P. Greenstein, *J. Biol. Chem.*, **116**, 463 (1936).

Although morpholine readily reacts with esters to form amides, no evidence of this reaction was found. The preparations of the esters are summarized in Table I.

The pure products were obtained in high yield by vacuum distillation with the exception of Ia which was purified by recrystallization. The liquid products were evaluated as plasticizers for vinyl resins, but their plasticizer properties were poor because they had relatively high brittle points. Some of these new compounds possess marked rodent repellent activity.⁴

Attempts to polymerize triallyl morpholinotricarballylate (Id) with benzoyl peroxide were unsuccessful, but the reaction of morpholine with polyallyl aconitate yielded an amorphous water-soluble resin.

Some related olefinic esters reacted with morpholine under similar conditions. Dibutyl maleate and dibutyl fumarate yielded the same compound, dibutyl morpholinotricarballylate (Ie). Similarly, dibutyl citraconate and dibutyl itaconate afforded the same compound, dibutyl morpholinopyrotartrate (If). In this case isomerization of the itaconic ester to the citraconic ester undoubtedly occurred before reaction with the amine, since 1,4-addition is preferred over 1,2-addition in reactions of this type.⁵ Furthermore, it is known that this isomerization is base-catalyzed.⁶ The analytical results for the morpholino esters are tabulated in Table II.

The mode of addition of morpholine to the aconitic esters was investigated by means of infrared spectra. All of the morpholinotricarballylate esters exhibited two absorption bands in the 1330–1350-cm.⁻¹ region; for example, two bands of medium intensity were found to occur at 1353 and 1328 cm.⁻¹ in tributyl morpholinotricarballylate. It has been proposed that absorption in the 1340-cm.⁻¹ region is due to the bending of a hydrogen atom attached to a tertiary carbon atom.⁷ Two such hydrogen atoms exist in α -morpholinotricarballylate esters and none in the beta position. Therefore, the alpha position is preferred. This conclusion agrees with the results of Greenstein,^{3b} who prepared α -aminotricarballylic acid from ammonia and triethyl aconitate.

Experimental⁸

Morpholine, dibutyl maleate, and dibutyl fumarate were obtained from Union Carbide Corp. and were used without further purification. The esters of aconitic acid, dibutyl

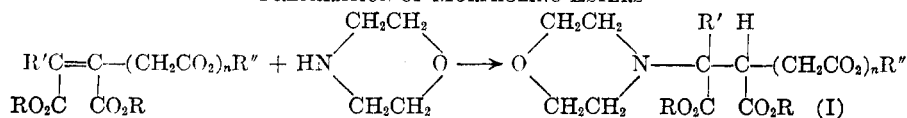
(4) E. J. Roberts and C. H. Mack (to U.S.A. as repr. by Sec. of Agr.), U.S. Patent 2,992,969 (1961).

(5) C. R. Noller, "Chemistry of Organic Compounds," Saunders, Philadelphia, 2nd ed., 1957, p. 763.

(6) R. P. Linstead, and J. T. Mann, *J. Chem. Soc.*, 726 (1931).

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 2nd ed., 1958, p. 21.

(8) Melting points and boiling points are uncorrected. Infrared spectra were obtained from chloroform solutions with the Perkin-Elmer spectrophotometer, Model 21.

TABLE I
 PREPARATION OF MORPHOLINO ESTERS


No.	Olefinic ester used				Distillation data			Yield, %	Sapon. equiv.	
	R	R'	R''	n	Temp., °C.	Press. μ	Rate DPM ^a		Calcd.	Found
Ia	CH ₃	H	CH ₃	1	^b	95
Ib	C ₂ H ₅	H	C ₂ H ₅	1	128 ^c	15	64	75	115	120
Ic	<i>n</i> -C ₄ H ₉	H	<i>n</i> -C ₄ H 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	<i>n</i> -C ₄ H ₉	H	H	0	130	75	100	66	157	157
If	<i>n</i> -C ₄ H 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, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	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 ₂ H ₅	H	C ₂ H ₅	1	C ₁₆ H ₂₇ NO ₇	55.65	55.95	7.83	7.84	4.05	4.03
Ic	<i>n</i> -C ₄ H ₉	H	<i>n</i> -C ₄ H 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	<i>n</i> -C ₄ H ₉	H	H	0	C ₁₆ H ₂₉ NO ₅	60.95	60.90	9.21	9.36	4.30	4.29
If	<i>n</i> -C ₄ H 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.

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γ-Isomethylionone

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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.

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