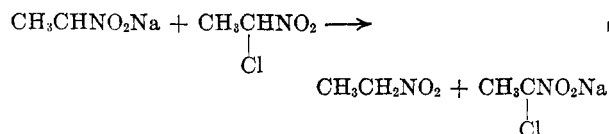TABLE I

CHLORINATIONS

Experiment No.	Nitroethane, g.	Cl₂, g.	NaOH, g.	H₂O, g.	NaCl, g.	Time, hr.	Temp., °C.	Crude product, g.	Conversions,[a] %	Remarks
1	90	78	40	250	..	3	15	94.5	20	Stirred reactor
2	90	78	49	250	..	3	15	102	65	No stirring
3	75	78	43	250	..	7	[b]	58	0	
4	75	78	40	280	30	1.7	0-5	107	94.5	Special chlorinator
5	89[c]	78	40	280	30	1.8	0	96.5	78	Special chlorinator
6	60[d]	50	40	300	30	1.0	0	80.1	80	Special chlorinator
7	75	78	40	280	30	1 0	0	101 7	93	Samples taken during run[e]

[a] To monochloro derivatives. [b] Not controlled. [c] 2-Nitropropane. [d] 1-Nitropropane. [e] CNE = 1-Chloro-1-nitro-ethane; DCNE = 1,1-Dichloro-1-nitroethane; NE = Nitroethane; see table below.

Time, min.	Wt., g.	% CNE	% DCNE	% NE
12	8.1	99.4	...	0.6
19	11.9	99.2	...	.8
25	8.3	99.0	0.3	.7
30	7.5	99.0	.4	.6
36	7.4	99.0	.3	.7
47	10.7	98.4	.7	.8
55	7.9	97.8	.9	.9

$$CH_3CHNO_2Na + CH_3\underset{\underset{Cl}{|}}{C}HNO_2 \longrightarrow$$

$$CH_3CH_2NO_2 + CH_3\underset{\underset{Cl}{|}}{C}NO_2Na$$

The sodium salt of chloronitroethane will then react with more chlorine or be hydrolyzed.

The hydrolysis of 1-chloro-1-nitroethane was studied by Hawthorne and Strahm,[4] who obtained acetic acid and nitrous oxide as products. In the

78 g. of nitroethane (99.8% from fractionation of an Eastman Organic Chemistry, Inc., product) in 140 ml. of water. When the nitroethane was dissolved, the solution was placed in the chlorinator and cooled to temperature. A measured amount of chlorine was added during 1-2 hr. The product came out of solution in droplets which settled to the bottom of the apparatus. This essentially pure 1-chloro-1-nitro-ethane was periodically removed. Chlorine was completely absorbed until all of the nitroethane had been consumed, whereupon the reaction solution became acid and chlorine escaped from the top of the reactor. The product was analyzed by infrared spectroscopy and gas chromatography.
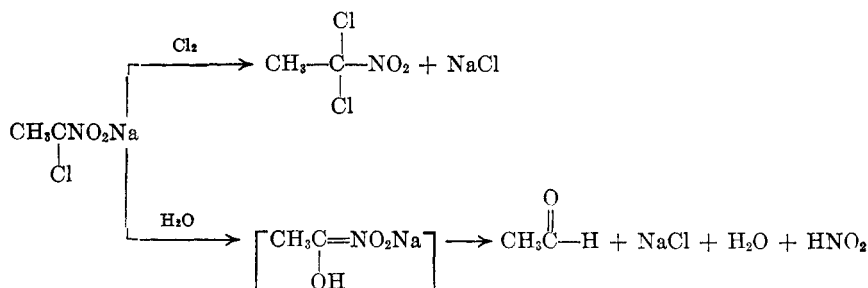
present work, both acetic acid and acetaldehyde were isolated. The exchange reaction occurs more readily if there is agitation, and the amount increases with temperature and time. The parallel increase in amounts of nitroethane and 1,1-dichloro-1-nitroethane in the products with time substantiates the conclusion that exchange is occurring.

Experimental

Examples of typical experiments are shown in Table I. The procedure which gives the highest yields is described below.

A special chlorinator was used, consisting of a 12-in. jacketed glass column 2 in. in diameter fitted with a stopcock at the bottom, a fritted glass chlorine inlet 1 in. from the bottom, and a thermometer and reflux condenser.

A solution of 40 g. of sodium hydroxide in 140 ml. of water was added to a stirred and cooled (ice bath) suspension of

(4) M. F. Hawthorne and R. D. Strahm, *J. Am. Chem. Soc.*, **79**, 3471 (1957).

Base-Catalyzed Rearrangement of Allylphenols and Haloallylphenols[1]

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The base-catalyzed rearrangement of olefinic double bonds has been the subject of several recent publications,[3-5] as well as that of some earlier

work.[6-8] Continuing our previous investigations of the potassium hydroxide-catalyzed rearrangement of allylphenols to propenylphenols, we now report the effect of solvents and of substituents in the allyl group on this double bond shift. Two model compounds were selected, the 3,3'-diallylhexestrol and the 3,3'-di(2-chloroallyl)hexestrol and water, ethanol, and 1-butanol were the reaction media.

It was found (Table I) that the double bond shift of 3,3'-diallylhexestrol could be achieved under milder conditions than previously employed[6,7] with ethanol and 1-butanol as the reaction media, but not with water. The same solvent effect was also observed in the rearrangement of 3,3'-di(2-chloroallyl)hexestrol, where the reaction product was identified as a benzofuran derivative.

I
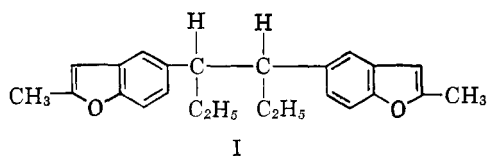
TABLE I[a]

FORMATION OF 3,3'-DIPROPENYLHEXESTROL FROM 3,3'-DIALLYLHEXESTROL IN 3 N POTASSIUM HYDROXIDE IN WATER, ETHANOL, AND 1-BUTANOL SOLUTIONS AT REFLUX TEMPERATURES

Solvent	Time, hr.	3,3'-Dipropenylhexestrol, %
Water	48	0
Ethanol	6	12
Ethanol	24	45
Ethanol	30	49
Ethanol	48	88
1-Butanol	1/4	47
1-Butanol	1/2	69
1-Butanol	3/4	79
1-Butanol	1	84
1-Butanol	1 1/3	89
1-Butanol	2	93
1-Butanol	4	93

[a] See ref. 10.

The progress of the isomerization was followed quantitatively in the case of the allylphenol by the absorption of the resulting propenylphenol in the infrared[9] at 960–970 cm.$^{-1}$ (Table I), or in the case of the haloallylphenol by the isolation of the product I identified as 3,4-bis[5-(2-methylbenzofuranyl)]hexane (Table II).

Evidence for structure I was obtained from the elementary analysis of the product, from the presence of a strong absorption peak at 1250 cm.$^{-1}$

(1) Presented in part at the 140th Meeting of the American Chemical Society, September, 1961, Abstracts, p. 10-O.

(2) Present address: Nalco Chemical Co., Chicago, Illinois.

(3) T. T. Prosser, J. Am. Chem. Soc. **83**, 1701 (1961).

(4) C. C. Price and W. H. Snyder, ibid., **83**, 1773 (1961).

(5) A. Schriesheim, J. E. Hofman, and C. A. Rowe, Jr., ibid., **83**, 3732 (1961).

(6) "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 19.

(7) E. Kaiser and J. J. Svarz, J. Am. Chem. Soc., **68**, 639 (1946).

(8) E. Kaiser and V. L. Koeing, ibid., **68**, 740 (1946).

(9) W. N. White and B. E. Norcross, ibid., **83**, 1968 (1961).

TABLE II

YIELDS OF I FROM 3,3'-DI(2-CHLOROALLYL)HEXESTROL IN 3 N POTASSIUM HYDROXIDE IN WATER, ETHANOL, AND 1-BUTANOL SOLUTIONS AT REFLUX TEMPERATURES

Solvent	Time, hr.	Yield, %
Water	16	1.7
Ethanol	2	42
1-Butanol	2	80

(ether linkage) in the infrared and from a strong peak at 288 mμ (double bond in conjugation with the aromatic nuclei) in the ultraviolet. The ease with which hydrogen bromide was generated during the bromination of (I) was also indicative of a benzofuran structure.[11] Finally, structure I was also synthesized from 3,3'-diallylhexestrol diacetate via bromination and alkaline treatment of the bromo derivative, a standard method for the preparation of benzofurans.[12]

Identity of the conditions, under which the allylphenol and the haloallylphenol rearranged, indicated that the removal of the vinylic halogen occurred in conjunction with the double bond shift. In the transition state of the allyl to propenyl rearrangement[3,4] the attachment of the chlorine to the double bond was weakened and thus the furan ring closure by nucleophylic attack of the phenolate group was made possible.

Experimental[13]

Since the procedures for the rearrangement of 3,3'-diallylhexestrol and 3,3'-di(2-chloroallyl)hexestrol with 3 N potassium hydroxide in water, ethanol, and 1-butanol solutions are essentially the same, only one representative method will be given for each of the two compounds.

Rearrangement of 3,3'-Diallylhexestrol with 3 N Potassium Hydroxide in Ethanol Solution.—To 25 ml. of a refluxing solution of 3 N potassium hydroxide in ethanol, 1.25 g. of 3,3'-diallylhexestrol was added with stirring. At time intervals shown in Table I, 5-ml. samples were withdrawn and added to dilute hydrochloric acid. The resulting precipitates were extracted with ether, and the combined ether extracts were washed with water, dried, and evaporated. From the dried solid residues, 2% solutions in chloroform were prepared and used for optical density measurements at 966 cm.$^{-1}$. The amounts of 3,3'-dipropenylhexestrol, corresponding to the respective optical densities, were calculated from a standard curve constructed from the optical densities of known quantities of specially purified 3,3'-dipropenylhexestrol. For this purification, 0.7 g. of 3,3'-dipropenylhexestrol, m.p. 153–154°,[7] was dissolved in a mixture of 1 part of ether and 3 parts of benzene and passed through a column of aluminum oxide (16 g. "Woelm" acid, activity grade 1). The absorbed material was eluted with a mixture of 1 part of ether and 1 part of benzene. The solvents were evaporated and the residue crystallized from benzene. The chromatographed 3,3'-dipropenylhexestrol melted at 158–159°.

(10) A detailed study of the kinetics of the allylphenol rearrangement will be published later.

(11) "Heterocyclic Compounds," R. C. Elderfield, ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 21.

(12) Ref. 11, p. 12.

(13) Analyses were performed by Midwest Microlab. Inc., Indianapolis 20, Indiana. Melting points were uncorrected. Ultraviolet spectra were determined in spectrograde methanol solutions with a Perkin-Elmer Spectrocord. For infrared spectra, a Perkin-Elmer recording infrared spectrophotometer, Model 21, was used.

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 esters[2] 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.

$$R'C{=}C(CH_2CO_2)_nR'' + HN\!\!<\!\!\begin{array}{c}CH_2CH_2\\[2pt]CH_2CH_2\end{array}\!\!>\!\!O \longrightarrow$$
$$\overset{|}{RO_2C}\ \ \overset{|}{CO_2R}$$

$$O\!\!<\!\!\begin{array}{c}CH_2CH_2\\[2pt]CH_2CH_2\end{array}\!\!>\!\!N{-}\overset{R'}{\underset{RO_2C}{C}}{-}\overset{H}{\underset{CO_2R}{C}}{-}(CH_2CO_2)_nR''$$

(I)

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 morpholinosuccinate (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.

Experimental[8]

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

(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).

(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.